

“Synthesis, Structure and Properties of Polyoxopalladates”

by

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Abstract

Polyoxometalates (POMs) represent a large class of discrete metal-oxo anions, usually formed by early transition elements in high oxidation states (e.g. Mo^{6+} , W^{6+} , V^{5+}). Recently Kortz and coworkers synthesized and structurally characterized the first discrete polyoxopalladate(II) $[\text{Pd}^{\text{II}}_{13}\text{As}^{\text{V}}_8\text{O}_{34}(\text{OH})_6]^{8-}$ (**Pd₁₃As₈**). This polyanion consists of 13 square-planar $\{\text{PdO}_4\}$ addenda units and hence represents a new POM subclass. Such late transition metal-based POMs are expected to be important, e.g. as precursors for nanoparticle synthesis, and also as models in the quest for understanding the true mechanism in noble metal (e.g. Pd, Pt, Au) based catalysis.

This dissertation summarizes the results obtained when trying to rationally modify **Pd₁₃As₈** in order to prepare other members of this class. In Chapter I a general introduction to POM chemistry is provided. Chapter II presents an overview of palladium(II)-containing heteropolytungstates and palladium-based polyoxopalladates. Chapter III describes the cuboid-shaped lanthanide- and 3d-transition metal-containing polyoxopalladates(II), $[\text{MO}_8\text{Pd}^{\text{II}}_{12}\text{L}_8]^n$, which can be subdivided in the following groups: 1) $\text{L} = \text{PhAsO}_3^{2-}$, $\text{M} = \text{Y}^{\text{III}}$, $\text{Pr}^{\text{III}} - \text{Lu}^{\text{III}}$, Sc^{III} , Mn^{II} , Fe^{III} , Co^{II} , Ni^{II} , Cu^{II} , Zn^{II} ; 2) $\text{L} = \text{SeO}_3^{2-}$, $\text{M} = \text{Mn}^{\text{II}}$, Fe^{III} , Co^{II} , Cu^{II} , Zn^{II} , Lu^{III} ; 3) $\text{L} = \text{PhPO}_3^{2-}$, $\text{M} = \text{Cu}^{\text{II}}$, Zn^{II} ; 4) $\text{L} = \text{PO}_4^{3-}$, $\text{M} = \text{Mn}^{\text{II}}$, Fe^{III} , Co^{II} , Cu^{II} , Zn^{II} . All these polyoxopalladate nanocubes have been prepared in simple one-pot reactions of $\text{Pd}_3(\text{CH}_3\text{COO})_6$, precursor of capping group L, and the respective salt of M^{n+} in aqueous medium. Chapter IV contains the synthesis and structural characterization of a double-cuboid-shaped, copper(II)-containing polyoxo-22-palladate(II), $[\text{Cu}_2\text{Pd}^{\text{II}}_{22}\text{P}_{12}\text{O}_{60}(\text{OH})_8]^{20-}$. This polyanion represents the first 3d transition metal containing polyoxopalladate, and contains more palladium ions than any other polyoxopalladate known to date. Also, central Cu^{II} ion is

in a very rare 8-coordination, which we investigated in detail by magnetic and EPR studies. Chapter V presents the synthesis and structural characterization of the yttrium-containing isopolytungstate $[\text{YW}_{10}\text{O}_{36}]^{9-}$. Chapter VI is devoted to three heteropolytungstates functionalized by organoantimony linkers, $[\{\text{PhSb}\}_4(\text{A}-\alpha-\text{XW}_9\text{O}_{34})_2]^{n-}$ ($\text{X} = \text{P}^{\text{V}}, \text{Ge}^{\text{IV}}$) and $[\{2-(\text{Me}_2\text{NCH}_2\text{C}_6\text{H}_4)\text{Sb}^{\text{III}}\}_3(\text{B}-\alpha-\text{AsW}_9\text{O}_{33})]^{3-}$. All compounds described above were characterized in the solid state by FT-IR spectroscopy, single-crystal XRD and thermogravimetric (TGA) analyses. The solution stability of the diamagnetic compounds was confirmed by multinuclear NMR spectroscopy (^1H , ^{13}C , ^{31}P , ^{77}Se , ^{183}W , ^{89}Y).

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Compound	Code
$\text{Na}_5[\text{YPd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}] \cdot 21\text{H}_2\text{O}$	Y-1a
$\text{Na}_5[\text{PrPd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}] \cdot 19\text{H}_2\text{O}$	Pr-1b
$\text{Na}_5[\text{NdPd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}] \cdot 24\text{H}_2\text{O}$	Nd-1c
$\text{Na}_5[\text{SmPd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}] \cdot 18\text{H}_2\text{O}$	Sm-1d
$\text{Na}_5[\text{EuPd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}] \cdot 21\text{H}_2\text{O}$	Eu-1e
$\text{Na}_5[\text{GdPd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}] \cdot 24\text{H}_2\text{O}$	Gd-1f
$\text{Na}_5[\text{TbPd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}] \cdot 22\text{H}_2\text{O}$	Tb-1g
$\text{Na}_5[\text{DyPd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}] \cdot 19\text{H}_2\text{O}$	Dy-1h
$\text{Na}_5[\text{HoPd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}] \cdot 16\text{H}_2\text{O}$	Ho-1i
$\text{Na}_5[\text{ErPd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}] \cdot 27\text{H}_2\text{O}$	Er-1j
$\text{Na}_5[\text{TmPd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}] \cdot 15\text{H}_2\text{O}$	Tm-1k
$\text{Na}_5[\text{YbPd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}] \cdot 18\text{H}_2\text{O}$	Yb-1l
$\text{Na}_5[\text{LuPd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}] \cdot 16\text{H}_2\text{O}$	Lu-1m
$\text{Na}_5[\text{Sc}^{\text{III}}\text{Pd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}] \cdot 21\text{H}_2\text{O}$	Sc-2a
$\text{Na}_6[\text{Mn}^{\text{II}}\text{Pd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}] \cdot 18\text{H}_2\text{O}$	Mn-2b
$\text{Na}_5[\text{Fe}^{\text{III}}\text{Pd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}] \cdot 21\text{H}_2\text{O}$	Fe-2c
$\text{Na}_6[\text{Co}^{\text{II}}\text{Pd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}] \cdot 24\text{H}_2\text{O}$	Co-2d
$\text{Na}_6[\text{Ni}^{\text{II}}\text{Pd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}] \cdot 22\text{H}_2\text{O}$	Ni-2e
$\text{Na}_6[\text{Cu}^{\text{II}}\text{Pd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}] \cdot 19\text{H}_2\text{O}$	Cu-2f
$\text{Na}_6[\text{Zn}^{\text{II}}\text{Pd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}] \cdot 37\text{H}_2\text{O}$	Zn-2g

$\text{Na}_{6-x}\text{H}_x[\text{Mn}^{\text{II}}\text{Pd}^{\text{II}}_{12}\text{Se}_8\text{O}_{32}]\cdot y\text{H}_2\text{O}$	Mn-3a
$\text{Na}_{5-x}\text{H}_x[\text{Fe}^{\text{III}}\text{Pd}^{\text{II}}_{12}\text{Se}_8\text{O}_{32}]\cdot y\text{H}_2\text{O}$	Fe-3b
$\text{Na}_{6-x}\text{H}_x[\text{Co}^{\text{II}}\text{Pd}^{\text{II}}_{12}\text{Se}_8\text{O}_{32}]\cdot y\text{H}_2\text{O}$	Co-3c
$\text{Na}_6[\text{Cu}^{\text{II}}\text{Pd}^{\text{II}}_{12}\text{Se}_8\text{O}_{32}]\cdot 12\text{H}_2\text{O}$	Cu-3d
$\text{Na}_6[\text{Zn}^{\text{II}}\text{Pd}^{\text{II}}_{12}\text{Se}_8\text{O}_{32}]\cdot 13\text{H}_2\text{O}$	Zn-3e
$\text{Na}_{5-x}\text{H}_x[\text{Lu}^{\text{III}}\text{Pd}^{\text{II}}_{12}\text{Se}_8\text{O}_{32}]\cdot y\text{H}_2\text{O}$	Lu-3f
$\text{Na}_6[\text{Cu}^{\text{II}}\text{Pd}^{\text{II}}_{12}(\text{C}_6\text{H}_5\text{P})_8\text{O}_{32}] \cdot 35\text{H}_2\text{O}$	Cu-4a
$\text{Na}_6[\text{Zn}^{\text{II}}\text{Pd}^{\text{II}}_{12}(\text{C}_6\text{H}_5\text{P})_8\text{O}_{32}] \cdot 36\text{H}_2\text{O}$	Zn-4b
$\text{Na}_9[\text{Mn}^{\text{II}}\text{Pd}^{\text{II}}_{12}\text{P}_8\text{O}_{35}(\text{OH})_5]\cdot 32\text{H}_2\text{O}$	Mn-5a
$\text{Na}_9[\text{Fe}^{\text{III}}\text{Pd}^{\text{II}}_{12}\text{P}_8\text{O}_{36}(\text{OH})_4]\cdot 16\text{H}_2\text{O}$	Fe-5b
$\text{Na}_{10}[\text{Co}^{\text{II}}\text{Pd}^{\text{II}}_{12}\text{P}_8\text{O}_{36}(\text{OH})_4]\cdot 30\text{H}_2\text{O}$	Co-5c
$\text{Na}_{10}[\text{Cu}^{\text{II}}\text{Pd}^{\text{II}}_{12}\text{P}_8\text{O}_{36}(\text{OH})_4]\cdot 31\text{H}_2\text{O}$	Cu-5d
$\text{Na}_9[\text{Zn}^{\text{II}}\text{Pd}^{\text{II}}_{12}\text{P}_8\text{O}_{35}(\text{OH})_5]\cdot 37\text{H}_2\text{O}$	Zn-5e
$\text{Na}_{20}[\text{Cu}^{\text{II}}_2\text{Pd}^{\text{II}}_{22}\text{P}^{\text{V}}_{12}\text{O}_{60}(\text{OH})_8]\cdot 58\text{H}_2\text{O}$	NaPd₂₂-6
$\text{Na}_9[\text{YW}_{10}\text{O}_{36}]\cdot 35\text{H}_2\text{O}$	Na-7
$(\text{NH}_4)_{12}[\{\text{PhSb}\}_4(\text{A}-\alpha-\text{GeW}_9\text{O}_{34})_2]\cdot 20\text{H}_2\text{O}$	NH₄-8
$\text{Rb}_9\text{Na}[\{\text{PhSb}\}_4(\text{A}-\alpha-\text{PW}_9\text{O}_{34})_2]\cdot 20\text{H}_2\text{O}$	RbNa-9
$\text{Rb}_3[\{2-(\text{Me}_2\text{NCH}_2\text{C}_6\text{H}_4)\text{Sb}^{\text{III}}\}_3(\text{B}-\alpha-\text{AsW}_9\text{O}_{33})]\cdot y\text{H}_2\text{O}$	Rb-10

Chapter I Introduction

Polyoxometalates (POMs) comprise a large class of polynuclear metal-oxygen clusters usually formed by early transition elements in high oxidation states, such as Mo^{6+} , W^{6+} or V^{5+} and mixtures of these elements. POMs have been known for a long time but the mechanism of their formation is not completely understood, and is usually described as “self-assembly”.¹ The synthesis of POMs can be affected by changing pH, temperature, ratio of reagents and the order of their adding, counter cations and ionic strength. That is why the development of the synthetic procedure of a target POM is quite difficult. Using the lacunary POM precursors in the reactions with different electrophiles (e.g. transition metal ions, lanthanides, organometallic species) sometimes helps to obtain needed compounds. The nature of the incorporated electrophilic units significantly influences on the redox, luminescence, magnetic characteristics of the resulting products.

The chemistry of POMs has intensively grown particularly over the last few decades, due to the development of the modern experimental techniques (e.g. single crystal XRD, NMR spectroscopy). Owing to the unique combination of properties, such as thermal and oxidative stability, tunability of acidity and redox activity, and solubility in various media, POMs have a wide range of potential applications, which include diverse fields such as catalysis, medicine, electronics, multifunctional materials, and analytical chemistry.²

1.1 Fundamental POM Structures

The class of POMs has been known since 1826, where Berzelius first noted the formation of yellow precipitate $(\text{NH}_4)_3[\text{PMo}_{12}\text{O}_{40}]$ as a result of the interaction of ammonium molybdate with phosphoric acid.³ Several attempts to understand the new class of compounds were made until 1933, where Keggin reported the first description of $\text{H}_3[\text{PW}_{12}\text{O}_{40}]\cdot 5\text{H}_2\text{O}$

structure on basis of data of X-ray diffraction.⁴ Later other types of structures (Anderson-Evans, Well-Dawson, Lindqvist) were published.

The class of POMs can be subdivided in isopolyanions and heteropolyanions. The former are composed of only addenda atoms (e.g. W, Mo, V, Ta) and oxygen ligands. A well-known example is the so called hexametallate or Lindqvist ion, $[\text{M}_6\text{O}_{19}]^{2-}$ ($\text{M} = \text{W}, \text{Mo}, \text{Ta}$), Fig. 1.1. This ion is composed of six edge-shared MO_6 octahedra, resulting in an overall octahedral assembly.

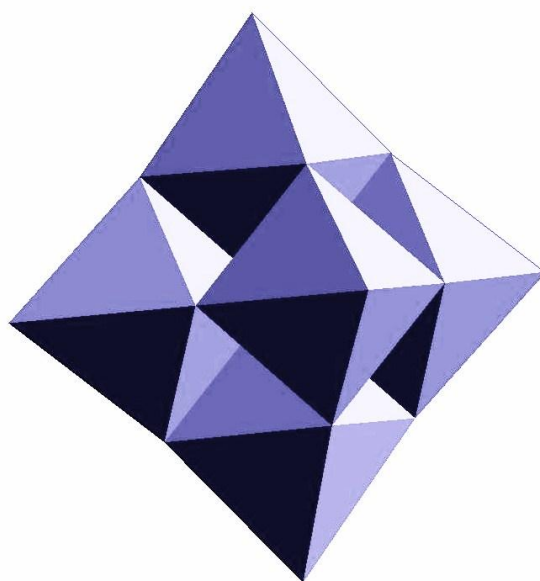


Figure 1.1 Polyhedral representation of the Lindqvist structure $[\text{M}_6\text{O}_{19}]^{2-}$.

On the other hand, heteropolyanions contain an additional hetero ion X, which can be P^{5+} , As^{5+} , Si^{4+} , Ge^{4+} , B^{3+} , etc. A common example of heteropolyanions is highly symmetrical Keggin ion, e.g. $[\text{SiW}_{12}\text{O}_{40}]^{4-}$, $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ (Fig. 1.2). This species is composed of a central, tetrahedral XO_4 hetero group surrounded by 12 MO_6 octahedra. The latter are arranged in four corner-shared M_3O_{13} triads with each triad being composed of three edge-shared MO_6 octahedra.

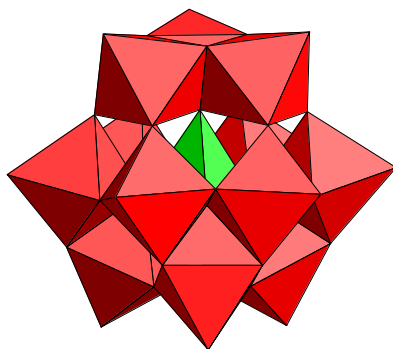


Figure 1.2 Polyhedral representation of the Keggin structure $[XM_{12}O_{40}]^{n-}$.

Another example of heteropolyanions is the Wells-Dawson species, $[X_2W_{18}O_{62}]^{n-}$, Fig. 1.3. This species contains two XO_4 hetero groups and a total of 18 addenda atoms.

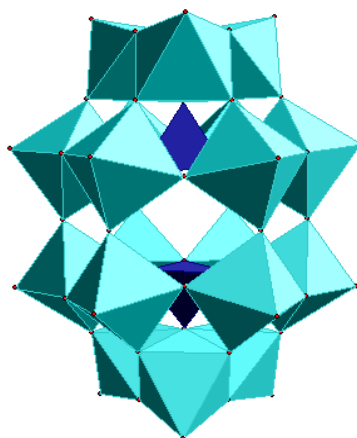


Figure 1.3 Polyhedral representation of the Wells-Dawson structure $[X_2W_{18}O_{62}]^{n-}$.

Heteropolyanions with an octahedral hetero group are also known, e.g. the Anderson-Evans ion $[XM_6O_{24}]^{n-}$ (Fig.1.4). The structure has planar arrangement of seven edge-shared octahedra.

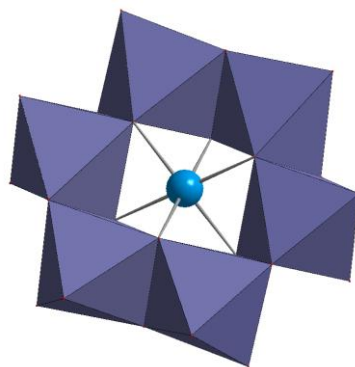


Figure 1.4 Polyhedral/ball-and-stick representation of the Anderson-Evans structure



It is also possible that in a POM more than one type of addenda atom is present (e.g. $[P_2W_{15}Mo_2VO_{62}]^{7-}$) and such species are called mixed-addenda polyanions.¹

1.2 Synthetic Strategies

Usually the approaches used to produce POMs are simple, consisting of a small number of steps, or even just one step. The main difficulties in POM synthesis are sometimes unpredictability of a product, due to the diversity of possible structures forming during a reaction, and the fact that the different compounds can be formed and even cristalized simultaneously.

Generally the acidification of aqueous solutions of tungstate and molibdate salts with or without heteroelements, are used for isopoly- and heteropolyoxometalate preparation. Depending on the reaction conditions, such as pH, ionic strength, reaction time, temperature and processing (e.g. microwave, hydrothermal, refluxing), counterions, concentration of reagents and the order of their addition to the reaction mixture etc. various POMs can be obtained.

Traditionally, POM synthesis is carried out in aqueous solution in presence of alkali metal cations, but using of different organic cations (e.g. $(\text{NH}_2)_2\text{C}=\text{NH}_2\text{Cl}$, Me_4NCl , Et_4NCl) and aqueous/organic solvent mixtures (e.g. water/EtOH, water/MeCN) for POM formation as well as for its precipitation or crystallisation is also known. Only one paper concerning utilization of ionic liquids for POM synthesis is known to date.^{1a,k}

1.3 General Properties

Usually POMs are air and water stable; they have large size and high molecular weight. The solubility of POMs depends on the counter cations; e.g. sodium salts are very water soluble while salts of organic cations such as tetrabutylammonium (TBA) are soluble in nonaqueous media. The polyanion salts and acids are commonly highly hydrated. The stability of the polyoxoanion structures in aqueous solution can vary widely (pH ~ 1-14) from one case to the other (e.g. $[\text{PW}_{12}\text{O}_{40}]^{3-}$ is stable at pH range < 1.5, for hexaniobate $[\text{Nb}_6\text{O}_{19}]^{8-}$ the stability range is pH 7 – 14). A number of POMs are strong oxidizing agents and undergo multiple one or two-electron reversible reductions resulting in mixed-valence species which are deeply colored and known as “heteropoly blues”.^{1a}

1.4 Analytical Techniques for the POM Characterization

The complexity of POM systems places extreme demands upon experimental techniques and upon interpretation of results. Structural X-ray crystallography has played a major role in the development of the field, and is up to date the most useful technique for POM characterization in the solid state. Single-crystal X-ray diffraction (XRD) analysis allows disclosing of the coordination arrangement of the atoms in the POM. FT-infrared spectroscopy is a very useful technique in POM chemistry especially if organic groups are a

part of POM not only for fingerprinting purposes but also for structural explanation. The most characteristic region of the spectrum is $\sim 1200 - 400 \text{ cm}^{-1}$ where absorptions due to metal- and nonmetal-oxygen stretching vibrations occur. Similarities of spectral band positions, shapes and relative intensities for two complexes indicate that they have identical structures.

Thermogravimetry delivers important information regarding thermal stability and brings also information on the species present; nevertheless elemental analysis is definitely the method to prove the purity of the bulk product.

For the identification and structural characterization of species in solution different analytical methods are used (e. g. cyclic voltammetry, multinuclear magnetic resonance spectroscopy). Several other techniques are employed for POM characterization such as electron paramagnetic resonance (EPR), electronic and X-ray photoelectron spectroscopy, electrospray ionization mass spectrometry (ESI-MS) and cryospray mass spectrometry (CSI-MS).^{1,5} Some works about theoretical investigation of POMs are also known.^{5d,6}

1.5 Applications

The applications of polyoxometalates in different areas such as catalysis, magnetism, bio- and nanotechnology, materials science, and medicine are mainly based on their previously discussed properties, including size, mass, electron- and proton-transfer/storage abilities, thermal stability and high Brønsted acidity (e.g. $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$).^{1,2}

1.5.1 Catalysis

Heteropolyoxometalates already showed their activity in acid- and redox catalysis. Keggin heteropolyacids and their salts are already used as industrial catalysts in homogeneous (the hydration of propene, synthesis of glycosides) as well as in heterogeneous systems (gas phase oxidation of methacrolein to methacrylic acid, alkylation of *p*-cresol with isobutene).⁷

Heteropolyacids are highly acidic (more than sulfuric acid) and thermally stable, which makes them so interesting for catalysis. Heteropolyacids can be used as catalysts for the broad scope of useful reactions (e.g. cracking or isomerization of alkanes,⁸ Friedel-Crafts reactions^{2b,7b}).

For oxygenation and oxidative dehydrogenation reactions a wide range of transition metal-containing POMs can be used. Nowadays the selective catalytic oxidation of organic compounds using the easily accessible “green” oxidants H_2O_2 and O_2 is of particular interest and POMs due to their properties (thermal and hydrolytic stability, solubility in various media, adjustable redox activity etc.) can play a role of catalysts for the purpose. It has been known that POMs catalyze various oxidations of organic substrates by H_2O_2 , such as epoxidation of olefins, oxidation of alcohols, glycols and phenols. Keggin type and related polyanions were widely applied in such systems and detailed examination lead to the discovery that POMs actually serve as precatalysts where they tend to be decomposed by excess of H_2O_2 to form oxo-peroxo species,⁹ e.g. the Ishii-Venturello complex $\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}^{3-}$,¹⁰ the titanium-containing POMs $[\text{PW}_{11}\text{Ti}(\text{OH})\text{O}_{39}]^{4-}$ which is active for the epoxidation of alkenes with H_2O_2 .¹¹

1.5.2 Medicine

Several POMs confirm biological activity due to their stability at physiological pH as well as their size, shape and electron- acceptor capability allow them to block the active centres of biomolecules (Fig. 1.5).¹² Based on the above mentioned characteristics, over the past few decades an important effort has been done in order to synthesize functionalized polyoxoanions with pharmacological interest.¹³

It has been observed, that POMs can inhibit or selectively activate a given number of enzymes, like dehydrogenase, phosphorylase, and protease.¹⁴ Another important feature

consists of their capability to mimic protein activity like insulin, as already some promising results have been reported about experiments conducted with diabetic mice.¹⁵ As anti-carcinogenic agents they have shown some satisfactory results against a number of tumours; however, potential applications as antiviral and antiretroviral agents have generated the most interest, since they have already shown activity against a broad spectrum of viruses, like herpes and retrovirus like the HIV in none citotoxic dosage; the latter in vivo as well as in vitro.¹⁶

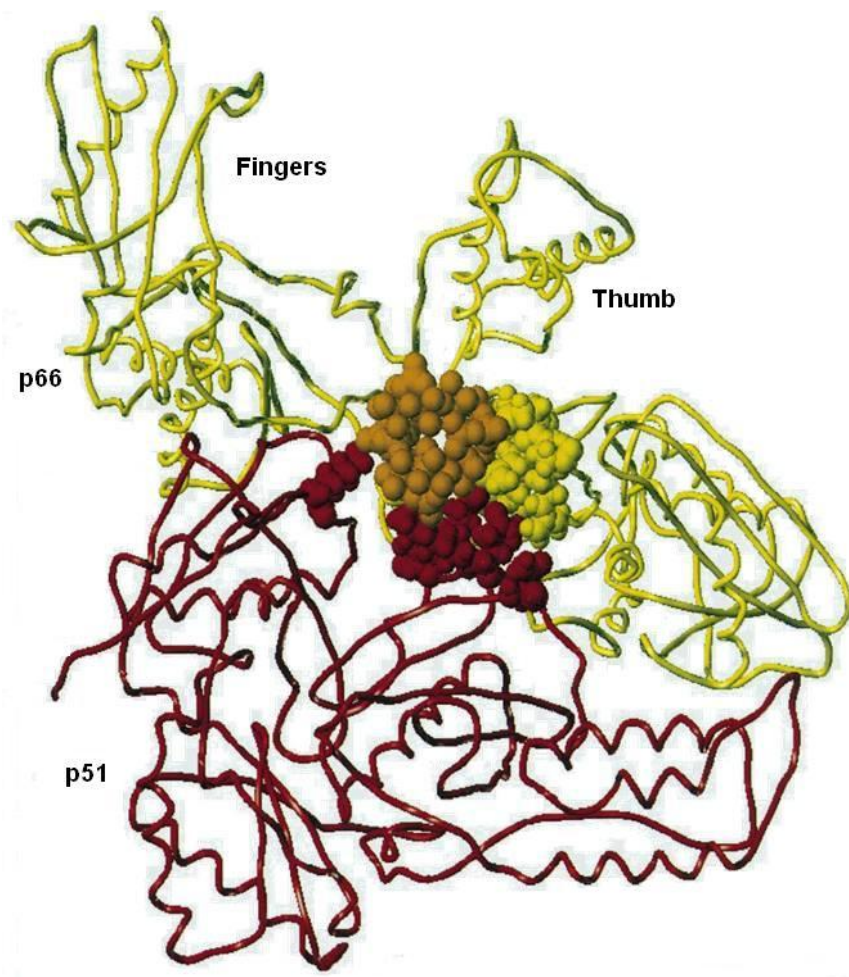


Figure 1.5 A model of the binding interactions of polyoxometalate $[(O_3POPO_3)_4W_{12}O_{36}]^{16-}$ at the DNA-binding cleft of HIV-1 RT.^{12a}

1.6 References

1. a) Pope, M.T. *Heteropoly and Isopoly Oxometalates*, Springer, Berlin, 1983; b) Day, V. W.; Klemperer, W. G., *Science*. **1985**, 228, 533-541; c) Pope, M.T.; Müller, A. *Angew. Chem.* **1991**, 103, 56–70; *Angew. Chem. Int. Ed.* **1991**, 30, 34–48; d) *Polyoxometalate Chemistry: From Topology Via self-Assembly to Applications*; Pope, M.T.; Müller, A., Eds.; Kluwer: Dordrecht, The Netherlands, 2001; e) *Polyoxometalate Chemistry for Nanocomposite Design*; Pope, M.T.; Yamase, T., Eds.; Kluwer: Dordrecht, The Netherlands, 2002; f) *Polyoxometalate Molecular Science*; Borrás- Almenar, J.J.; Coronado, E.; Müller, A.; Pope, M.T., Eds.; Kluwer: Dordrecht, The Netherlands, 2003; g) Talismanov, S. S.; Eremenko, I. L., *Russ. Chem. Rev.* **2003**, 72, 555–569; h) Cronin, L. in *Comprehensive Coordination Chemistry II*, Vol. 7 (Eds.: McCleverty, J. A.; Meyer, T. J.), Elsevier, Amsterdam, 2004, 1-57; i) Hasenknopf, B.; Micoine, K.; Lacote, E.; Thorimbert, S.; Malacria, M.; Thouvenot R. *Eur. J. Inorg. Chem.* **2008**, 5001-5013; j) Kortz, U., Guest Ed.; *Eur. J. Inorg. Chem.* **2009**, 34, issue dedicated to polyoxometalates; k) Long, D.-L.; Tsunashima, R.; Cronin, L. *Angew. Chem.* **2010**, 122, 1780-1803; *Angew. Chem. Int. Ed.* **2010**, 49, 1736-1758.
2. a) *Polyoxometalates: From Platonic Solids to Antiretroviral Activity*; Pope, M. T.; Müller, A., Eds.; Kluwer: Dordrecht, The Netherlands, 1994; b) Okuhara, T.; Mizuno, N.; Misono, M. *Adv. Catal.* **1996**, 41, 113-252; c) Hill, C. L., Ed.; *Chem. Rev.* **1998**, 98 (1), special thematic issue; d) Müller, A.; Roy, S. *Coord. Chem. Rev.*, **2003**, 245, 153-166; e) Coronado, E.; Day, P. *Chem. Rev.* **2004**, 104, 5419-5448; f) Hill, C. L. *J. Mol. Catal. A. Chem.* **2007**, 262, 2-6; g) Kortz, U.; Müller, A.; Slagereen, J.; Schnack, J.; Dalal, N. S.; Dressel, M. *Coord. Chem. Rev.* **2009**, 253, 2315-2327.
3. Berzelius, J. J. *Poggendorffs Ann. Phys. Chem.* **1826**, 6, 369-380.

4. Keggin, J. F. *Nature*. **1933**, *131*, 908–909.
5. a) Moffat, J.B. *Metal-Oxygen Clusters. The Surface and catalytic properties of Heteropoly Oxometalates*; Kluwer Academic/Plenum Publishers: New York, USA, 2001; b) Wilson, E.F.; Abbas, H.; Duncombe, B.J.; Streb, C.; Long, D.-L.; Cronin, L. *J. Am. Chem. Soc.* **2008**, *130*, 13876–13884; c) Miras, H. N.; Wilson, E.F.; Cronin, L. *Chem. Commun.* **2009**, 1297–1311; d) Izarova, N. V.; Vankova, N.; Banerjee, A.; Jameson, G. B.; Heine, T.; Schinle, F.; Hampe, O.; Kortz, U. *Angew. Chem.* **2010**, *122*, 7975 – 7980; *Angew. Chem. Int. Ed.* **2010**, *49*, 7807 – 7811.
6. a) Poblet, J.M.; López, X.; Bo, C. *Chem. Soc. Rev.* **2003**, *32*, 297–308; b) Brodbeck, R; Andrae, D. in *High Performance Computing in Science and Engineering, Garching/Munich 2007* (Eds.: Wagner, S; Steinmetz, M.; Bode, A.; Brehm, M.), Springer Berlin Heidelberg, Germany, 2009, 129–142; c) Barsukova, M.; Izarova, N. V.; Biboum, R. N.; Keita, B.; Nadjo, L.; Ramachandran, V.; Dalal, N. S.; Antonova, N. S.; Carbó, J.J.; Poblet, J. M.; Kortz, U. *Chem. Eur. J.* **2010**, *16*, 9076-9085; d) Vilà-Nadal, L.; Wilson, E. F.; Miras, H. N.; Rodríguez-Forteza, A.; Cronin, L.; Poblet, J. M. *Inorg. Chem.* **2011**, *50*, 7811-7819; e) Aparicio-Anglès, X.; Clotet, A.; Bo C.; Poblet, J.M. *Phys. Chem. Chem. Phys.* **2011**, *13*, 15143–15147; f) Banerjee, A.; Raad, F.S.; Vankova, N.; Bassil, B. S.; Heine, T.; Kortz, U. *Inorg. Chem.* **2011**, dx.doi.org/10.1021/ic201652h.
7. a) Misono, M.; Nojiri, N. *Appl. Catal.* **1990**, *64*, 1-30; b) Kozhevnikov, I. V. *Stud. Surf. Sci. Catal.* **1994**, *90*, 21-34; *Russ.Chem. Rev.* **1993**, *62*, 473-491.
8. a) Oulmekki, A.; Lefebvre, F. *React. Kinet. Catal. Lett.* **1992**, *48*, 593-600; b) Oulmekki, A.; Lefebvre, F. *React. Kinet. Catal. Lett.* **1992**, *48*, 601-606; c) Oulmekki, A.; Lefebvre, F. *React. Kinet. Catal. Lett.* **1992**, *48*, 607-612; d) Kuang, W.; Rives, A.; Tayeb, B.O.B.; Fournier, M.; Hubaut, R. *J. Colloid Interface Sci.* **2002**, *248*, 123-129; e) Essayem, N.; Ben Taarit, Y.; Feche, C.; Gayraud, P.Y.; Sapaly, G.; Naccache, C. *J. Catal.* **2003**, *219*, 97-106;

- f) Ivanov, A.V.; Vasina, T.V.; Nissenbaum, V.D.; Kustov, L.M.; Timofeeva, M.N.; Houzvicka, J.I. *Appl. Catal. A: Gen.* **2004**, *259*, 65-72.
9. Kozhevnikov, I. *Catalysis by polyoxometalates*; J. Wiley: Chichester, England, 2002.
10. Venturello, C.; D'Aloisio, R.; Bart, J. C. J.; Ricci, M. *J. Mol. Cat.* **1985**, *32*, 107-110.
11. Kholdeeva, O. A. *Top. Cat.* **2006**, *40*, 229-243.
12. a) Sarafianos, S. G.; Kortz, U.; Pope, M. T.; Modak, M. J. *Biochem. J.* **1996**, *319*, 619-626; b) Rhule, J. T.; Hill, C. L.; Judd, D. A.; Schinazi, R. F. *Chem. Rev.* **1998**, *98*, 327-357; c) Hu, D.; Shao, C.; Guan, W.; Su, Z.; Sun, J. *J. Inorg. Biochem.* **2007**, *101*, 89-94; d) Zhang, G.; Keita, B.; Craescu, C. T.; Miron, S.; Oliveira, P.; Nadjo, L. *Biomacromolecules.* **2008**, *9*, 812-817; d) Prudent, R.; Moucadel, V.; Laudet, B.; Barette, C.; Lafanechere, L.; Hasenknopf, B.; Li, J.; Bareyt, S.; Lacote, E.; Thorimbert, S.; Malacria, M.; Gouzerh, P.; Cochet, C. *Chem. Biol.* **2008**, *15*, 683-692; e) Wall, M. J.; Wigmore, G.; Lopatar, J.; Frenguelli, B. G.; Dale, N. *Neuropharmacology* **2008**, *55*, 1251-1258.
13. a) Inoue, M.; Yamase, T. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2863-2868; b) Kortz, U. Savelieff, M.G.; Ghali, F.Y.A.; Khalil, L.M.; Maalouf, S.A.; Sinno, D.I. *Angew. Chem. Int. Ed.* **2002**, *41*, 4070-4073; c) Kortz, U.; Marquer, C.; Thouvenot, R.; Nierlich, M. *Inorg. Chem.* **2003**, *42*, 1158-1162.
14. Crans, D. C. *Comments Inorg. Chem.* **1994**, *16*, 35-76.
15. a) Heyliger, C.E.; Tahiliani, A.G.; McNeill, J.H. *Science* **1985**, *227*, 1474-1477; b) Barberá, A.; Fernández-Alvarez, J.; Truc, A.; Gomis, R.; Guinovart, J.J. *J. Biol. Chem.* **1994**, *269*, 20047-20053; c) Palanivel, R.; Sundravel, S.; Ravichandran, P.; Govindasamy, S. *Med. Sci. Res.* **1998**, *26*, 541-544; d) Foster, J.D.; Wiedemann, J.M.; Pang, C.J.; Chou, J.Y.; Nordlie, R.C. *Arch. Biochem. Biophys.* **1998**, *393*, 117-122; e) Nomiya, K.; Torii, H.; Hasegawa, T.; Nemoto, Y.; Nomura, K.; Hashino, K.; Uchida, M.; Kato, Y.; Shimizu, K.;

- Oda, M. *J. Inorg. Biochem.* **2001**, 86, 657-667; f) Shechter, Y.; Goldwasser, I.; Mironchik, M.; Fridkin, M.; Gefel, D. *Coord. Chem. Rev.* **2003**, 237, 3-11.
16. a) Yamase, T. Fujita, H.; Fukushima, K. *Inorg. Chim. Acta.* **1988**, 151, 15-18; b) Yamase, T.; Tomita, Y.; Fujita, H. *Biomed. Pharm. Appl.* **1991**, 13, 187-212; c) Tajima, Y. *Biol. Pharm. Bull.* **2001**, 24, 1079-1084; d) Tajima, Y. *Biomed. Res.* **2002**, 23, 115-125; e) Tajima, Y. *J. Inorg. Biochem.* **2003**, 94, 155-160.

Chapter II Palladium-containing Polyoxometalates

Palladium-containing materials are known as catalysts for numerous industrial chemical processes.¹ The combination of noble metal catalytic properties with the ability of POMs to activate the easily accessible “green” oxidants H_2O_2 and O_2 , their oxidative and thermal stability, solubility in various solvents, adjustable redox activity etc. can result in competitive catalytic systems for different homogeneous as well as heterogeneous nonpolluting oxidation processes.² Noble metal containing POMs should be useful as precursors for preparing mixed metal oxide catalysts and finely distributed metal clusters in a highly reproducible manner. Soluble discrete palladium-oxo species are of particular interest nowadays due to their potential for the explanation of the mechanism of catalysis by noble metal based materials.³

Known noble metal containing POMs can be subdivided on two classes: late transition metal substituted polyanions, where one or more late transition metal centers are incorporated in the lacunary polyoxotungstate, -molybdate or -vanadate structures, and recently discovered class of noble metal based POMs, which are built exclusively with d^8 late transition metal centers.⁴ Several palladium-containing polyoxotungstates and the polyoxopalladates will be reviewed below.

2.1 Palladium-containing Polyoxotungstates

2.1.1 $[\text{Pd}_2\text{W}_{10}\text{O}_{36}]^{8-}$

Angus-Dunne *et al.* described the preparation and characterization of a palladium-substituted sandwich-type POM $[\text{Pd}_2\text{W}_{10}\text{O}_{36}]^{8-}$. The mixed potassium sodium salt of this polyanion $\text{K}_2\text{Na}_6[\text{Pd}_2\text{W}_{10}\text{O}_{36}] \cdot 22\text{H}_2\text{O}$ was obtained from the reaction of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ with K_2PdCl_2 in aqueous medium with addition of H_2SO_4 (pH 5.5). Dark-brown crystals of the compound were obtained in good yield after *ca.* 6 months and characterized by single crystal

X-ray analysis, cyclic voltammetry and IR spectroscopy (IR spectrum (KBr disk, ν/cm^{-1}): 933(s), W=O stretching; 868 (s), 841 (m), 774 (ms), 710 (s), 614 (w), W-O-W and Pd-O-W stretching; 486 (w), W-O-W or W-O-Pd bending). $\text{K}_2\text{Na}_6[\text{Pd}_2\text{W}_{10}\text{O}_{36}]\cdot 22\text{H}_2\text{O}$ crystallizes in triclinic system, space group P-1, $a = 9.229(2) \text{ \AA}$, $b = 11.277(3) \text{ \AA}$, $c = 15.102(4) \text{ \AA}$, $\alpha = 108.33(1)^\circ$, $\beta = 96.15(2)^\circ$, $\gamma = 109.74(1)^\circ$, $V = 1363.8(7) \text{ \AA}^3$, $Z=1$.

$[\text{Pd}_2\text{W}_{10}\text{O}_{36}]^{8-}$ (Fig. 2.1) is composed of two monolacunary Lindqvist type $[\text{W}_5\text{O}_{18}]^{6-}$ moieties linked by two Pd(II) ions in square-planar environments. The symmetry of the anion is approximately D_{2h} .⁵

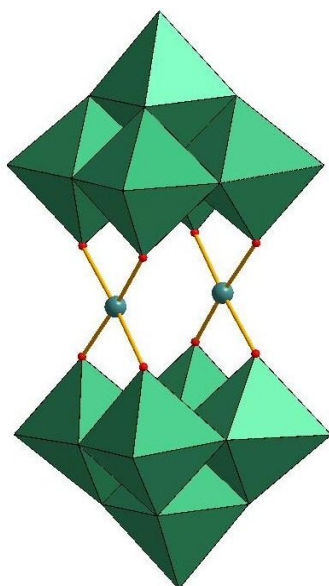


Figure 2.1 Combined polyhedral/ball-and-stick representation of $[\text{Pd}_2\text{W}_{10}\text{O}_{36}]^{8-}$.

The WO_6 octahedra are shown in green, and the balls represent Pd (aqua).

2.1.2 $[\text{Pd}_3(\alpha\text{-X}^{\text{III}}\text{W}_9\text{O}_{33})_2]^{12-}$ (X= Sb,As), $[\text{Pd}_2\text{WO}(\text{H}_2\text{O})(\text{A-}\alpha\text{-Si}^{\text{IV}}\text{W}_9\text{O}_{34})_2]^{12-}$ and $[\text{PdWO}(\text{H}_2\text{O})(\alpha\text{-As}^{\text{III}}\text{W}_9\text{O}_{33})_2]^{12-}$

Kortz and coworkers reported several Pd(II)-substituted polyoxoanions $[\text{Pd}_3(\alpha\text{-Sb}^{\text{III}}\text{W}_9\text{O}_{33})_2]^{12-}$,⁶ $[\text{Pd}_2\text{WO}(\text{H}_2\text{O})(\text{A-}\alpha\text{-Si}^{\text{IV}}\text{W}_9\text{O}_{34})_2]^{12-}$,⁷ $[\text{Pd}_3(\alpha\text{-As}^{\text{III}}\text{W}_9\text{O}_{33})_2]^{12-}$ and $[\text{PdWO}(\text{H}_2\text{O})(\alpha\text{-As}^{\text{III}}\text{W}_9\text{O}_{33})_2]^{12-}$,⁸ composed of two trilacunary Keggin moieties $[\alpha\text{-XW}_9\text{O}_{33}]^{9-}$ (X = As^{III} , Sb^{III}) or $[\alpha\text{-SiW}_9\text{O}_{34}]^{10-}$ linked via a central belt consisting of Pd(II)

centers and in two cases a $\{\text{WO}(\text{H}_2\text{O})\}^{4+}$ group. All Pd(II) centers in these compounds have square-planar coordination geometry and coordinate two oxygen atoms of each trilacunary Keggin subunit.

The palladium-substituted tungstoantimonate(III) $[\text{Cs}_2\text{Na}(\text{H}_2\text{O})_{10}\text{Pd}_3(\alpha\text{-SbW}_9\text{O}_{33})_2]^{9-}$ and tungstoarsenate(III) $[\text{Cs}_2\text{Na}(\text{H}_2\text{O})_8\text{Pd}_3(\alpha\text{-AsW}_9\text{O}_{33})_2]^{9-}$ have been synthesized with good yield by reaction of $\text{Pd}(\text{CH}_3\text{COO})_2$ with $\text{Na}_9[\text{X}^{\text{III}}\text{W}_9\text{O}_{33}]$ ($\text{X} = \text{Sb}, \text{As}$) in aqueous acidic medium (pH 4.8). Single-crystal X-ray analysis was carried out for $\text{Cs}_3\text{KNa}_5[\text{Cs}_2\text{Na}(\text{H}_2\text{O})_{10}\text{Pd}_3(\alpha\text{-SbW}_9\text{O}_{33})_2] \cdot 16.5\text{H}_2\text{O}$, which crystallizes in the monoclinic system, space group $P2_1/m$, with $a = 13.3963(13) \text{ \AA}$, $b = 19.5970(19) \text{ \AA}$, $c = 18.1723(17) \text{ \AA}$, $\beta = 100.416(2)^\circ$, and $Z = 2$; and $\text{Cs}_3\text{Na}_6[\text{Cs}_2\text{Na}(\text{H}_2\text{O})_8\text{Pd}_3(\alpha\text{-AsW}_9\text{O}_{33})_2] \cdot \text{NaCl} \cdot 15\text{H}_2\text{O}$ which also crystallizes in the monoclinic system, space group $P2_1/m$, with $a = 13.1842(5) \text{ \AA}$, $b = 19.6584(7) \text{ \AA}$, $c = 18.2377(6) \text{ \AA}$, $\beta = 100.7660(10)^\circ$, and $Z = 2$.

The polyanions consist of two lone-pair containing $\{\alpha\text{-X}^{\text{III}}\text{W}_9\text{O}_{33}\}$ ($\text{X} = \text{Sb}, \text{As}$) trilacunary Keggin moieties linked via three square-planar Pd(II) ions leading to a sandwich-type structure (Fig. 2.2). The palladium centers are equivalent and coordinate two oxygen atoms of each $\{\alpha\text{-X}^{\text{III}}\text{W}_9\text{O}_{33}\}$ subunit (Pd–O 1.974–1.990(10) $\text{ \AA}$ for $[\text{Cs}_2\text{Na}(\text{H}_2\text{O})_{10}\text{Pd}_3(\alpha\text{-SbW}_9\text{O}_{33})_2]^{9-}$). The central belt of the polyanions is completed by two Cs^+ and one Na^+ ions which occupy the vacancies between the adjacent palladium centers, reducing the symmetry of the polyanion to C_{2v} .^{6,8}

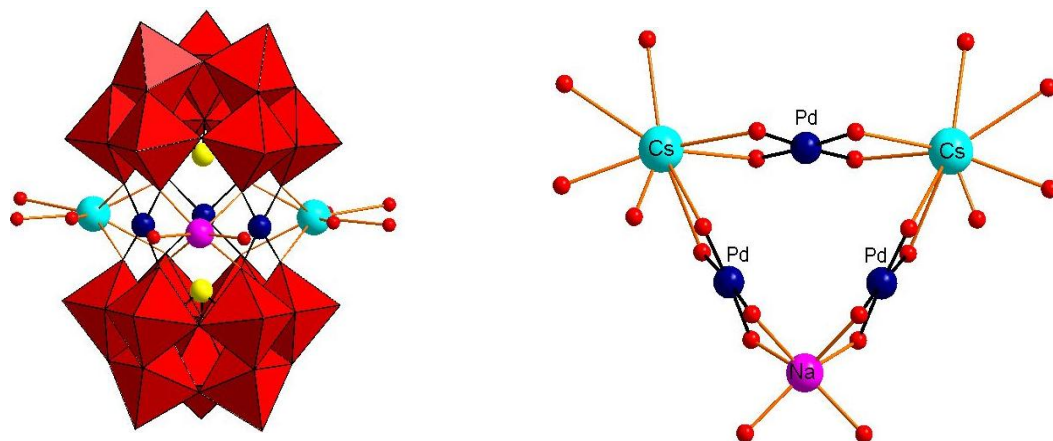


Figure 2.2 Combined polyhedral/ball-and-stick representation of $[\text{Cs}_2\text{Na}(\text{H}_2\text{O})_{10}\text{Pd}_3(\alpha\text{-SbW}_9\text{O}_{33})_2]^{9-}$ (left), ball-and-stick representation of the central belt in the polyanion (right). The WO_6 octahedra are shown in red, and the balls represent Pd (dark blue), Sb (yellow), Cs (sky blue), Na (purple), and O (red).

The di-palladium(II) substituted polyanion $[\text{Cs}_2\text{K}(\text{H}_2\text{O})_7\text{Pd}_2\text{WO}(\text{H}_2\text{O})(\text{A-}\alpha\text{-SiW}_9\text{O}_{34})_2]^{9-}$ (Fig. 2.3) has been prepared by reaction of $\text{Pd}(\text{CH}_3\text{COO})_2$ with $\text{K}_{10}[\text{A-}\alpha\text{-SiW}_9\text{O}_{34}]$ in aqueous acidic medium (pH 4.8). Single-crystal X-ray analysis was carried out for $\text{Cs}_3\text{K}_2\text{Na}_4[\text{Cs}_2\text{K}(\text{H}_2\text{O})_7\text{Pd}_2\text{WO}(\text{H}_2\text{O})(\text{A-}\alpha\text{-SiW}_9\text{O}_{34})_2] \cdot 5\text{H}_2\text{O}$, which crystallizes in the monoclinic system, space group $P2_1/n$, with $a=16.655(3)$ Å, $b=19.729(4)$ Å, $c=25.995(5)$ Å, $\beta = 95.46(3)^\circ$, and $Z = 4$.

The title polyanion composed of two $\{\text{A-}\alpha\text{-SiW}_9\text{O}_{34}\}$ lacunary Keggin moieties which are linked via a central belt consisting of a $\{\text{WO}(\text{H}_2\text{O})\}^{4+}$ group, two Pd(II) centers, one potassium ion and two cesium ions. The palladium(II) ions exhibit square-planar coordination geometry as they are bonded only to four oxo groups of the polyanion backbone. The potassium and cesium ions are also coordinated by terminal water molecules.⁷

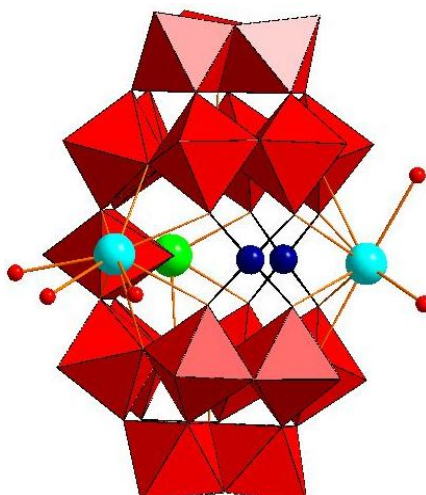


Figure 2.3 Combined polyhedral/ball-and-stick representation of $[\text{Cs}_2\text{K}(\text{H}_2\text{O})_7\text{Pd}_2\text{WO}(\text{H}_2\text{O})(\text{A}-\alpha\text{-SiW}_9\text{O}_{34})_2]^{9-}$. The WO_6 octahedra are shown in red, and the balls represent Pd (dark blue), K (green), Cs (sky blue), and O (red).

One more Pd(II) containing polyanion $[\text{Na}_2(\text{H}_2\text{O})_2\text{PdWO}(\text{H}_2\text{O})(\alpha\text{-AsW}_9\text{O}_{33})_2]^{10-}$ (Fig. 2.4) with the sandwich-like structure has been obtained by reaction of Pd(II) ions with $[\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{14-}$ in aqueous acidic medium (pH 4.8). The mixed cesium sodium salt of the polyanion, $\text{Cs}_3\text{Na}_7[\text{Na}_2(\text{H}_2\text{O})_2\text{PdWO}(\text{H}_2\text{O})(\alpha\text{-AsW}_9\text{O}_{33})_2] \cdot 1.5\text{NaCl} \cdot 22\text{H}_2\text{O}$, crystallizes in the triclinic system, space group $P\bar{1}$, with $a=13.2465(16)$ Å, $b=16.873(2)$ Å, $c=23.080(3)$ Å, $\alpha = 107.315(2)^\circ$, $\beta = 95.025(3)^\circ$, $\gamma = 98.040(3)^\circ$, and $Z = 2$.

The polyanion is composed of two trilacunary Keggin fragments $\{\text{B}-\alpha\text{-AsW}_9\text{O}_{33}\}$ connected by a central belt consisting of a $\{\text{WO}(\text{H}_2\text{O})\}^{4+}$ group, a square-planar Pd(II) center and two sodium ions, which leads to a structure with nominal C_s symmetry. One of the two sodium ions in the central belt is located in an addenda atom position, which appears to decrease the stability of this polyanion in solution.⁸

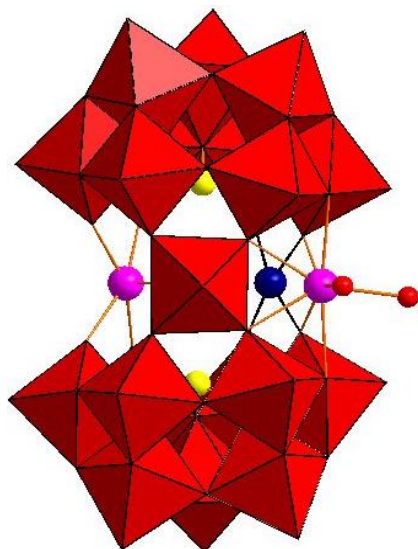


Figure 2.4 Combined polyhedral/ball-and-stick representation of $[\text{Na}_2(\text{H}_2\text{O})_2\text{PdWO}(\text{H}_2\text{O})(\alpha\text{-AsW}_9\text{O}_{33})_2]^{10-}$. The WO_6 octahedra are shown in red, and the balls represent Pd (dark blue), As (yellow), Na (purple), and O (red).

2.1.3 $[\text{Pd}_x\{\text{WO}(\text{H}_2\text{O})\}_{3-x}\{\alpha\text{-PW}_9\text{O}_{34}\}_2]^{(6+2x)-}$ ($x = 1 - 3$)

Very recently Villanneau *et al.* described the synthesis and characterization of a series of related sandwich-type complexes of Pd(II) ions and the trilacunary Keggin-type tungstophosphates with the general formula $[\text{Pd}_x\{\text{WO}(\text{H}_2\text{O})\}_{3-x}\{\alpha\text{-PW}_9\text{O}_{34}\}_2]^{(6+2x)-}$ ($x = 1-3$).^{9a} In these compounds two $[\text{A-}\alpha\text{-PW}_9\text{O}_{34}]^{9-}$ fragments are bonded by a central belt containing from one to three square-planar coordinated Pd(II) ions (Fig. 2.5). The synthesis of the tri-palladium(II)-substituted polyanion $[\text{Pd}_3(\text{PW}_9\text{O}_{34})_2]^{12-}$ was already reported more than 20 years ago by Knoth *et al.*,^{9b} but no structural characterization of this complex was provided, only chemical analysis.

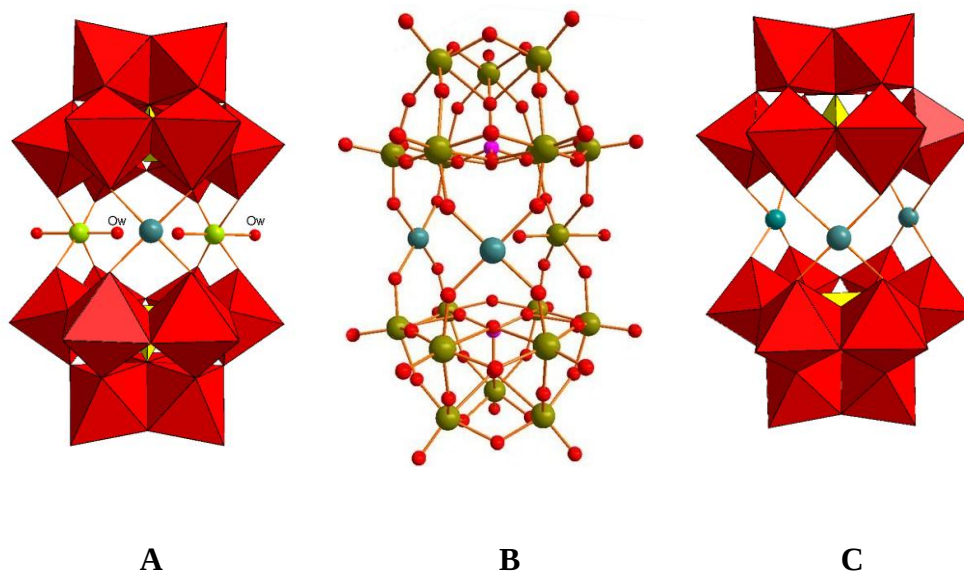


Figure 2.5 Polyhedral/ball-and-stick representation of

$[\text{Pd}_x\{\text{WO}(\text{H}_2\text{O})\}_{3-x}\{\alpha\text{-PW}_9\text{O}_{34}\}_2]^{(6+2x)-}$ for $x=1$ (**A**), $x=2$ (**B**), $x=3$ (**C**).

The WO_6 octahedra are shown in red and PO_4 tetrahedra – in yellow, and the balls represent Pd (aqua), W (yellow and olive green), P (purple) and O (red).

2.1.4 $[\text{Pd}_3(\text{H}_2\text{O})_9\text{Bi}_2\text{W}_{22}\text{O}_{76}]^{8-}$

Also very recently Kortz's group reported a 22-tungsto-2-bismuthate(III) with the Krebs-type structure decorated by three Pd(II) ions, $[\text{Pd}_3(\text{H}_2\text{O})_9\text{Bi}_2\text{W}_{22}\text{O}_{76}]^{8-}$. Three palladium centers are grafted to the terminal oxygens of the two external $\{\text{WO}_3\}$ groups in the $\{\text{Bi}_2\text{W}_{22}\}$ assembly. The important feature of this compound is the coordination of three water ligands to each of the Pd(II) ions which are bound to the tungstobismuthate core.^{10a}

The palladium(II) decorated tungstobismuthate(III) $[\text{Pd}_3(\text{H}_2\text{O})_9\text{Bi}_2\text{W}_{22}\text{O}_{76}]^{8-}$ has been prepared by a simple one-pot reaction of PdCl_2 with $[\text{Bi}_2\text{W}_{22}\text{O}_{74}(\text{OH})_2]^{12-}$ or $[\text{BiW}_9\text{O}_{33}]^{9-}$ in aqueous acidic medium at pH 4.8. Single-crystal X-ray analysis was carried out for the mixed sodium palladium(II) salt $\text{Na}_5\text{Pd}_{1.5}[\text{Pd}_3(\text{H}_2\text{O})_9\text{Bi}_2\text{W}_{22}\text{O}_{76}] \cdot 22\text{H}_2\text{O}$, which crystallizes in the triclinic system, space group $P\bar{1}$, with $a=12.8207(12)$ Å, $b=13.1305(14)$ Å, $c=17.407(2)$ Å, $\alpha = 108.610(7)^\circ$, $\beta = 98.928(7)^\circ$, $\gamma = 109.550(6)^\circ$, and $Z = 1$.

The polyanion is composed of two trilacunary Keggin fragments $[B\text{-}\beta\text{-BiW}_9\text{O}_{33}]^{9-}$ which are connected by two inner $\{\text{WO}_2\}$ and two outer $\{\text{WO}_3\}$ groups, resulting in the well-known Krebs type structure $[\text{Bi}_2\text{W}_{22}\text{O}_{74}(\text{OH})_2]^{12-}$.^{10b} This assembly is decorated by three square-planar Pd(II) centers disordered over six positions (see Fig. 2.6). The Pd(II) ions are grafted to the terminal oxygens of the external WO_3 group of the polyanion via a Pd–O–W bond (average Pd–O 1.959 Å). The remaining three coordination sites of Pd(II) are occupied by terminal water ligands (average Pd–OH₂ = 2.03 Å). This feature distinguishes the polyanion from all other known palladium containing POMs which have the Pd(II) ions fully incorporated into the POM framework. The external, highly accessible positions of the palladium ions in the polyanion, combined with the fact that they have terminal, presumably labile water ligands, render the polyanion highly interesting for heterogeneous catalytic applications.^{10a}

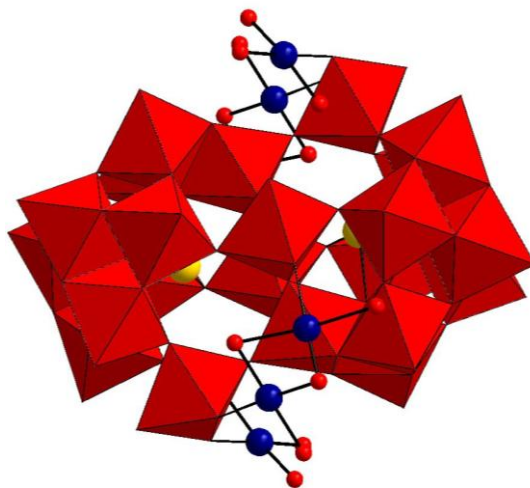


Figure 2.6 Combined polyhedral/ball-and-stick representation of $[\text{Pd}_3(\text{H}_2\text{O})_9\text{Bi}_2\text{W}_{22}\text{O}_{76}]^{8-}$.

The WO_6 octahedra are shown in red, and the balls represent Pd (dark blue), Bi (yellow), and O (red).

2.1.5 $[\text{Pd}^{\text{IV}}(\text{O})(\text{OH})\text{WO}(\text{OH}_2)(\text{PW}_9\text{O}_{34})_2]^{13-}$

Recently, Hill's group disclosed the preparation of a Pd(IV)-oxo compound, $\text{K}_{10}\text{Na}_3[\text{Pd}^{\text{IV}}(\text{O})(\text{OH})\text{WO}(\text{OH}_2)(\text{PW}_9\text{O}_{34})_2]$, by reaction of PdSO_4 with $[\text{A}-\alpha\text{-PW}_9\text{O}_{34}]^{9-}$ yielding $[\text{Pd}^{\text{II}}_3(\text{PW}_9\text{O}_{34})_2]^{12-}$ which undergoes rapid loss of Pd(II) to form $[\text{Pd}^{\text{II}}\text{WO}(\text{OH}_2)(\text{PW}_9\text{O}_{34})_2]^{12-}$ and air oxidation of this compound resulted in the Pd(IV)-oxo complex. This polyanion is composed of two $[\text{A}-\alpha\text{-PW}_9\text{O}_{34}]^{9-}$ Keggin moieties which are linked by a central belt consisting of a $\{\text{WO}(\text{H}_2\text{O})\}^{4+}$ group and a $\{\text{PdO}(\text{OH})\}^+$ group (Fig. 2.7). The tungsten center in the belt has an internal oxo ligand and an external aqua ligand, whereas the Pd center has an internal oxo and an external hydroxy ligand.^{11a,b} It must be noted that to date neither our group nor others have been able to reproduce this compound.^{9a,11c}

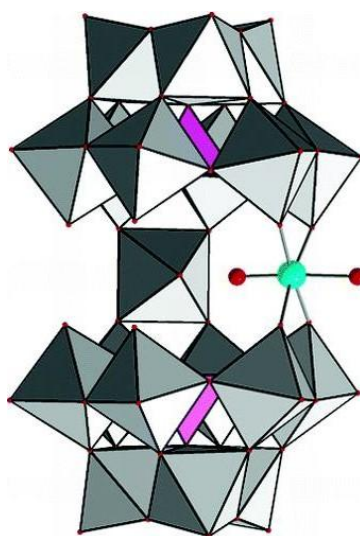


Figure 2.7 Combined polyhedral/ball-and-stick representation of $[\text{Pd}^{\text{IV}}(\text{O})(\text{OH})\text{WO}(\text{OH}_2)(\text{PW}_9\text{O}_{34})_2]^{13-}$. The WO_6 octahedra are shown in grey and PO_4 tetrahedra – in purple, the balls represent Pd (light green) and O (red).

2.1.6 $[\text{Pd}_2(\alpha\text{-PW}_{11}\text{O}_{39}\text{H}_{0.5})_2]^{9-}$, $[\text{anti-Pd}_2(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}\text{H}_{0.5})_2]^{15-}$ and
 $[\text{syn-Pd}_2(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}\text{H}_3)_2]^{10-}$

Several months ago Izarova, Kortz and co-workers published three Pd^{II} -containing tungstophosphates: $[\text{Pd}_2(\alpha\text{-PW}_{11}\text{O}_{39}\text{H}_{0.5})_2]^{9-}$ and two structural isomers of $[\text{Pd}_2(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}\text{H}_n)_2]^{(16-2n)-}$ (Fig. 2.8).¹² The compounds were prepared via simple synthetic procedures and their potassium salts were characterized by single-crystal X-ray diffraction, elemental analysis, IR and multinuclear (^{31}P and ^{183}W) NMR spectroscopy. This study sheds light on the long-standing question about the nature and structure of the actual products formed in the reaction of Pd^{II} ions with monolacunary Keggin-type $[\alpha\text{-XW}_{11}\text{O}_{39}]^{n-}$ and Wells-Dawson-type $[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ heteropolytungstates.

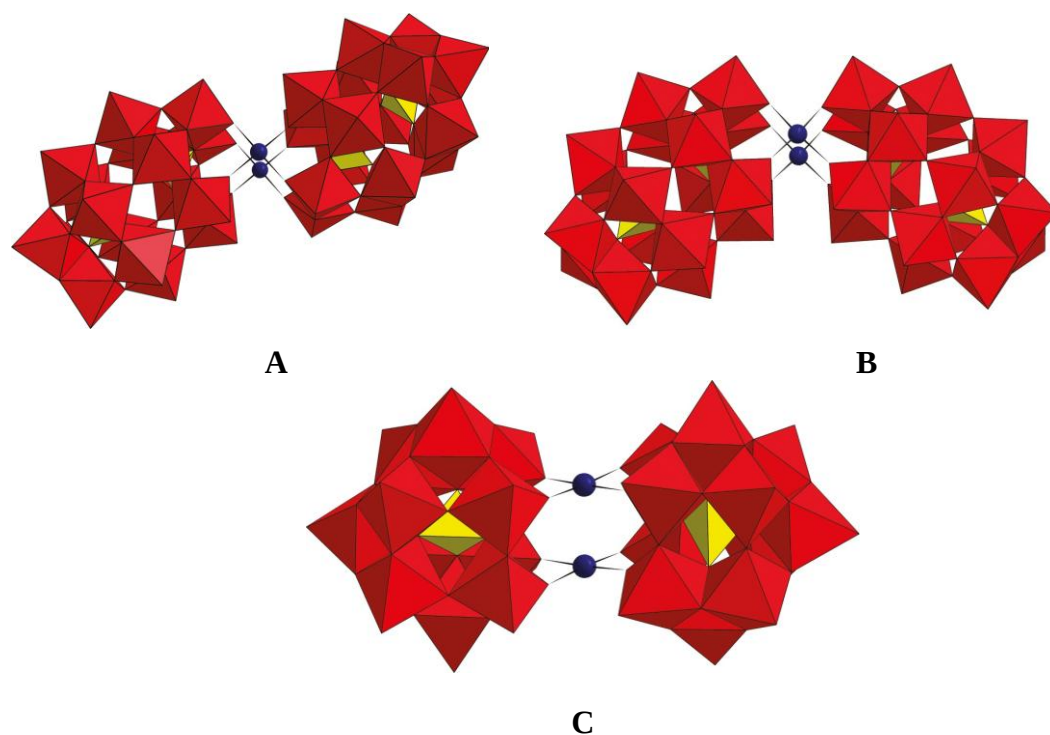


Figure 2.8 Combined polyhedral/ball-and-stick representation of $[\text{anti-Pd}_2(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}\text{H}_{0.5})_2]^{15-}$ (**A**), $[\text{syn-Pd}_2(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}\text{H}_3)_2]^{10-}$ (**B**) and $[\text{Pd}_2(\alpha\text{-PW}_{11}\text{O}_{39}\text{H}_{0.5})_2]^{9-}$ (**C**). Color legend: WO_6 , red octahedra; PO_4 , yellow tetrahedra; Pd, dark blue balls.

2.2 Polyoxopalladates

2.2.1 $[\text{Pd}^{\text{IV}}_2\text{Te}_4\text{O}_{22}(\text{OH})_2]^{14-}$ and $[\text{Pd}^{\text{IV}}_2(\text{IO}_6)_2\{\text{IO}_5(\text{OH})\}_2]^{10-}$

In 1991 Levason and co-workers prepared the first fully inorganic discrete tetratelluratodipalladate(IV) complex $[\text{Pd}^{\text{IV}}_2\text{Te}_4\text{O}_{22}(\text{OH})_2]^{14-}$ (Fig. 2.9) by boiling of prepared *in situ* $[\text{PdCl}_6]^{2-}$ and telluric acid in 4 M sodium hydroxide. The single crystal X-ray investigation of $\text{Na}_8\text{K}_2\text{H}_4[\text{Pd}^{\text{IV}}_2\text{Te}^{\text{VI}}_4\text{O}_{22}(\text{OH})_2]\cdot 20\text{H}_2\text{O}$ showed that the structure of $[\text{Pd}^{\text{IV}}_2\text{Te}^{\text{VI}}_4\text{O}_{22}(\text{OH})_2]^{14-}$ is based on two octahedral Pd^{IV} centres linked together via two $\mu_3\text{-}\{\text{TeO}_6\}$ groups.^{13a} Somewhat later the same authors obtained its periodate analogue $[\text{Pd}^{\text{IV}}_2(\text{IO}_6)_2\{\text{IO}_5(\text{OH})\}_2]^{10-}$, which has the structure very close to that of the tellurium containing complex.^{13b}

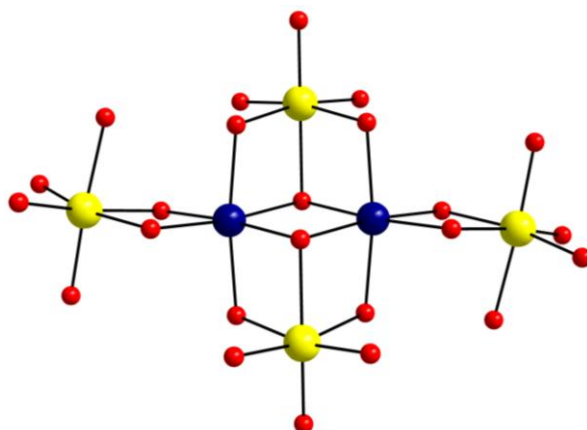


Figure 2.9 The structure of $[\text{Pd}^{\text{IV}}_2\text{Te}^{\text{VI}}_4\text{O}_{22}(\text{OH})_2]^{14-}$ (ball-and-stick representation).

Colour legend: Pd dark blue, Te yellow, O red.

2.2.2 $[\text{Pd}^{\text{II}}_{13}\text{As}^{\text{V}}_8\text{O}_{34}(\text{OH})_6]^{8-}$

In 2008 Kortz and co-workers discovered a simple open-beaker procedure for the synthesis of late-transition-metal based POMs.^{14a} The approach is based on the condensation of $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$ or $[\text{Au}(\text{OH})_4]^-$ complexes in aqueous media and allows to obtain the water soluble polyoxopalladates(II) and –aurates (II).¹⁴ The first POM built exclusively by Pd(II)

ions $[\text{Pd}_{13}\text{As}^{\text{V}}\text{O}_{34}(\text{OH})_6]^{8-}$ (**Pd₁₃As**) is readily formed in a one-pot self-assembly reaction of PdCl_2 and As_2O_5 in aqueous acetic medium (pH 6.1). The single crystal X-ray analysis was carried out for the sodium salt $\text{Na}_8[\text{Pd}_{13}\text{As}_8\text{O}_{34}(\text{OH})_6]\cdot 42\text{H}_2\text{O}$, which crystallizes in the triclinic system, space group *P*-1, with $a=12.7477(8)$ Å, $b=13.1633(10)$ Å, $c=14.4539(16)$ Å, $\alpha=105.069(5)^\circ$, $\beta=109.731(5)^\circ$, $\gamma=105.814(4)^\circ$, and $Z=1$. The polyanion was also characterized by elemental analysis, IR, TGA and electrochemistry. It was also shown that the polyanion is a stable and active catalyst for oxidation of benzylalcohol by O_2 in aqueous solution.

The structure of the polyanion can be described in terms of Platonic and Archimedean solids (regular polyhedra and polyhedra with two types of faces but only one type of vertex, respectively) such as the cube, truncated cube, and cuboctahedron, which are arranged one inside another (Fig. 2.10, left). One of the 13 Pd(II) ions is located in the center of the structure. It is surrounded by eight oxygen atoms situated at the vertices of a distorted cube, four of which are coordinated by the central Pd(II) ion. The other twelve palladium(II) ions surround the $\{\text{PdO}_8\}$ motif, resulting in an approximate cuboctahedron arrangement. The 24 “outer” oxygen atoms form a truncated cube-shaped shell, which is capped by eight positively charged $\text{As}^{\text{V}}\text{O}^{3+}$ groups forming an external, cube-shaped shell. The resulting “molecular nanocube” **Pd₁₃As** has an edge length of about 1 nm and hence a volume of about 1 nm^3 (Fig. 2.10, right). Interestingly, all thirteen palladium(II) ions in the polyanion retain square-planar coordination geometry, in marked contrast to all other discrete POMs, which generally contain metals in octahedral environments.^{14a}

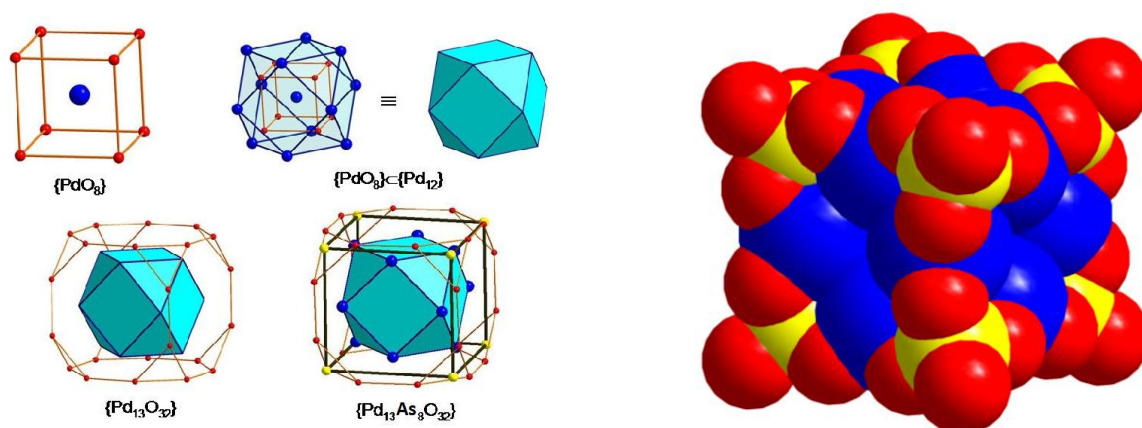


Figure 2.10 Structural representation of $[\text{Pd}^{\text{II}}_{13}\text{As}^{\text{V}}_8\text{O}_{34}(\text{OH})_6]^{8-}$ (**Pd₁₃As**)

in terms of Platonic and Archimedean solids (left). Space-filling view of **Pd₁₃As** (right).

Colour code: Pd (blue), As (yellow), and O (red).

2.2.3 $[\text{Pd}_{13}(\text{PhAs})_8\text{O}_{32}]^{6-}$ and $[\text{Pd}_{13}\text{Se}_8\text{O}_{32}]^{6-}$

Later on following the synthetic approach described in previous paragraph 2.2.2, Kortz and co-workers prepared two derivatives of **Pd₁₃As**, namely $[\text{Pd}^{\text{II}}_{13}(\text{PhAs})_8\text{O}_{32}]^{6-}$ (**Pd₁₃PhAs**) and $[\text{Pd}^{\text{II}}_{13}\text{Se}_8\text{O}_{32}]^{6-}$ (**Pd₁₃Se**), where eight AsO_4^{3-} capping groups are replaced by phenylarsonate $\text{PhAs}^{\text{V}}\text{O}_3^{2-}$ and lone pair containing selenite $\text{Se}^{\text{IV}}\text{O}_3^{2-}$ respectively. Interestingly the nature of the external heterogroup influences the coordination geometry of the central Pd^{II} leading to unusual coordination numbers 6 and 8 for this ion in the **Pd₁₃Se** and **Pd₁₃PhAs**, correspondingly.

Two heteropolyoxopalladates **Pd₁₃PhAs** and **Pd₁₃Se** were prepared by self-assembly reactions of $\text{Pd}(\text{OAc})_2$ with PhAsO_3H_2 or SeO_2 , respectively, and isolated as the hydrated sodium salts $\text{Na}_6[\text{Pd}^{\text{II}}_{13}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}] \cdot 24\text{H}_2\text{O}$ and $\text{Na}_6[\text{Pd}^{\text{II}}_{13}\text{Se}^{\text{IV}}_8\text{O}_{32}] \cdot 10\text{H}_2\text{O}$, respectively.

The structure of the polyoxopalladate core $\{\text{Pd}_{13}\text{X}_8\text{O}_{32}\}$ ($\text{X} = \text{As}^{\text{V}}, \text{Se}^{\text{IV}}$) in **Pd₁₃PhAs** and **Pd₁₃Se** is very similar to that in **Pd₁₃As** (Fig. 2.11).

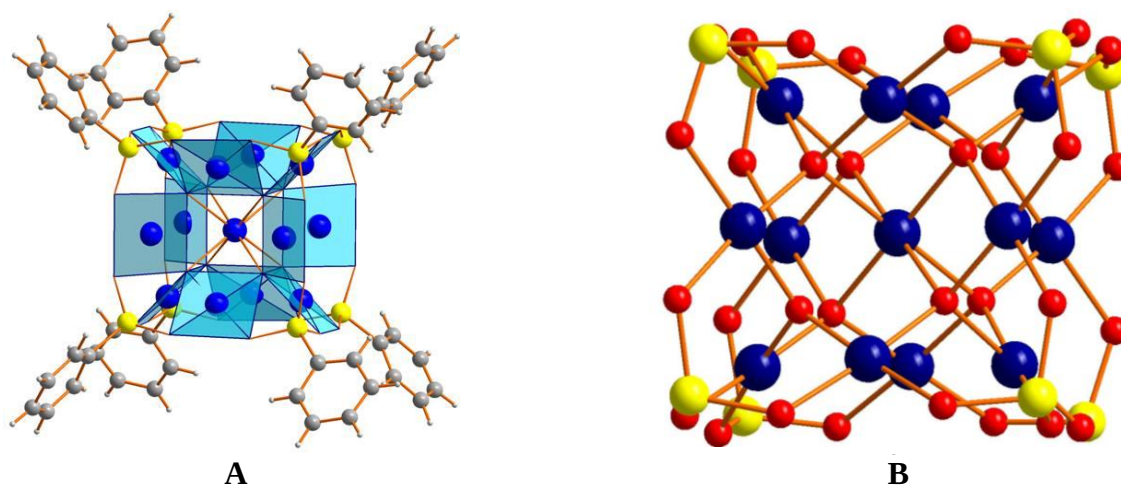


Figure 2.11 Combined polyhedral/ball-and-stick representation of $[\text{Pd}^{\text{II}}_{13}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}]^{6-}$ (**A**) and ball-and-stick structure of $[\text{Pd}^{\text{II}}_{13}\text{Se}^{\text{IV}}_8\text{O}_{32}]^{6-}$ (**B**).

Colour code: Pd blue, As and Se yellow, O red, C grey, H light grey.

The main difference between these three polyanions is the coordination environment of the central Pd(II) ion. In **Pd₁₃As** the central palladium has square-planar coordination geometry, as the remaining 12 outer metal centers. The four central Pd–O distances in **Pd₁₃As** are 2.081(5) and 2.090(5) Å and about 2.874 to 2.879 Å for the other four (non-coordinated) oxygen atoms of the “inner” distorted cube-shaped shell. The coordination number of the central Pd(II) in **Pd₁₃PhAs** is eight (coordination polyhedron is a cube). In the Se derivative **Pd₁₃Se** the coordination number of the central Pd(II) is six with a trigonally compressed octahedral coordination sphere. What we have observed for **Pd₁₃PhAs** is apparently the first example of an eight-coordinate Pd(II) ion. Thus, surprisingly, the palladium-oxo shells can stabilize high coordination numbers (6 and 8) for the central Pd(II).

Hence, polyanion $[\text{Pd}^{\text{II}}_{13}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}]^{6-}$ is the first example of a palladium(II) based complex where Pd coordinates 8 ligands. Magnetic/EPR measurements indeed proved that the compound $\text{Na}_6[\text{Pd}^{\text{II}}_{13}(\text{PhAs})_8\text{O}_{32}] \cdot 24\text{H}_2\text{O}$ is paramagnetic with $S=1$, which is in full agreement with our proposed model of an 8-coordinated central Pd^{II} ion.^{14b}

2.2.4 $[\text{Pd}^{\text{II}}_{15}\text{P}^{\text{V}}_{10}\text{O}_{50}]^{20-}$

Kortz and co-workers reported that the self-assembly reaction of $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$ in phosphate buffer (pH 6.5) leads to a star-shaped polyoxo-15-palladate (II) $[\text{Pd}^{\text{II}}_{15}\text{P}^{\text{V}}_{10}\text{O}_{50}]^{20-}$ (**Pd₁₅P₁₀**). Polyanion **Pd₁₅P₁₀** has been obtained as a hydrated sodium salt $\text{Na}_{12}[\text{Pd}_{0.4}\text{Na}_{0.6}\text{Pd}_{15}\text{P}_{10}\text{O}_{50}\text{H}_{6.6}]\cdot 36\text{H}_2\text{O}$ and characterized by single-crystal XRD, elemental analysis, IR, TGA, ^{31}P NMR and electrochemistry.

The $\text{Na}_{12}[\text{Pd}_{0.4}\text{Na}_{0.6}\text{Pd}_{15}\text{P}_{10}\text{O}_{50}\text{H}_{6.6}]\cdot 36\text{H}_2\text{O}$ crystallizes in the monoclinic system, space group $P2_1/n$, with $a = 15.9596(10)$ Å, $b = 27.0477(18)$ Å, $c = 25.8721(17)$ Å, $\beta = 103.405(4)^\circ$, and $Z = 8$.

The idealized structure of **Pd₁₅P₁₀** has 5-fold symmetry and contains 15 Pd^{II} centers and 10 P heteroatoms. The fifteen Pd^{II} ions form a pentacapped pentagonal prism (a pentagonal prism with every square face capped by one additional vertex) which encapsulates an $\{\text{O}_{10}\}$ pentagonal prism. Every oxygen from the inner $\{\text{O}_{10}\}$ motif is coordinated to three Pd^{II} ions forming a trigonal face in the $\{\text{Pd}_{15}\}$ polyhedron (Fig. 2.12).

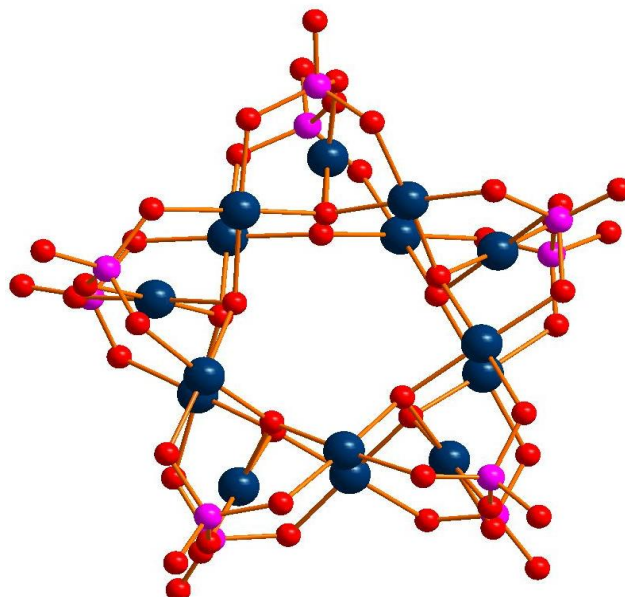


Figure 2.12 Ball-and-stick representation of $[\text{Pd}_{15}\text{P}_{10}\text{O}_{50}]^{20-}$ (**Pd₁₅P₁₀**).

Color code: Pd blue, P pink, O red.

The polyoxopalladate shell **Pd₁₅P₁₀** has the shape of a double five-point star with an approximate diameter of 1.5 nm and possesses idealized D_{5h} symmetry.

The preliminary catalytic studies of $\text{Na}_{12}[\text{Pd}_{0.4}\text{Na}_{0.6}\text{Pd}_{15}\text{P}_{10}\text{O}_{50}\text{H}_{6.6}]\cdot 36\text{H}_2\text{O}$ showed that this compound is active as a catalyst in alcohol oxidation by dioxygen.^{14c}

2.2.5 $[\text{NaPd}_{15}\text{Se}_{10}\text{O}_{40}]^{9-}$

Very recently Delferro *et al.* reported a structural analogue of pentagonal star-shaped polyoxopalladate **Pd₁₅P₁₀** $[\text{NaPd}_{15}\text{Se}_{10}\text{O}_{40}]^{9-}$ comprised of 15 Pd^{II} metal centers and 10 selenite heterogroups instead of 10 phosphate moieties in the former one. In addition a Na^+ cation is placed in the center of the cyclic **Pd₁₅Se₁₀** polyanion (Fig. 2.13). The **Pd₁₅Se₁₀** derivative was prepared by self-assembly of $\text{Pd}(\text{CH}_3\text{COO})_2$ and Na_2SeO_3 in a $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (5:1) mixture at room temperature thus suggesting one more synthetic route (a condensation of noble metal salt with an appropriate heterogroup in organic or mixed organic-aqueous media with further recrystallization of the obtained solid from water) to noble metal based POMs.¹⁵

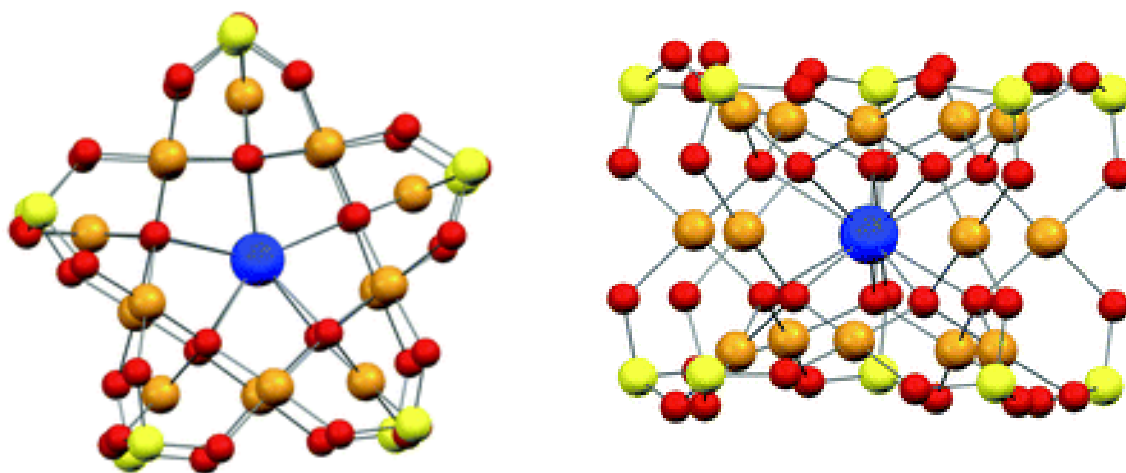


Figure 2.13 Ball-and-stick representations of $[\text{NaPd}_{15}\text{Se}_{10}\text{O}_{40}]^{9-}$.

View along 5-fold axis (left) and perpendicular to the 5-fold axis (right).

Colour legend: Pd orange, Se yellow, O red and Na blue balls.

2.2.6 $[\text{Pd}_2\text{C}\text{H}_7\text{Pd}^{\text{II}}_{15}\text{O}_{10}(\text{P}^{\text{V}}\text{O}_4)_{10}]^{13-}$

Recently Cronin's group was able to obtain $[\text{H}_7\text{Pd}^{\text{II}}_{15}\text{O}_{10}(\text{P}^{\text{V}}\text{O}_4)_{10}]^{13-}$ (**Pd₁₅**) and place two additional Pd^{II} ions in the center of **Pd₁₅** macrocycle resulting in $[\text{Pd}_2\text{C}\text{H}_7\text{Pd}^{\text{II}}_{15}\text{O}_{10}(\text{P}^{\text{V}}\text{O}_4)_{10}]^{13-}$ polyanion (**Pd₁₇**). Both of the compounds were characterized by X-ray crystallographic analysis, ^{31}P NMR (see Fig. 2.14), CSI-MS and XPS. Solution studies indicate that the empty host and filled guest complex are in equilibrium with each other.¹⁶

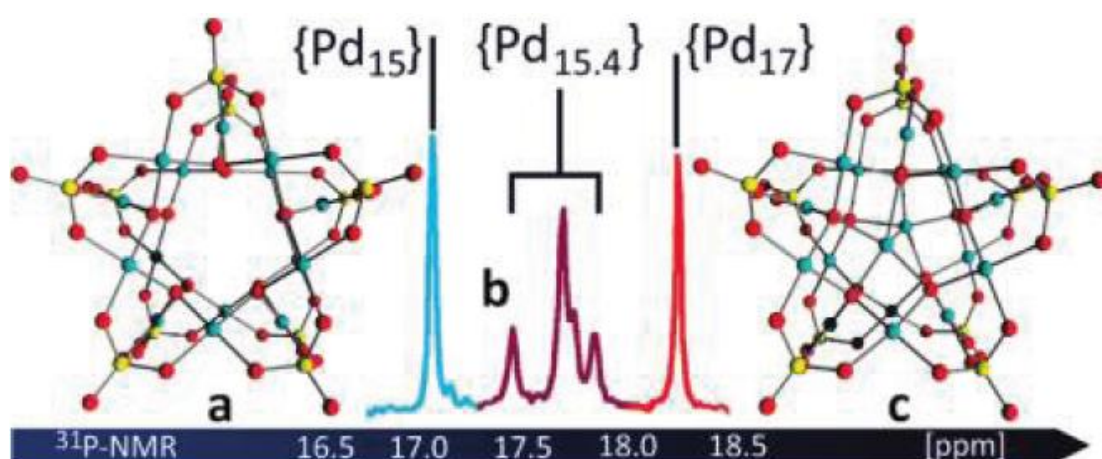


Figure 2.14 (a) Top view of the structure $[\text{H}_7\text{Pd}^{\text{II}}_{15}\text{O}_{10}(\text{P}^{\text{V}}\text{O}_4)_{10}]^{13-}$; (b) ^{31}P NMR chemical shifts of phosphate ligand in the structures $\{\text{Pd}_{15}\}$ (blue), $\{\text{Pd}_2\text{C}\text{Pd}_{15}\}$ (red), and reported $\{\text{Pd}_{15.4}\}$ (purple); (c) Top view of the structure of $[\text{Pd}_2\text{C}\{\text{H}_7\text{Pd}^{\text{II}}_{15}\text{O}_{10}(\text{P}^{\text{V}}\text{O}_4)_{10}\}]^{9-}$.

Colour legend: Pd = blue, P = yellow, O = red spheres.

2.2.7 $[\text{Pd}^{\text{II}}_7\text{V}^{\text{V}}_6\text{O}_{24}(\text{OH})_2]^{6-}$

The condensation of $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$ in the presence of vanadate ion resulted in a mixed-metal POM $[\text{Pd}^{\text{II}}_7\text{V}^{\text{V}}_6\text{O}_{24}(\text{OH})_2]^{6-}$ (**Pd₇V₆**) comprising seven square-planar $\text{Pd}^{\text{II}}\text{O}_4$, four tetrahedral $\text{V}^{\text{V}}\text{O}_4$ and two square-pyramidal $\text{V}^{\text{V}}\text{O}_5$ addenda units. The title polyoxoanion has a shape of a bowl (Fig. 2.15, upper left) and consists of two identical $\{\text{Pd}_3\text{V}_3\text{O}_{11}\}$ units (Fig. 2.15, upper middle), linked through four μ_2 -oxo-bridges, and one additional Pd^{II} center that forms the bottom of the “bowl” (Fig. 2.15, lower left).

The solution stability of **Pd₇V₆** has been demonstrated by ⁵¹V NMR spectroscopy. The ⁵¹V NMR spectrum of **Pd₇V₆** exhibits two peaks ($\delta = -284.8$ and -485.3 ppm) with approximate relative intensities 1:2 in full agreement with the solid state structure of $\text{K}_6[\text{Pd}^{\text{II}}_7\text{V}^{\text{V}}_6\text{O}_{24}(\text{OH})_2] \cdot 6\text{H}_2\text{O}$ (Fig. 2.15, right).

The DFT calculations of ⁵¹V NMR chemical shifts of **Pd₇V₆** suggested that the polyoxo-6-vanado(V)-7-palladate(II) in aqueous solution is most probably present as a $[\text{K}_7\text{HPd}_7\text{V}_6\text{O}_{25}(\text{OH})]^+$ assembly involving a counter-charged shell of potassium cations.^{14d}

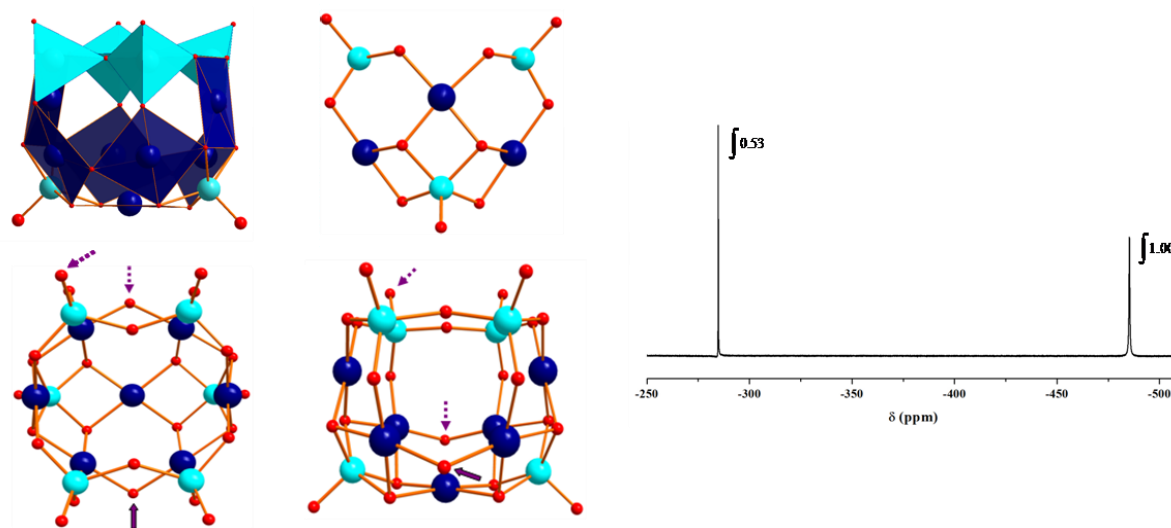


Figure 2.15 Combined ball-and-stick/polyhedral representation of $[\text{Pd}^{\text{II}}_7\text{V}^{\text{V}}_6\text{O}_{24}(\text{OH})_2]^{6-}$ (top left). Ball-and-stick representation of the $\{\text{Pd}_3\text{V}_3\text{O}_{11}\}$ fragment (top right) in **Pd₇V₆**.

Polyanion **Pd₇V₆** is also shown with a view into the cavity along the 2-fold axis and from the side (bottom). Colour legend: Pd dark blue, V turquoise, O red balls; $\{\text{PdO}_4\}$ blue squares, $\{\text{VO}_4\}$ turquoise tetrahedra. Protonated oxygens are highlighted by a solid arrow and partially protonated oxygens by a dashed arrow.

⁵¹V NMR spectrum measured at room temperature on $\text{K}_6[\text{Pd}^{\text{II}}_7\text{V}^{\text{V}}_6\text{O}_{24}(\text{OH})_2] \cdot 6\text{H}_2\text{O}$ redissolved in $\text{H}_2\text{O} / \text{D}_2\text{O}$ (right). The peak area integrals are also shown.

2.3 References

1. a) Somorjai, G. A. *Introduction to Surface Chemistry and Catalysis*; Wiley&Sons: New York, 1994; b) Shelef, M. *Chem. Rev.* **1995**, 95, 209-225; c) Malleron, J.-L.; Fiaud, J.-C.; Legros, J.-Y. *Handbook of Palladium-Catalyzed Organic Reactions: Synthetic Aspects and Catalytic Cycles*; Academic Press: San Diego, CA, 1997; d) Aggarwal, S.; Monga, A. P.; Perusse, S. R.; Ramesh, R.; Ballarotto, V.; Williams, E. D.; Chalamala, B. R.; Wei, Y.; Reuss, R. H. *Science* **2000**, 287, 2235-2237; e) Nishihata, Y.; Mizuki, J.; Akao, T.; Tanaka, H.; Uenishi, M.; Kimura, M.; Okamoto, T.; Hamada, N. *Nature* **2002**, 418, 164-167; f) Stuchinskaya, T. L.; Kozhevnikov, I. V. *Catal. Commun.* **2003**, 4, 417-422; g) Mallat, T.; Baiker, A. *Chem. Rev.* **2004**, 104, 3037-3058; h) Beccalli, E. M.; Broggini, G.; Martinelli, M.; Sollocornola, S. *Chem. Rev.* **2007**, 107, 5318-5365.
2. a) Brink, G.-J.; Arends, I.W.C.E.; Sheldon, R.A. *Science* **2000**, 287, 1636-1639; b) Weinstock, I.A.; Barbuzzi, E.M.G.; Wemple, M.W.; Cowan, J.J.; Reiner, R.S.; Sonnen, D.M.; Heintz, R.A.; Bond, J.S.; Hill, C.L. *Nature* **2001**, 414, 191-195; c) Boring, E.; Geletii, Y.; Hill, C.L. in *Catalytic Activation of Dioxygen*; Simandi, L.I. Ed.; Kluwer: Dordrecht, **2001**; d) Neumann, R. in *Transition Metals for Fine Chemicals and Organic Synthesis*, Vol. 2, 2nd ed.; Bolm, C.; Beller, M. Eds.; Wiley-VCH: Weinheim, **2004**, 415-426; e) Nakagawa, Y.; Kamata, K.; Kotani, M.; Yamaguchi, K.; Mizuno, N. *Angew. Chem. Int. Ed.* **2005**, 44, 5136-5141; f) Okun, N.M.; Tarr, J.C.; Hilleshiem, D.A.; Zhang, L.; Hardcastle, K.I.; Hill, C.L. *J. Mol. Catal. A. Chem.* **2006**, 246, 11-17; g) Hill, C.L.; Anderson, T.M.; Han, J.W.; Hillesheim, D.A.; Geletii, Y.V.; Okun, N.M.; Cao, R.; Botar, B.; Musaev, D.G.; Morokuma, K. *J. Mol. Catal. A. Chem.* **2006**, 251, 234-238.
3. a) Pham, N.T.S.; Van Der Sluys, M.; Jones, C.W. *Adv. Synth. Catal.* **2006**, 348, 609-679; b) Goloboy, J. C.; Klemperer, W. G. *Angew. Chem. Int. Ed. Engl.* **2009**, 48, 3562-3564.

4. Putaj, P.; Lefebvre, F. *Coord. Chem. Rev.* **2011**, 255, 1642–1685.
5. Angus-Dunne, S.J.; Burns, R.C.; Craig, D.C.; Lawrance, G.A. *Chem. Commun.* **1994**, 523–524.
6. Bi, L.-H.; Reicke, M.; Kortz, U.; Keita, B.; Nadjo, L.; Clark, R.J. *Inorg. Chem.* **2004**, 43, 3915–3920.
7. Bi, L.-H.; Kortz, U.; Keita, B.; Nadjo, L.; Borrmann, H. *Inorg. Chem.* **2004**, 43, 8367–8372.
8. Bi, L.-H.; Kortz, U.; Keita, B.; Nadjo, L.; Daniels, L. *Eur. J. Inorg. Chem.* **2005**, 3034–3041.
9. a) Villanneau, R.; Renaudineau, S.; Herson, P.; Boubekeur, K.; Thouvenot, R.; Proust, A. *Eur. J. Inorg. Chem.* **2009**, 479–488; b) 22. Knoth, W. H.; Domaille, P.; Harlow, R. L. *Inorg. Chem.* **1986**, 25, 1577–1584.
10. a) Bi, L.-H.; Dickman, M.H.; Kortz, U. *Cryst.Eng.Comm.* **2009**, 11, 965–966; b) Bösing, M.; Loose, I.; Pohlmann, H.; Krebs, B. *Chem. Eur. J.*, **1997**, 3, 1232–1237.
11. a) Anderson, T.M.; Cao, R.; Slonkina, E.; Hedman, B.; Hodgson, K.O.; Hardcastle, K.I.; Neiwert, W.A.; Wu, S.; Kirk, M.L.; Knottenbelt, S.; Depperman, E.C.; Keita, B.; Nadjo, L.; Musaev, D.G.; Morokuma, K.; Hill, C.L. *J. Am. Chem. Soc.* **2005**, 127, 11948–11949; b) Anderson, T.M.; Cao, R.; Slonkina, E.; Hedman, B.; Hodgson, K.O.; Hardcastle, K.I.; Neiwert, W.A.; Wu, S.; Kirk, M.L.; Knottenbelt, S.; Depperman, E.C.; Keita, B.; Nadjo, L.; Musaev, D.G.; Morokuma, K.; Hill, C.L. *J. Am. Chem. Soc.* **2008**, 130, 2877–2877 (addition/correction); c) Kortz, U.; Lee, U.; Joo, H.-C.; Park, K.-M.; Mal, S.S.; Dickman, M.H.; Jameson, G.B. *Angew. Chem. Int. Ed.* **2008**, 47, 9383–9384.
12. Izarova, N. V.; Banerjee, A.; Kortz, U. *Inorg. Chem.* **2011**, 50, 10379–10386.
13. a) Levason, W.; Spicer, M.D.; Webster, M. *Inorg. Chem.* **1991**, 30, 967–971; b) Hector, A L.; Levason, W.; Webster, M. *Inorg. Chim. Acta.* **2003**, 343, 90–94.

14. a) Chubarova, E. V.; Dickman, M. H.; Keita, B.; Nadjó, L.; Miserque, F.; Mifsud, M.; Arends, I. W. C. E.; Kortz, U. *Angew. Chem.* **2008**, *120*, 9685-9689; *Angew. Chem. Int. Ed. Engl.* **2008**, *47*, 9542-9546; b) Izarova, N. V.; Dickman, M. H.; Biboum, R. N.; Keita, B.; Nadjó, L.; Ramachandran, V.; Dalal, N. S.; Kortz, U. *Inorg. Chem.* **2009**, *48*, 7504-7506; c) Izarova, N. V.; Biboum, R. N.; Keita, B.; Mifsud, M.; Arends, I.W.C.E.; Jameson, G. B.; Kortz, U. *Dalton Trans.* **2009**, *43*, 9385-9387; d) Izarova, N. V.; Vankova, N.; Banerjee, A.; Jameson, G. B.; Heine, T.; Schinle, F.; Hampe, O.; Kortz, U. *Angew. Chem.* **2010**, *42*, 7975-7980; *Angew. Chem. Int. Ed.* **2010**, *49*, 7807-7811; e) Barsukova, M.; Izarova, N. V.; Biboum, R. N.; Keita, B.; Nadjó, L.; Ramachandran, V.; Dalal, N. S.; Antonova, N. S.; Carbó, J.J.; Poblet, J. M.; Kortz, U. *Chem. Eur. J.* **2010**, *16*, 9076-9085; f) Izarova, N.V.; Vankova, N.; Heine, T.; Biboum, R.N.; Keita, B.; Nadjó, L.; Kortz, U. *Angew. Chem.* **2010**, *122*, 1930-1933; *Angew. Chem. Int. Ed. Engl.* **2010**, *49*, 1886-1889; g) Barsukova-Stuckart, M.; Izarova, N. V.; Jameson, G. B.; Ramachandran, V.; Wang, Z.; van Tol, J.; Dalal, N. S.; Ngo Biboum, R.; Keita, B.; Nadjó, L.; Kortz, U. *Angew. Chem.* **2011**, *123*, 2688-2692; *Angew. Chem. Int. Ed. Engl.* **2011**, *50*, 2639-2642.
15. Delferro, M.; Graiff, C.; Elviri, L.; Predieri, G. *Dalton Trans.* **2010**, *39*, 4479-4481.
16. Xu, F.; Scullion, R. A.; Yan, J.; Miras, H. N.; Busche, C.; Scandurra, A.; Pignataro, B.; Long, D.; Cronin, L. *J. Am. Chem. Soc.* **2011**, *133*, 4684-4686.

Chapter III Results

Synthesis and Characterization of Cuboid-shaped Lanthanide- and Transition Metal-containing Polyoxopalladates(II)

The work was mainly focused on the synthesis of various derivatives of the polyoxopalladate $[\text{Pd}^{\text{II}}_{13}\text{As}_8\text{O}_{34}(\text{OH})_6]^{8-}$ (**Pd₁₃As**) replacing the AsO_4 capping units by other groups (e.g. PO_4^{3-} , SbO_3^{3-} , PhPO_3^{2-}) and incorporating different kinds of metal ions (e.g. main group, transition metal, lanthanide) in the middle of the $\{\text{Pd}_{12}\text{L}_8\}$ (L=capping groups) structure type to study the structural and electronic flexibility and stability of the polyoxo-12-palladate shell. Used analytical techniques, synthesis and characterization of obtained compounds are described in this chapter.

3.1 General Methods and Materials

All reagents were purchased from commercial sources and used without further purification.

All of the obtained compounds were characterized by FT-IR spectroscopy, single crystal X-Ray diffraction (XRD) and thermogravimetric analysis (TGA). For some of the compounds the elemental analysis and solution study by multinuclear NMR spectroscopy were already done.

The combined results of three analytical methods namely single crystal XRD, elemental analysis and TGA were taken into account to determine the molecular formulas of the compounds.

3.1.1 Single Crystal X-Ray Diffraction (XRD) Analysis

Crystal data for the structures of obtained compounds were collected on a Bruker Kappa X8 APEX CCD single-crystal diffractometer equipped with a sealed Mo tube and a graphite monochromator ($\lambda = 0.71073 \text{ \AA}$). The crystals were mounted in Hampton cryoloops using light oil for data collection at 173 K and 100 K or on glass fiber using glue for data collection at room temperature. The SHELX software package (Bruker) was used to solve and refine the structures.¹ An empirical absorption correction was applied using the SADABS program.² The structures were solved by direct methods and refined by the full-matrix least-squares method ($\sum w(|F_o|^2 - |F_c|^2)^2$) with anisotropic thermal parameters for all atoms included in the model. The H atoms of the crystal waters were not located.

3.1.2 Fourier Transform Infrared (FT-IR) Spectroscopy

The IR spectra were recorded on KBr disk using a Nicolet-Avatar 370 spectrometer between 400 and 4000 cm^{-1} . The following abbreviation was used to assign the peak intensities: w: weak; m: medium; s: strong; vs: very strong; b: broad; sh: shoulder.

3.1.3 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was carried out on a TA Instruments SDT Q600 thermobalance with 10-30 mg samples in 100 μL alumina pans under a 100 $\text{mL}\cdot\text{min}^{-1}$ flow of nitrogen; the temperature was ramped from 20 $^{\circ}\text{C}$ to 1000 $^{\circ}\text{C}$ at a rate of 5 $^{\circ}\text{C}\cdot\text{min}^{-1}$.

3.1.4 Nuclear Magnetic Resonance (NMR) Spectroscopy

The NMR spectra of several obtained compounds were recorded in $\text{H}_2\text{O}/\text{D}_2\text{O}$ solution on a 400 MHz JEOL ECX instrument at room temperature using 5 mm tubes for ^1H , ^{13}C , ^{31}P , ^{77}Se and 10 mm tubes for ^{183}W and ^{89}Y NMR. The respective resonance frequencies were 399.78 MHz (^1H), 100.71 MHz (^{13}C), 162.14 MHz (^{31}P), 76.39 MHz (^{77}Se), 16.69 MHz (^{183}W) and 19.63 MHz (^{89}Y). The chemical shifts are reported with respect to the

references Si(CH₃)₄ (¹H and ¹³C), 85% H₃PO₄ (³¹P), H₂SeO₃ (⁷⁷Se, δ = 1302 ppm), Na₂WO₄ (¹⁸³W) and Y(NO₃)₃ (⁸⁹Y).

3.1.5 Bond Valence Sum (BVS) Calculations

The BVS calculations were performed with a program copyrighted by Chris Hormillosa & Sean Healy and distributed by I. D. Brown.³

3.2 Lanthanide- and Yttrium-containing Polyoxopalladates

with Phenylarsonate Capping Groups

The previous results showed that the {Pd₁₂L₈} polyoxopalladate shell can adjust to the coordination requirements of the encapsulated guest cation. Interestingly, the nature of the capping group influences the coordination geometry of the central Pd^{II} ion leading to unusual coordination numbers for palladium(II), such as six in [Pd₁₃Se₈O₃₂]⁶⁻ (**Pd₁₃Se**) and even eight in [Pd₁₃(PhAs)₈O₃₂]⁶⁻ (**Pd₁₃PhAs**).⁴ This prompted us to study the possibility to incorporate in the center of the polyoxo-12-palladate shell the ions for which large coordination number is more common, such as lanthanides. The incorporation of lanthanide ions into POM frameworks has already led to compounds with interesting luminescence, magnetic, and Lewis acid catalytic properties.⁵ Moreover, using lanthanide ions has allowed the construction of solid 1D, 2D, or 3D POM assemblies as well as very large discrete polyanions.⁶

Thus a series of novel yttrium and lanthanide containing polyoxopalladates with general formula Na₅[M^{III}Pd^{II}₁₂(As^VPh)₈O₃₂]⁻·yH₂O, where M = Y (**Y-1a**), Pr (**Pr-1b**), Nd (**Nd-1c**), Sm (**Sm-1d**), Eu (**Eu-1e**), Gd (**Gd-1f**), Tb (**Tb-1g**), Dy (**Dy-1h**), Ho (**Ho-1i**), Er (**Er-1j**), Tm (**Tm-1k**), Yb (**Yb-1l**), Lu (**Lu-1m**), y=15–27 has been obtained. The compounds **Y-1a** – **Lu-1m** have been synthesized by reaction of Pd₃(CH₃COO)₆, phenylarsonic acid and the respective salt of the M³⁺ ion in 0.5 M aqueous sodium acetate solution (pH 6.9) in yields

ranging from 9% (for **Pr-1b**) to 43% (for **Y-1a**), and characterized in the solid state by FT-IR spectroscopy, TGA, single-crystal XRD and elemental analysis. These compounds are stable towards air and light in the solid state and can be successfully recrystallized several times from water.

3.2.1 Synthetic Procedures

Na₅[YPd^{II}₁₂(As^VPh)₈O₃₂]·21H₂O (Y-1a**):** Pd₃(CH₃COO)₆ (0.140 g, 0.208 mmol), PhAsO₃H₂ (0.125 g, 0.619 mmol) and Y(NO₃)₃·6H₂O (0.060 g, 0.156 mmol) were dissolved in 5 ml of sodium acetate solution (0.5 M, pH 6.9). While stirring, the solution was heated to 80°C for 90 min. Then it was cooled to room temperature, filtered and allowed to crystallize at room temperature. Dark red-brown crystals were obtained after several days, filtered off and air dried. Yield: 0.170 g (43 % based on {Pd}). Elemental analysis calcd (%): Na 3.20, Y 2.48, Pd 35.60, As 16.71, C 16.07, H 2.30; found: Na 3.21, Y 2.51, Pd 35.50, As 16.70, C 15.80, H 2.43. IR (2% KBr pellet, ν/cm^{-1}): 1629 (m), 1480 (w), 1439 (m), 1178 (w), 1094 (m), 1024 (w), 800 (s), 744 (s), 694 (s), 611 (s), 543 (s), 438 (s).

Na₅[PrPd^{II}₁₂(As^VPh)₈O₃₂]·19H₂O (Pr-1b**):** The compound was prepared by exactly the same procedure as **Y-1a**, but by using Pr(CH₃COO)₃·H₂O (0.052 g, 0.156 mmol) instead of Y(NO₃)₃·6H₂O. Dark red-brown crystals were obtained. Yield: 0.035 g (9 % based on {Pd}). Elemental analysis calcd (%): Na 3.19, Pr 3.91, Pd 35.44, As 16.63, C 16.00, H 2.18; found: Na 3.31, Pr 3.90, Pd 35.30, As 16.40, C 15.80, H 2.41. IR (2% KBr pellet, ν/cm^{-1}): 1629(m), 1479(w), 1438(m), 1180(w), 1096(m), 1024(w), 795(s), 745(s), 694(s), 596(s), 545(s), 431(s).

Na₅[NdPd^{II}₁₂(As^VPh)₈O₃₂]·24H₂O (Nd-1c**):** The compound was prepared by exactly the same procedure as **Y-1a**, but by using Nd(CH₃COO)₃·H₂O (0.053 g, 0.156 mmol). Dark red-brown crystals were obtained. Yield: 0.100 g (26 % based on {Pd}). Elemental analysis calcd (%): Na 3.11, Nd 3.90, Pd 34.54, As 16.21, C 15.60, H 2.40; found: Na 3.15, Nd 3.65,

Pd 34.30, As 16.10, C 15.30, H 2.39. IR (2% KBr pellet, ν/cm^{-1}): 1627 (m), 1479 (w), 1438 (m), 1180 (w), 1094 (m), 1024 (w), 795 (s), 744 (s), 693 (s), 598 (s), 545 (s), 434 (s).

$\text{Na}_5[\text{SmPd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}] \cdot 18\text{H}_2\text{O}$ (Sm-1d): The compound was prepared by exactly the same procedure as **Y-1a**, but by using $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.069 g, 0.156 mmol). Dark red-brown crystals were obtained. Yield: 0.090 g (23 % based on {Pd}). Elemental analysis calcd (%): Na 3.20, Sm 4.18, Pd 35.52, As 16.67, C 16.04, H 2.13; found: Na 3.24, Sm 4.18, Pd 35.30, As 16.70, C 16.10, H 2.27. IR (2% KBr pellet, ν/cm^{-1}): 1629 (m), 1481 (w), 1438 (m), 1176 (w), 1096 (m), 1024 (w), 797 (s), 745 (s), 694 (s), 602 (s), 544 (s), 435 (s).

$\text{Na}_5[\text{EuPd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}] \cdot 21\text{H}_2\text{O}$ (Eu-1e): The compound was prepared by exactly the same procedure as **Y-1a**, but by using $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (0.057 g, 0.156 mmol). Dark red-brown crystals were obtained. Yield: 0.120 g (32 % based on {Pd}). Elemental analysis calcd (%): Na 3.15, Eu 4.16, Pd 34.98, As 16.42, C 15.79, H 2.26; found: Na 3.15, Eu 4.16, Pd 34.90, As 16.30, C 15.80, H 2.34. IR (2% KBr pellet, ν/cm^{-1}): 1627 (m), 1477 (w), 1438 (m), 1178 (w), 1096 (m), 1024 (w), 797 (s), 745 (s), 694 (s), 603 (s), 543 (s), 435 (s).

$\text{Na}_5[\text{GdPd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}] \cdot 24\text{H}_2\text{O}$ (Gd-1f): The compound was prepared by exactly the same procedure as **Y-1a**, but by using $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ (0.058 g, 0.156 mmol). Dark red-brown crystals were obtained. Yield: 0.130 g (34 % based on {Pd}). Elemental analysis calcd (%): Na 3.10, Gd 4.24, Pd 34.42, As 16.16, C 15.54, H 2.39; found: Na 3.14, Gd 4.21, Pd 34.30, As 16.30, C 15.60, H 2.45. IR (2% KBr pellet, ν/cm^{-1}): 1629 (m), 1479 (w), 1438 (m), 1176 (w), 1094 (m), 1024 (w), 798 (s), 745 (s), 694 (s), 604 (s), 543 (s), 436 (s).

$\text{Na}_5[\text{TbPd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}] \cdot 22\text{H}_2\text{O}$ (Tb-1g): The compound was prepared by exactly the same procedure as **Y-1a**, but by using $\text{Tb}(\text{CH}_3\text{COO})_3 \cdot \text{H}_2\text{O}$ (0.055 g, 0.156 mmol). Dark red-brown crystals were obtained. Yield: 0.125 g (31 % based on {Pd}). Elemental analysis calcd (%): Na 3.13, Tb 4.32, Pd 34.75, As 16.31, C 15.69, H 2.3; found: Na 3.23, Tb 4.30, Pd

34.70, As 16.10, C 15.70, H 2.41. IR (2% KBr pellet, ν/cm^{-1}): 1627 (m), 1481 (w), 1440 (m), 1178 (w), 1094 (m), 1024 (w), 798 (s), 744 (s), 694 (s), 606 (s), 543 (s), 436 (s).

$\text{Na}_5[\text{DyPd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}]\cdot 19\text{H}_2\text{O}$ (Dy-1h): The compound was prepared by exactly the same procedure as **Y-1a**, but by using $\text{DyCl}_3\cdot 6\text{H}_2\text{O}$ (0.059 g, 0.156 mmol). Dark red-brown crystals were obtained. Yield: 0.095 g (24 % based on {Pd}). Elemental analysis calcd (%): Na 3.17, Dy 4.48, Pd 35.23, As 16.53, C 15.90, H 2.17; found: Na 3.20, Dy 4.47, Pd 35.20, As 16.30, C 15.80, H 2.24. IR (2% KBr pellet, ν/cm^{-1}): 1629 (m), 1479 (w), 1436 (m), 1180 (w), 1096 (m), 1024 (w), 798 (s), 745 (s), 694 (s), 607 (s), 542 (s), 437 (s).

$\text{Na}_5[\text{HoPd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}]\cdot 16\text{H}_2\text{O}$ (Ho-1i): The compound was prepared by exactly the same procedure as **Y-1a**, but by using $\text{HoCl}_3\cdot 6\text{H}_2\text{O}$ (0.059 g, 0.156 mmol). Dark red-brown crystals were obtained. Yield: 0.130 g (34 % based on {Pd}). Elemental analysis calcd (%): Na 3.22, Ho 4.69, Pd 35.74, As 16.77, C 16.13, H 2.03; found: Na 3.18, Ho 4.71, Pd 35.50, As 16.70, C 16.20, H 2.45. IR (2% KBr pellet, ν/cm^{-1}): 1627 (m), 1479 (w), 1438 (m), 1178 (w), 1094 (m), 1024 (w), 799 (s), 744 (s), 694 (s), 609 (s), 543 (s), 437 (s).

$\text{Na}_5[\text{ErPd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}]\cdot 27\text{H}_2\text{O}$ (Er-1j): The compound was prepared by exactly the same procedure as **Y-1a**, but by using $\text{Er}(\text{CH}_3\text{COO})_3\cdot \text{H}_2\text{O}$ (0.057 g, 0.156 mmol). Dark red-brown crystals were obtained. Yield: 0.155 g (40 % based on {Pd}). Elemental analysis calcd (%): Na 3.05, Er 4.43, Pd 33.84, As 15.88, C 15.28, H 2.51; found: Na 3.51, Er 4.35, Pd 33.70, As 15.70, C 15.90, H 2.92. IR (2% KBr pellet, ν/cm^{-1}): 1627 (m), 1479 (w), 1440 (m), 1178 (w), 1094 (m), 1026 (w), 799 (s), 744 (s), 694 (s), 610 (s), 542 (s), 436 (s).

$\text{Na}_5[\text{TmPd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}]\cdot 15\text{H}_2\text{O}$ (Tm-1k): The compound was prepared by exactly the same procedure as **Y-1a**, but by using $\text{TmCl}_3\cdot \text{H}_2\text{O}$ (0.060 g, 0.156 mmol). Dark red-brown crystals were obtained. Yield: 0.085 g (23 % based on {Pd}). Elemental analysis calcd (%): Na 3.23, Tm 4.75, Pd 35.88, As 16.84, C 16.20, H 1.98; found: Na 2.99, Tm 4.67, Pd 35.90,

As 16.90, C 16.40, H 2.43. IR (2% KBr pellet, ν/cm^{-1}): 1625 (m), 1479 (w), 1440 (m), 1178 (w), 1094 (m), 1026 (w), 799 (s), 744 (s), 694 (s), 612 (s), 542 (s), 437 (s).

$\text{Na}_5[\text{YbPd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}]\cdot 18\text{H}_2\text{O}$ (Yb-1l): The compound was prepared by exactly the same procedure as **Y-1a**, but by using $\text{Yb}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ (0.070 g, 0.156 mmol). Dark red-brown crystals were obtained. Yield: 0.160 g (42 % based on {Pd}). Elemental analysis calcd (%): Na 3.18, Yb 4.78, Pd 35.3, As 16.57, C 15.94, H 2.12; found: Na 2.97, Yb 4.62, Pd 35.30, As 16.20, C 16.10, H 2.47. IR (2% KBr pellet, ν/cm^{-1}): 1629 (m), 1481 (w), 1440 (m), 1180 (w), 1094 (m), 1026 (w), 799 (s), 744 (s), 693 (s), 613 (s), 542 (s), 437 (s).

$\text{Na}_5[\text{LuPd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}]\cdot 16\text{H}_2\text{O}$ (Lu-1m): The compound was prepared by exactly the same procedure as **Y-1a**, but by using $\text{LuCl}_3\cdot 6\text{H}_2\text{O}$ (0.061 g, 0.156 mmol). Dark red-brown crystals were obtained. Yield: 0.120 g (32 % based on {Pd}). Elemental analysis calcd (%): Na 3.21, Lu 4.88, Pd 35.64, As 16.73, C 16.09, H 2.03; found: Na 3.10, Lu 4.30, Pd 35.50, As 16.20, C 16.10, H 2.20. IR (2% KBr pellet, ν/cm^{-1}): 1625 (m), 1481 (w), 1436 (m), 1176 (w), 1096(m), 1026 (w), 800 (s), 743 (s), 693 (s), 614 (s), 542 (s), 437 (s).

3.2.2 Single Crystal XRD

The compounds **Y-1a** – **Lu-1m** are all isomorphous and crystallize in the tetragonal crystal system in the space group $I4/m$. The structure of the $\{\text{MPd}_{12}(\text{AsPh})_8\text{O}_{32}\}$ core is very similar to that in the previously reported **$\text{Pd}_{13}\text{PhAs}$** and can be described in terms of Platonic and Archimedean solids.⁴ The main difference is that the central Pd^{II} ion in the latter has been replaced by a Ln^{III} or Y^{III} ion (see Fig. 3.1).

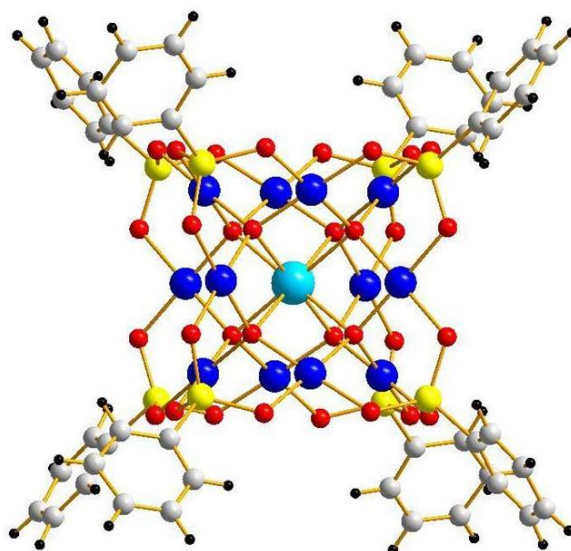


Figure 3.1 Ball-and-stick representation of $[M^{III}Pd^{II}_{12}(AsPh)_8O_{32}]^{5-}$.

Colour code: M turquoise, Pd blue, As yellow, O red, C grey, and H black.

This central yttrium or lanthanide ion in **Y-1a** – **Lu-1m** is coordinated by eight oxygen atoms situated at the vertices of a cube. The twelve palladium(II) ions surrounding the central $\{MO_8\}$ fragment form a cuboctahedron. Each oxygen atom of the “inner” $\{MO_8\}$ cube (μ_4 -O) is coordinated by the lanthanide ion and by three palladiums, situated on a trigonal face of the cuboctahedron. Each of the twelve Pd^{II} ions exhibits the expected square-planar coordination by two μ_4 -O and two “outer” oxygen atoms (μ_2 -O). The 24 “outer” oxygen atoms form a truncated cube-shaped shell, which is capped by eight positively charged $AsPh^{4+}$ groups. The eight As atoms possess tetrahedral coordination geometry and form in fact an external, cube-shaped shell. Selected bond distances for the polyanion in **Y-1a** – **Lu-1m** are shown in Table 3.1.

Thus, small, medium and large lanthanide ions can be incorporated in the center of the polyoxopalladate $[M^{III}Pd^{II}_{12}(AsPh)_8O_{32}]^{5-}$. The M–O bond lengths in these polyanions decrease from **Pr-1b** to **Lu-1m**, following the expected trend of the lanthanide series (see

Table 3.1). Moreover the Pd...Pd distances in the $\{\text{Pd}^{\text{II}}_{12}\text{O}_{32}\}$ noble metalate host increase with increasing size of the encapsulated metal guest and vice versa. This feature of the encapsulating $\{\text{Pd}^{\text{II}}_{12}\text{O}_{32}\}$ polyoxopalladate shell is exciting and suggests a certain “structural elasticity”, meaning that the host matrix adjusts to the size and coordination requirements of the incorporated guest cation.

Table 3.1 Selected bond lengths [Å] for the polyanions in **Y-1a** – **Lu-1m**.

	M – (μ_4 -O)	Pd – (μ_4 -O) (mean)	Pd – (μ -O) (mean)	As – (μ -O) (mean)	As – C
Y-1a	2.346(6)	1.994(6)	2.034(7)	1.689(7)	1.897(6)
Pr-1b	2.431(4)	1.995(4)	2.022(5)	1.693(5)	1.883(3)
Nd-1c	2.420(4)	1.996(4)	2.027(5)	1.693(5)	1.885(4)
Sm-1d	2.386(9)	1.990(8)	2.016(10)	1.694(10)	1.899(13)
Eu-1e	2.382(5)	1.991(5)	2.023(6)	1.694(6)	1.886(4)
Gd-1f	2.379(8)	1.989(7)	2.022(8)	1.681(9)	1.880(6)
Tb-1g	2.350(7)	2.000(7)	2.031(9)	1.695(9)	1.882(7)
Dy-1h	2.349(8)	1.991(8)	2.024(10)	1.698(10)	1.885(16)
Ho-1i	2.335(7)	1.992(7)	2.025(8)	1.700(8)	1.887(6)
Er-1j	2.332(11)	1.991(11)	2.028(12)	1.693(13)	1.89(2)
Tm-1k	2.320(9)	1.994(9)	2.025(10)	1.697(11)	1.891(8)
Yb-1l	2.329(7)	1.990(7)	2.029(8)	1.696(9)	1.882(6)
Lu-1m	2.303(11)	1.994(10)	2.023(12)	1.703(12)	1.877(9)

In the solid state the polyanions in **Y-1a** – **Lu-1m** form a hexagonal-packing framework with channels along the *a* and *b* axes (see Fig. 3.2). The channels are occupied by crystal water molecules and sodium counter cations. Neighboring polyanions interact through weak CH/ π hydrogen bonds,⁷ which are directed along diagonals between the *b* and *c*, and the $-b$ and $-c$ axes. There are no π - π stacking interactions between the phenyl groups, possibly because of steric hindrance or repulsion between the hydrophilic polyoxopalladate core and the hydrophobic aromatic groups.

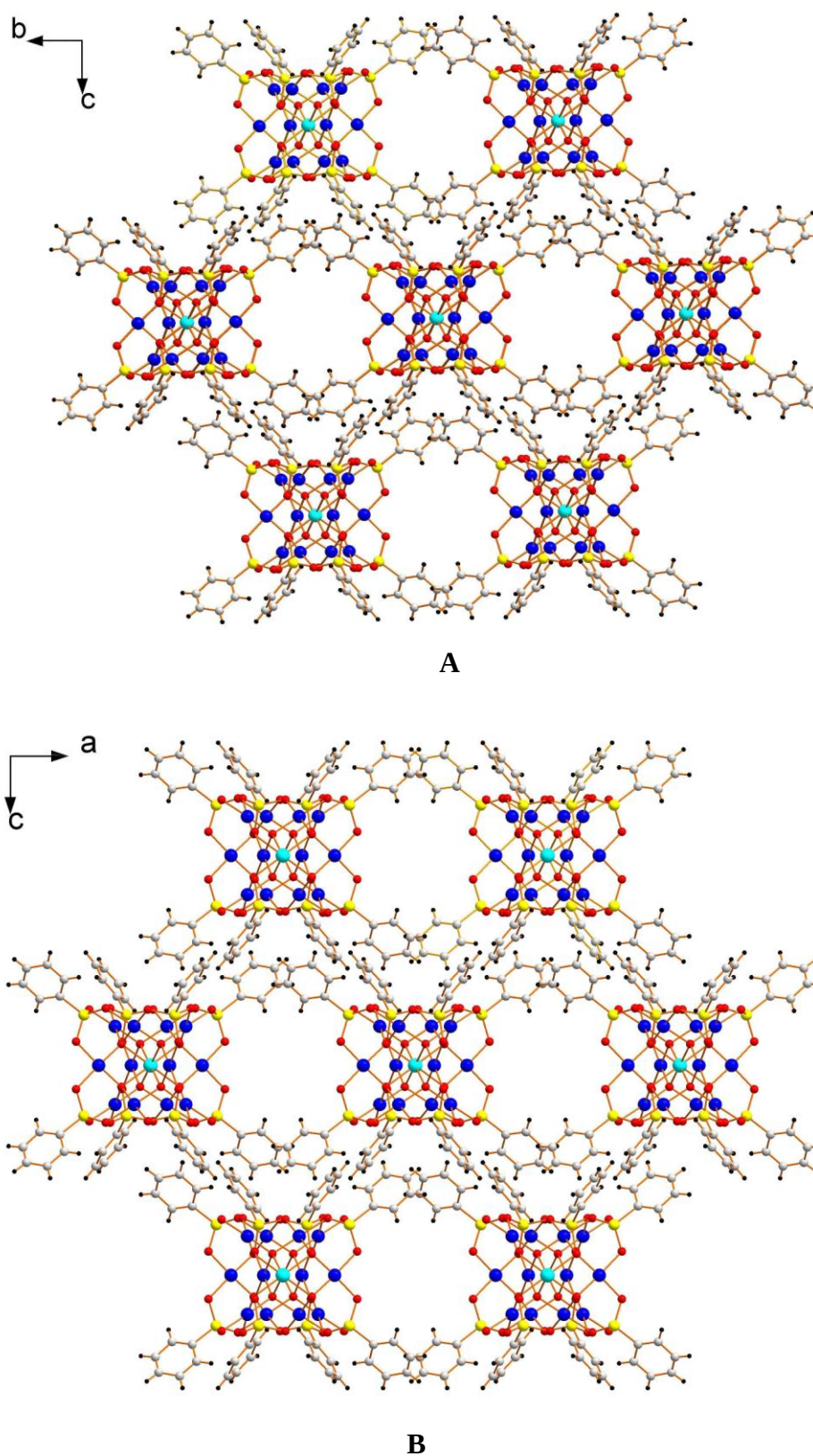


Figure 3.2 The hexagonal packing arrangement of $[M^{III}Pd^{II}_{12}(AsPh)_8O_{32}]^{5-}$ along the *a* (**A**) and *b* (**B**) axis. Colour code: M turquoise, Pd blue, As yellow, O red, C grey, and H black.

Tables 3.2 – 3.4 include further crystallographic data for **Y-1a** – **Lu-1m**.

Table 3.2 Crystal data and structure refinement for **Y-1a** – **Eu-1e**.

	Y-1a	Pr-1b	Nd-1c	Sm-1d	Eu-1e
empirical formula	C ₄₈ H ₁₀₄ As ₈ Na ₅ O ₆₄ Pd ₁₂ Y	C ₄₈ H ₁₁₆ As ₈ Na ₅ O ₇₀ Pd ₁₂ Pr	C ₄₈ H ₈₈ As ₈ Na ₅ O ₅₆ Pd ₁₂ Nd	C ₄₈ H ₉₂ As ₈ Na ₅ O ₅₈ Pd ₁₂ Sm	C ₄₈ H ₈₄ As ₈ Na ₅ O ₅₄ Pd ₁₂ Eu
molecular weight [g mol ⁻¹]	3785.3	3945.7	3696.5	3738.7	3668.2
crystal system	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal
space group	I4/m	I4/m	I4/m	I4/m	I4/m
<i>a</i> [Å]	15.911(3)	15.8804(19)	15.8621(4)	15.8590(13)	15.8843(5)
<i>b</i> [Å]	15.911(3)	15.8804(19)	15.8621(4)	15.8590(13)	15.8843(5)
<i>c</i> [Å]	25.097(4)	25.137(4)	25.1029(7)	25.049(2)	25.0817(7)
<i>V</i> [Å ³]	6353.6(19)	6339.3(14)	6316.0(3)	6299.9(9)	6328.4(3)
<i>Z</i>	2	2	2	2	2
<i>T</i> [K]	173(2)	173(2)	173(2)	173(2)	173(2)
ρ_{calcd} [Mg m ⁻³]	1.979	2.062	1.944	1.971	1.925
μ [mm ⁻¹]	4.270	4.210	4.236	4.303	4.311
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]					
<i>R</i> ₁ ^[a]	0.0579	0.0542	0.0537	0.0734	0.0581
<i>wR</i> ₂ ^[b]	0.1588	0.1415	0.1529	0.1937	0.1686
<i>R</i> indices (all data)					
<i>R</i> ₁ ^[a]	0.1014	0.1113	0.1096	0.1378	0.1070
<i>wR</i> ₂ ^[b]	0.1851	0.1768	0.1930	0.2753	0.2267

$$^{[a]} R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^{[b]} wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$

Table 3.3 Crystal data and structure refinement for **Gd-1f** – **Ho-1i**.

	Gd-1f	Tb-1g	Dy-1h	Ho-1i
empirical formula	C ₄₈ H ₈₈ As ₈ Na ₅ O ₅₆ Pd ₁₂ Gd	C ₄₈ H ₁₀₄ As ₈ Na ₅ O ₆₄ Pd ₁₂ Tb	C ₄₈ H ₁₀₄ As ₈ Na ₅ O ₆₄ Pd ₁₂ Dy	C ₄₈ H ₈₈ As ₈ Na ₅ O ₅₆ Pd ₁₂ Ho
molecular weight [gmol ⁻¹]	3709.5	3855.3	3858.9	3717.2
crystal system	Tetragonal	Tetragonal	Tetragonal	Tetragonal
space group	I4/m	I4/m	I4/m	I4/m
<i>a</i> [Å]	15.857(2)	15.993(2)	15.9390(19)	15.9485(14)
<i>b</i> [Å]	15.857(2)	15.993(2)	15.9390(19)	15.9485(14)
<i>c</i> [Å]	25.049(5)	25.108(4)	25.060(3)	25.0606(18)
<i>V</i> [Å ³]	6298.3(18)	6421.9(15)	6366.7(13)	6374.3(9)
<i>Z</i>	2	2	2	2
<i>T</i> [K]	173(2)	173(2)	173(2)	173(2)
ρ_{calcd} [Mgm ⁻³]	1.956	1.994	2.013	1.937
μ [mm ⁻¹]	4.363	4.321	4.390	4.411
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]				
<i>R</i> ₁ ^[a]	0.0706	0.0655	0.0663	0.0679
<i>wR</i> ₂ ^[b]	0.2140	0.1716	0.1763	0.1658
<i>R</i> indices (all data)				
<i>R</i> ₁ ^[a]	0.1295	0.1285	0.1028	0.1030
<i>wR</i> ₂ ^[b]	0.2527	0.2037	0.2068	0.1885

$$^{[a]} R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^{[b]} wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$

Table 3.4 Crystal data and structure refinement for **Er-1j** – **Lu-1m**.

	Er-1j	Tm-1k	Yb-1l	Lu-1m
empirical formula	C ₄₈ H ₈₈ As ₈ Na ₅ O ₅₆ Pd ₁₂ Er	C ₄₈ H ₈₀ As ₈ Na ₅ O ₅₂ Pd ₁₂ Tm	C ₄₈ H ₈₀ As ₈ Na ₅ O ₅₂ Pd ₁₂ Yb	C ₄₈ H ₇₂ As ₈ Na ₅ O ₄₈ Pd ₁₂ Lu
molecular weight [gmol ⁻¹]	3719.6	3649.2	3653.3	3583.1
crystal system	Tetragonal	Tetragonal	Tetragonal	Tetragonal
space group	I4/m	I4/m	I4/m	I4/m
<i>a</i> [Å]	15.965(2)	15.927(2)	15.8721(10)	15.9426(11)
<i>b</i> [Å]	15.965(2)	15.927(2)	15.8721(10)	15.9426(11)
<i>c</i> [Å]	25.053(5)	25.043(5)	25.0420(15)	25.0593(14)
<i>V</i> [Å ³]	6385.5(18)	6352.4(18)	6308.7(7)	6369.2(7)
<i>Z</i>	2	2	2	2
<i>T</i> [K]	173(2)	173(2)	173(2)	173(2)
ρ_{calcd} [Mgm ⁻³]	1.935	1.908	1.923	1.868
μ [mm ⁻¹]	4.441	4.498	4.567	4.560
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]				
<i>R</i> ₁ ^[a]	0.0695	0.0847	0.0618	0.0862
<i>wR</i> ₂ ^[b]	0.1812	0.2355	0.1804	0.2476
<i>R</i> indices (all data)				
<i>R</i> ₁ ^[a]	0.1214	0.1434	0.1162	0.1480
<i>wR</i> ₂ ^[b]	0.2158	0.2837	0.2107	0.2885

$$^{[a]} R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^{[b]} wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$

3.2.3 FT-IR Spectroscopy

The polyoxopalladate salts **Y-1a** – **Lu-1m** and the parent $\text{Na}_6[\text{Pd}^{\text{II}}_{13}(\text{PhAs})_8\text{O}_{32}]\cdot 24\text{H}_2\text{O}$ (**Na-Pd₁₃PhAs**) have similar FT-IR spectra showing only slight shifts in some band positions (see Fig. 3.3a – 3.3m).⁴ As an example, for **Y-1a** the strong bands at 438, 543, and 611 cm^{-1} correspond to the vibrational modes of the Pd–O groups, which could be superimposed with bands associated with the Y–O vibrations. The strong band at 800 cm^{-1} is attributed to the vibrations of the $\{\text{AsO}_3\}$ fragments. The stretching and bending vibrations of the C–H and C–C bonds of the phenyl rings appear in the regions between 1480 and 1094 cm^{-1} and 744 – 694 cm^{-1} , respectively. The broad band at 1629 cm^{-1} belongs to asymmetric vibrations of the crystal waters.⁸

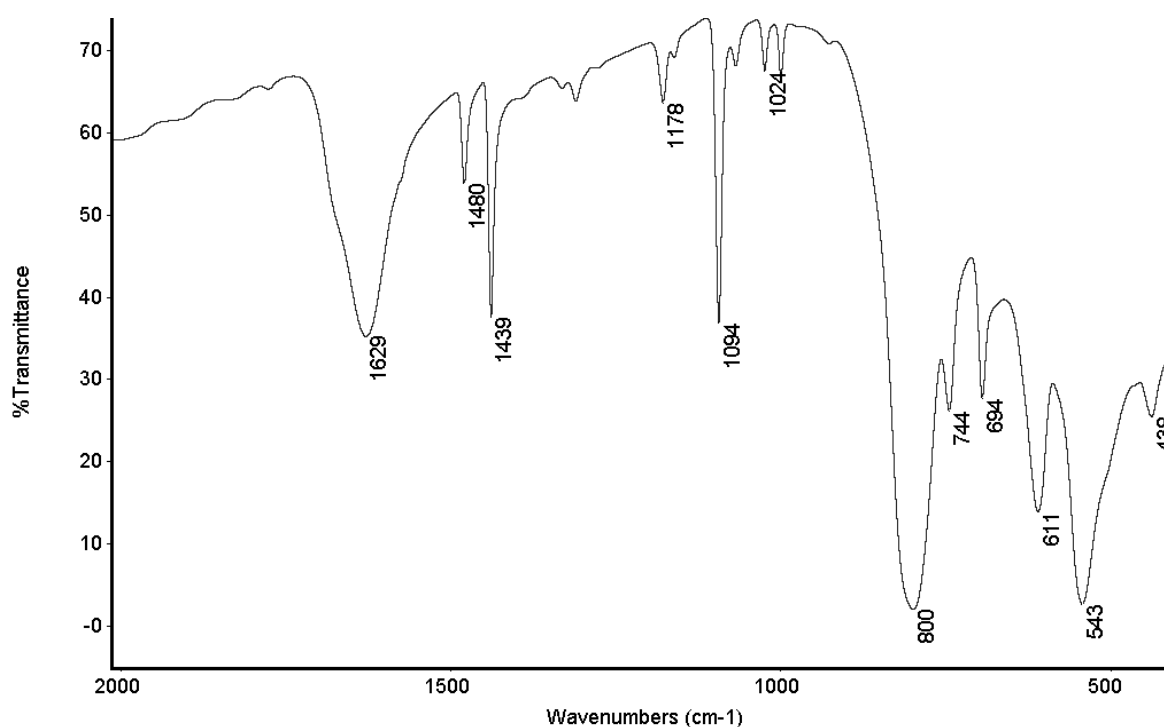


Figure 3.3a FT-IR spectrum of **Y-1a**.

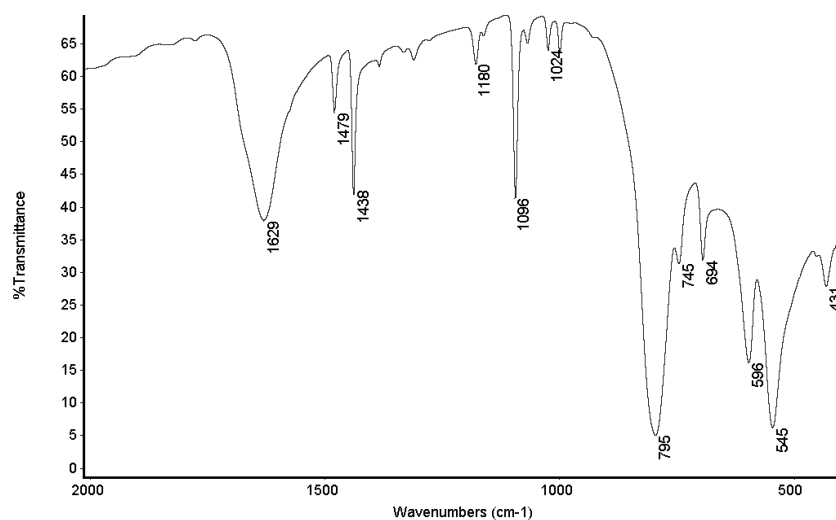


Figure 3.3b FT-IR spectrum of Pr-1b.

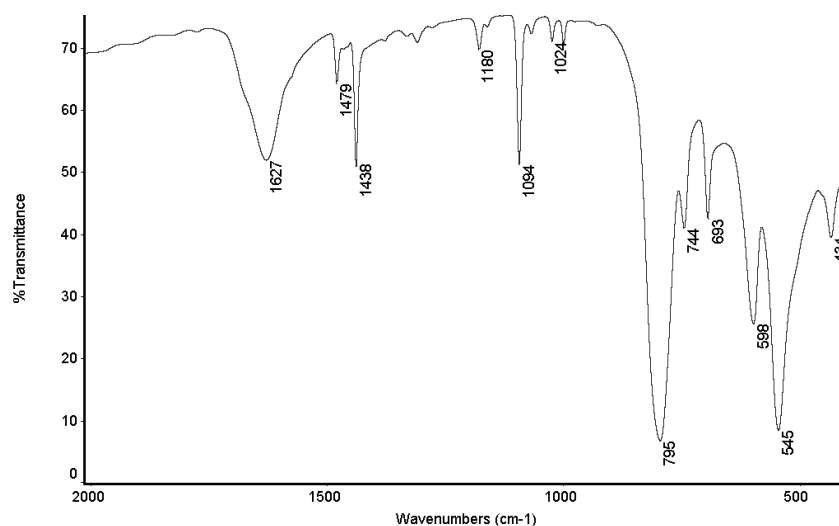


Figure 3.3c FT-IR spectrum of Nd-1c.

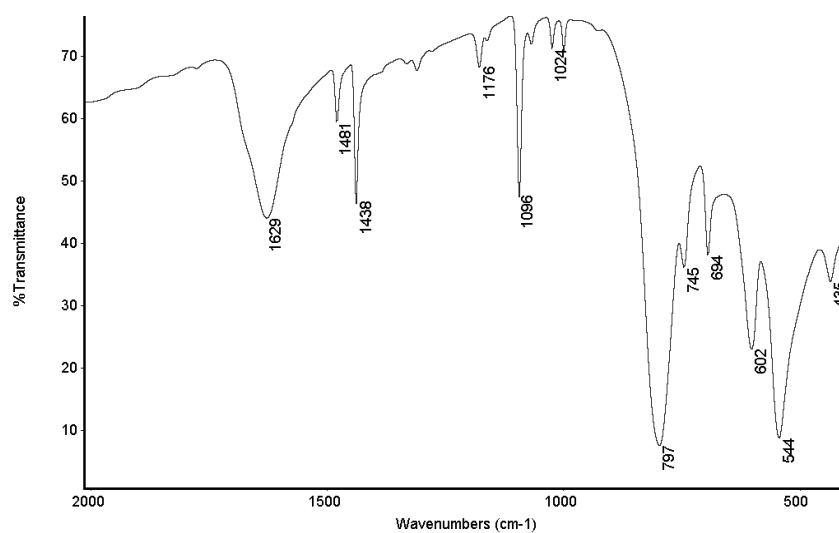


Figure 3.3d FT-IR spectrum of Sm-1d.

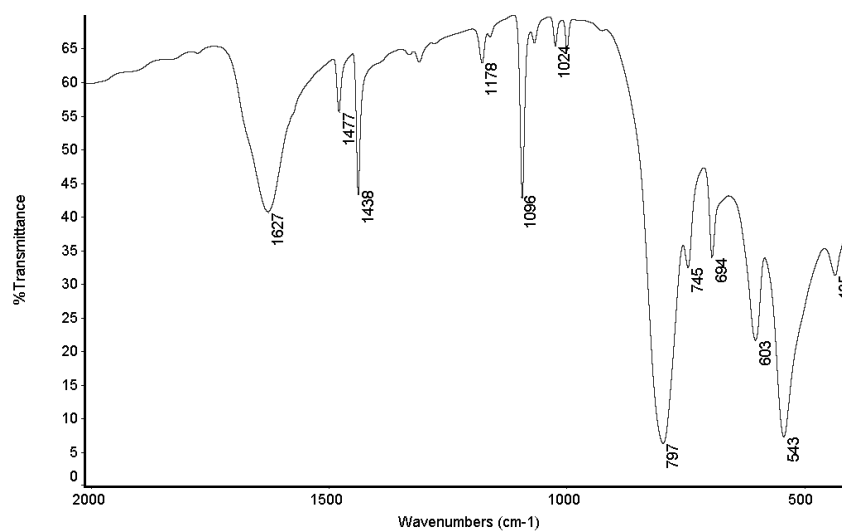


Figure 3.3e FT-IR spectrum of Eu-1e.

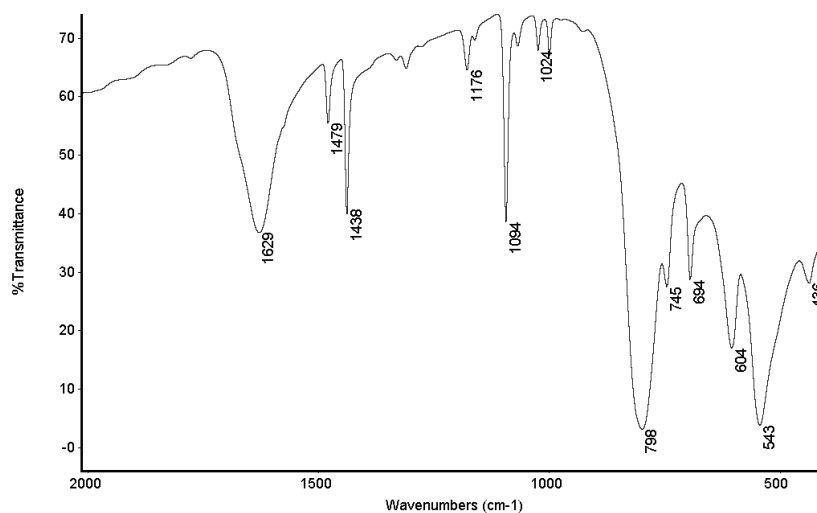


Figure 3.3f FT-IR spectrum of Gd-1f.

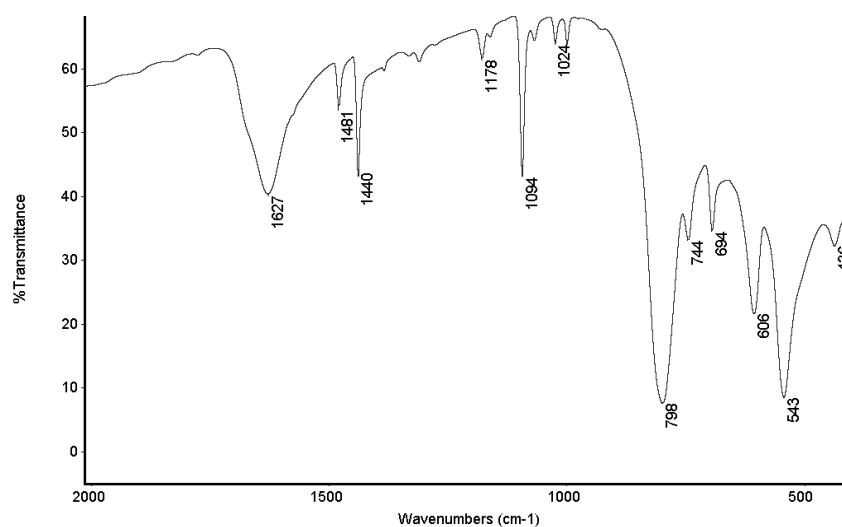


Figure 3.3g FT-IR spectrum of Tb-1g.

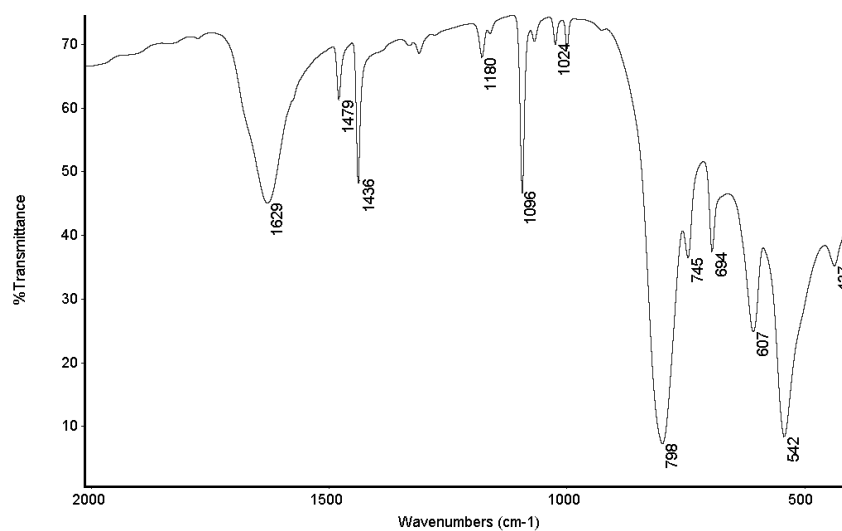


Figure 3.3h FT-IR spectrum of **Dy-1h**.

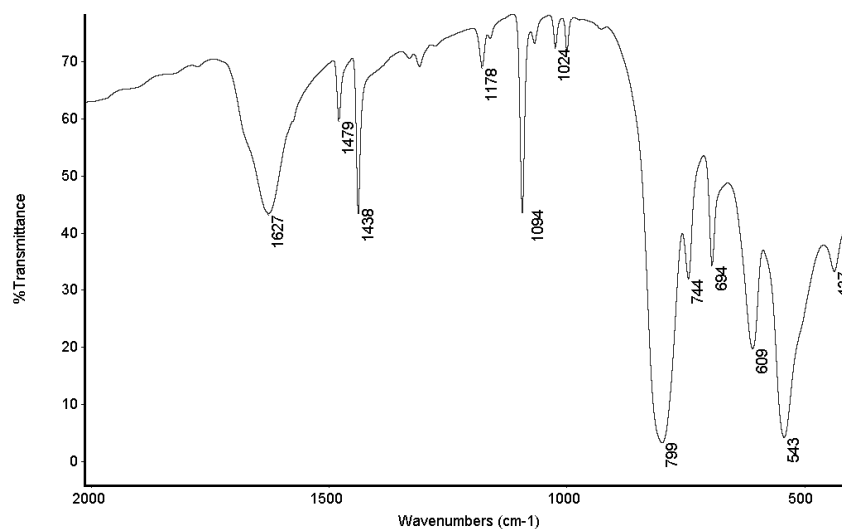


Figure 3.3i FT-IR spectrum of **Ho-1i**.

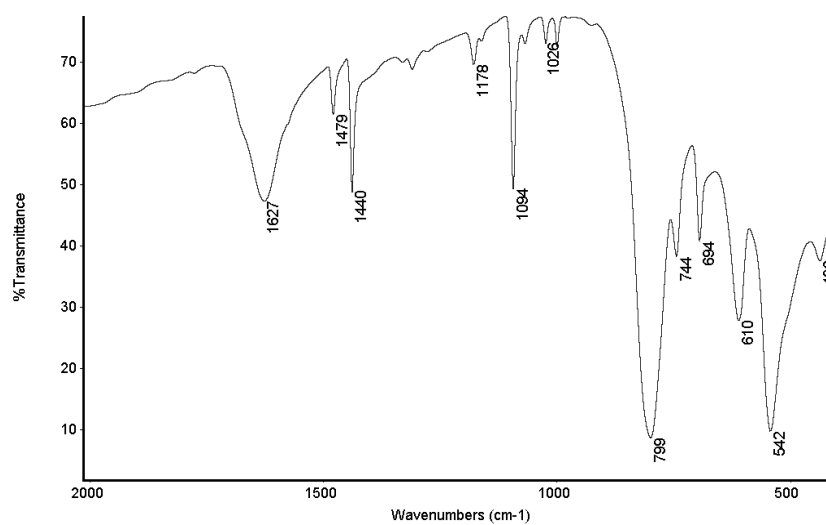


Figure 3.3j FT-IR spectrum of **Er-1j**.

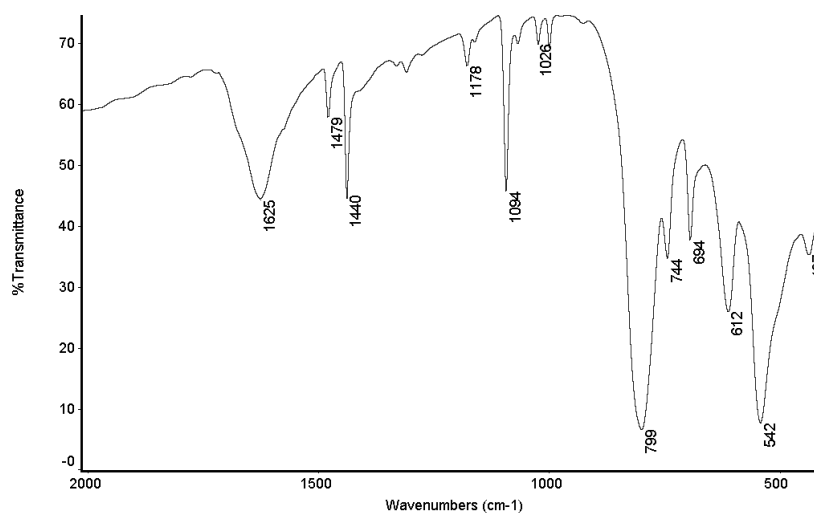


Figure 3.3k FT-IR spectrum of Tm-1k.

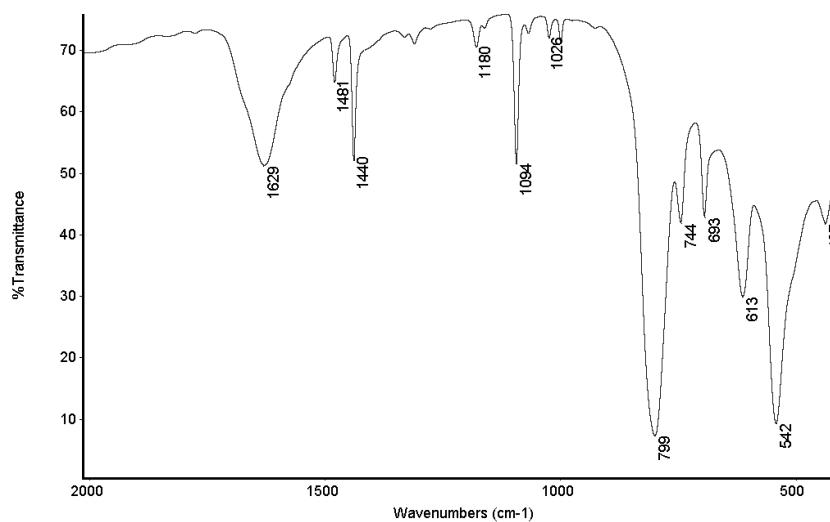


Figure 3.3l FT-IR spectrum of Yb-1l.

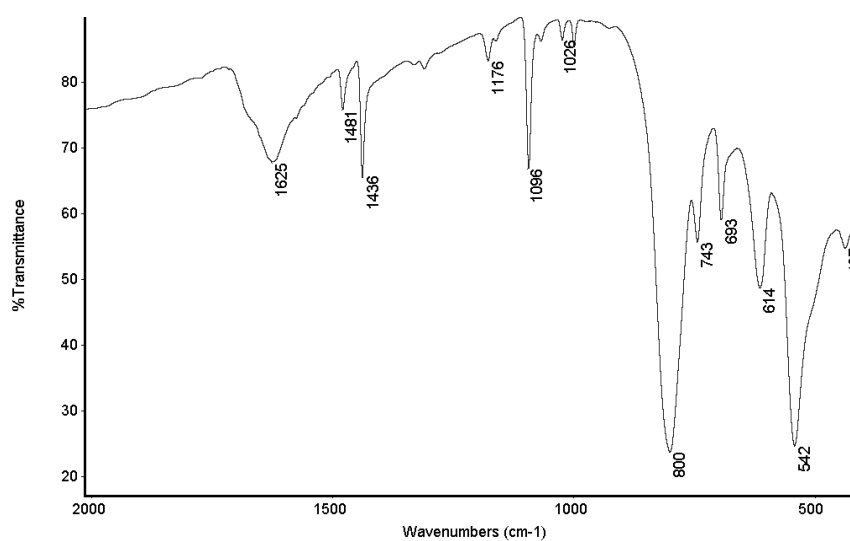


Figure 3.3m FT-IR spectrum of Lu-1m.

3.2.4 Thermogravimetric Analysis

The thermogravimetric processes of **Y-1a** – **Lu-1m** are very similar and reveal several weight-loss steps (see Fig. 3.4a-3.4m). For example, for **Y-1a** (Fig. 3.4a) the first step occurs between 25 and 227 °C and corresponds to the loss of 26 water molecules per formula unit. The number of water molecules determined by TGA is slightly lower than that obtained by crystallography (32 molecules). This fact can be easily explained by partial loss of crystal waters during sample drying. Single crystals for XRD measurements were taken directly from the mother liquid, put in oil and frozen under nitrogen flow on the diffractometer, whereas the samples for TGA were air-dried for at least one day. The combustion of eight phenyl groups per formula unit proceeds in the temperature range of 227 – 455 °C. The additional smooth weight loss before 525 °C is assigned to the removal of oxygen associated with the decomposition of As_2O_5 with formation of As_2O_3 and O_2 . Several consecutive weight-loss steps covering the temperature range of 550 – 775 °C are attributed to arsenic volatility, most likely in the form of As_4O_6 .^{4,9}

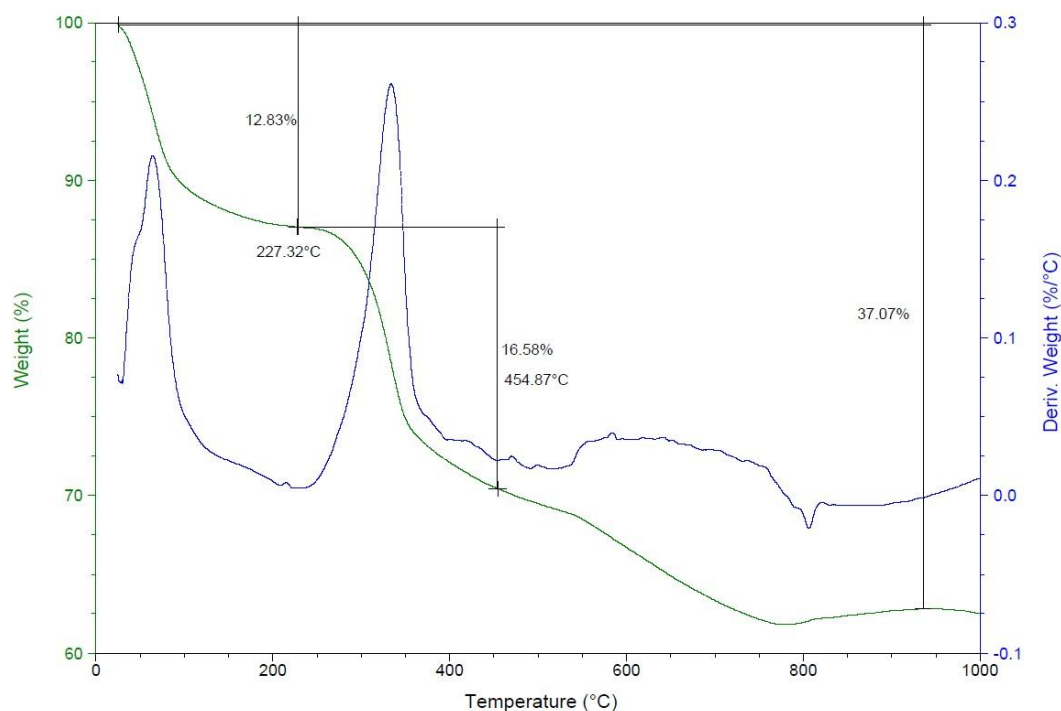


Figure 3.4a Thermogram of **Y-1a**.

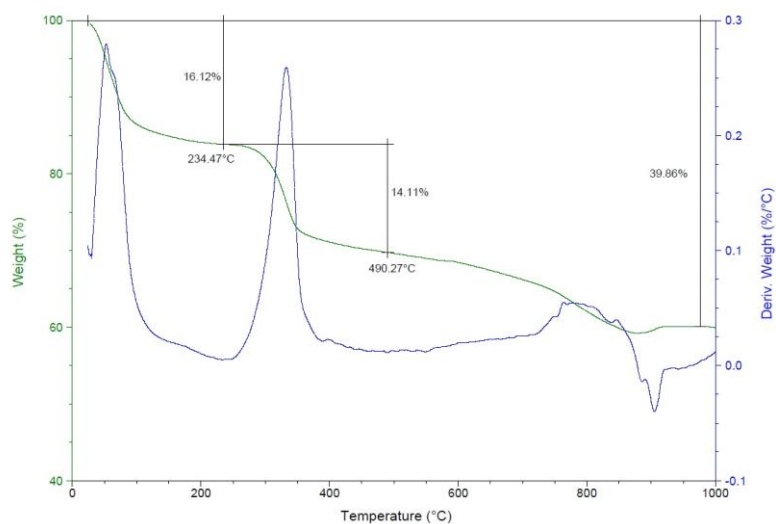


Figure 3.4b Thermogram of Pr-1b.

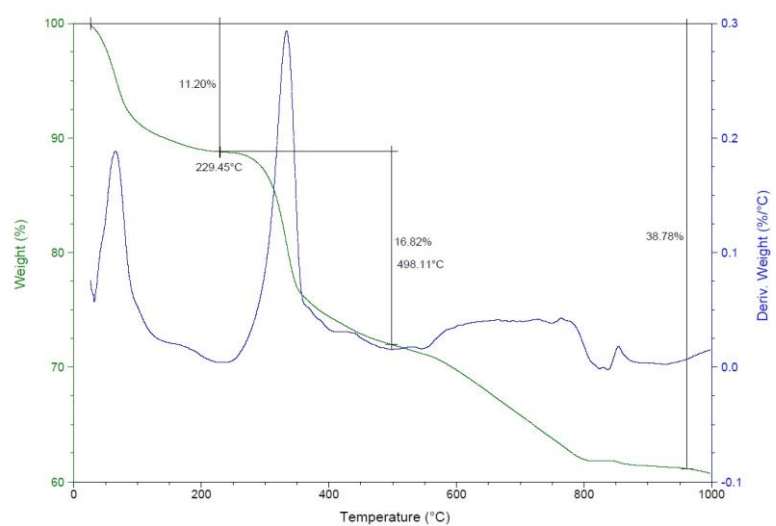


Figure 3.4c Thermogram of Nd-1c.

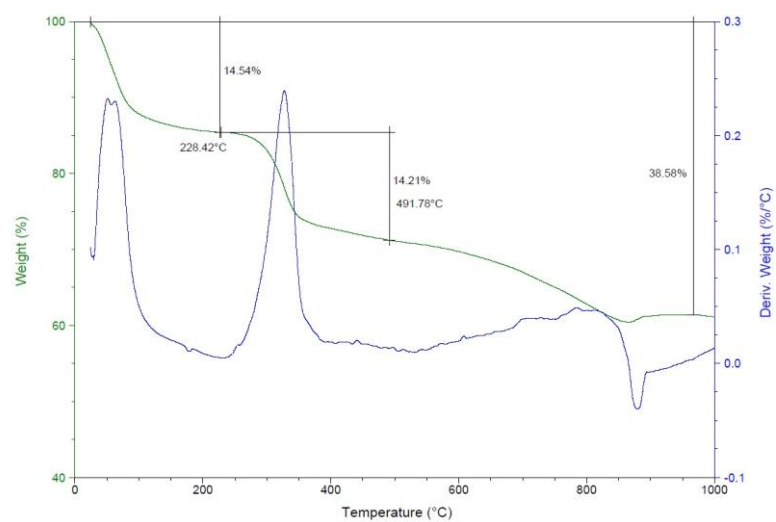


Figure 3.4d Thermogram of Sm-1d.

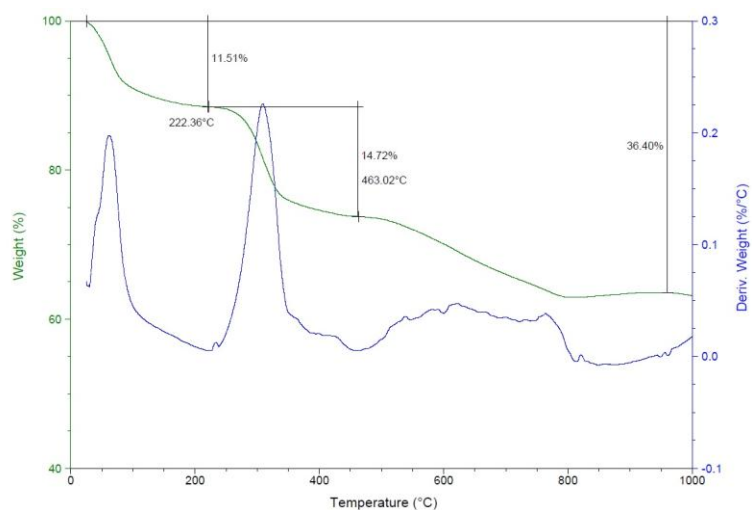


Figure 3.4e Thermogram of Eu-1e.

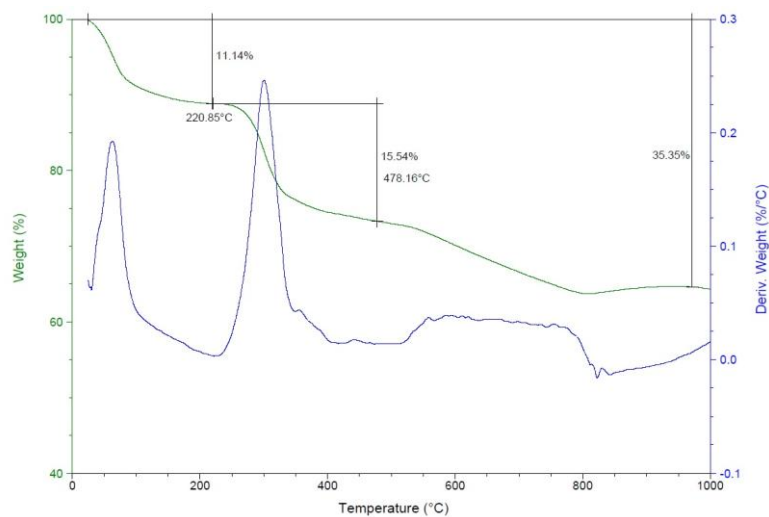


Figure 3.4f Thermogram of Gd-1f.

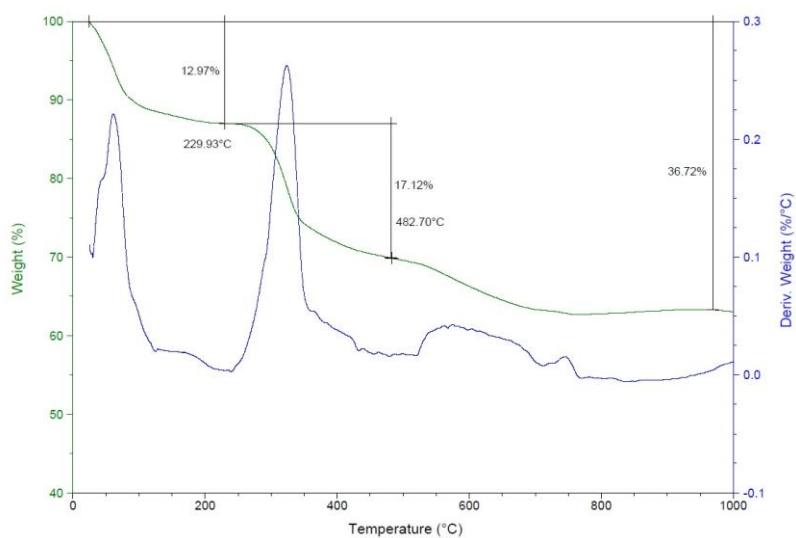


Figure 3.4g Thermogram of Tb-1g.

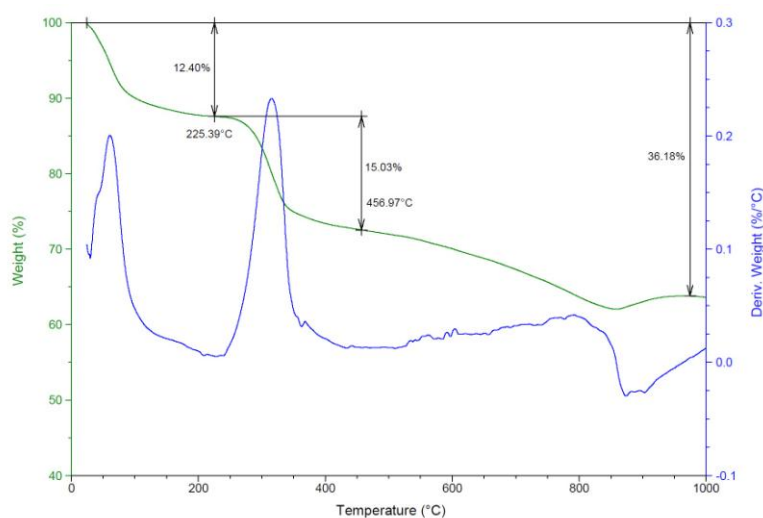


Figure 3.4h Thermogram of Dy-1h.

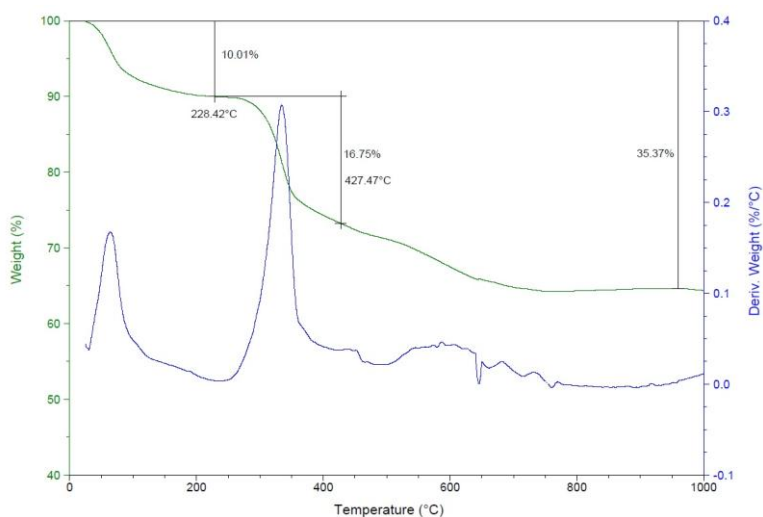


Figure 3.4i Thermogram of Ho-1i.

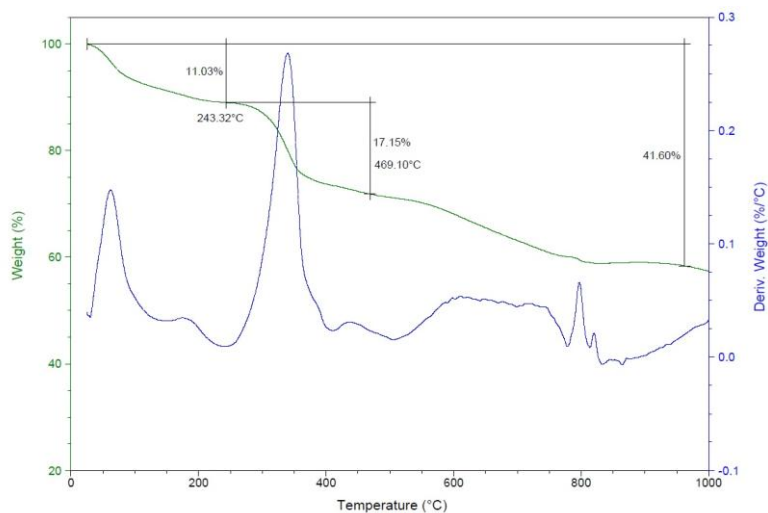


Figure 3.4j Thermogram of Er-1j.

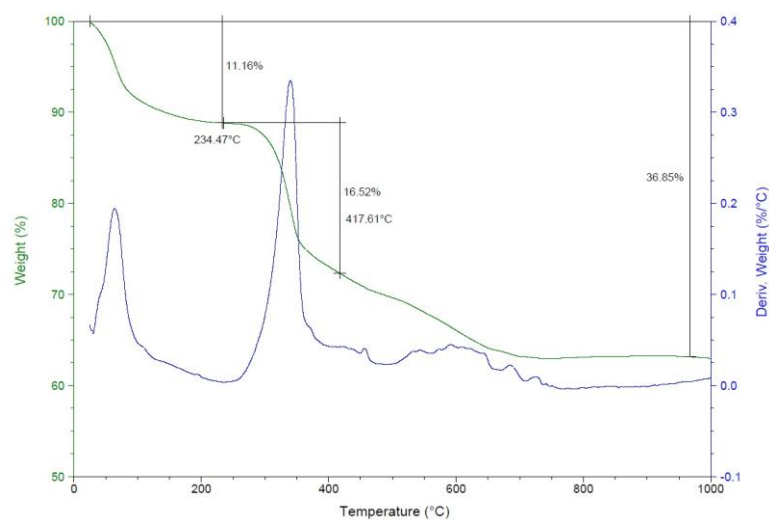


Figure 3.4k Thermogram of Tm-1k.

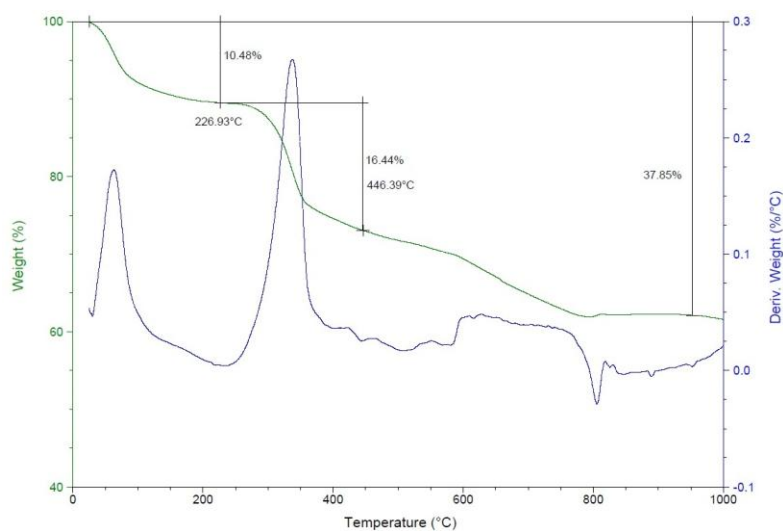


Figure 3.4l Thermogram of Yb-1l.

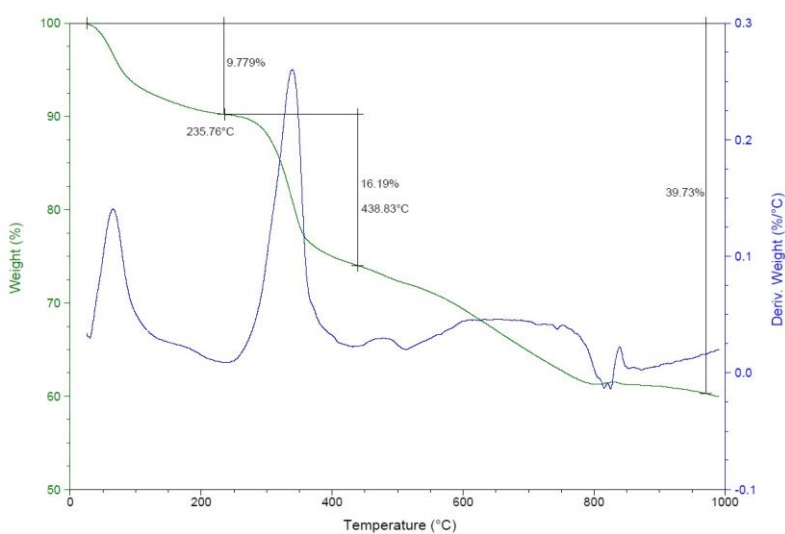


Figure 3.4m Thermogram of Lu-1m.

3.2.5 Conclusions

We have expanded the class of noble metalates by the discovery of a novel family of yttrium(III)- and lanthanide(III)-containing polyoxopalladates, $[M^{III}Pd^{II}_{12}(AsPh)_8O_{32}]^{5-}$ ($M = Y, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb$ and Lu). The polyanions $[M^{III}Pd^{II}_{12}(As^VPh)_8O_{32}]^{5-}$ consist of a cuboid framework of twelve Pd^{II} ions with eight phenylarsonate capping groups located at the vertices and a central guest ion M . The 13 polyanions have similar structure as **Pd₁₃PhAs**, but the central, eight-coordinated Pd^{II} has now been replaced by the larger Y^{III} or Ln^{III} ions ($Ln =$ lanthanide) for which eight-coordination is more common. This is also supported by the yields for **Y-1a** – **Lu-1m**, which, in general, are significantly higher than for **Na-Pd₁₃PhAs**. It was demonstrated that small, medium, and also large lanthanide ions can be incorporated in the center of the novel polyoxopalladate $[M^{III}Pd^{II}_{12}(As^VPh)_8O_{32}]^{5-}$. The $Ln-O$ bond lengths follow the expected trend decreasing from left to right in the lanthanide series. This indicates that the $\{Pd^{II}_{12}O_{32}\}$ shell can adjust to the coordination requirements of the encapsulated guest cation. Compounds **Nd-1c** and **Eu-1e** were selected for electrochemical studies, which were done by the group of Prof. Louis Nadjo (Université Paris-Sud, Orsay Cedex, France). Their cyclic voltammetry in a lithium acetate buffer at pH 5.9 showed a Pd^0 deposition process on the glassy carbon electrode surface. Coulometry indicated that all Pd^{II} centers were reduced to Pd^0 . The film was stable and could be taken out of the deposition medium and characterized in pure lithium acetate buffer (pH 5.9). Magnetic susceptibility and EPR measurements were carried out on **Eu-1e** and **Gd-1f** by the group of Prof. Naresh S. Dalal (Florida State University, USA). The former was confirmed to be diamagnetic and the latter strongly paramagnetic with a $S=7/2$ ground state. DFT calculations for **Y-1a**, **Gd-1f** and **Lu-1m** have been also performed by Prof. Josep M. Poble and co-workers (Universitat Rovira i Virgili, Tarragona, Spain).

The $\{\text{Pd}_{12}\text{L}_8\}$ structure type is a fascinating host which can accommodate a variety of coordination modes of the guests, namely square-planar coordinated Pd^{II} (in $[\text{Pd}^{\text{II}}_{13}\text{As}_8^{\text{V}}\text{O}_{34}(\text{OH})_6]^{8-}$), octahedrally coordinated Pd^{II} (in $[\text{Pd}^{\text{II}}_{13}\text{Se}_8\text{O}_{32}]^{6-}$), cubic coordinated Pd^{II} (in $[\text{Pd}^{\text{II}}_{12}(\text{AsPh})_8\text{O}_{32}]^{6-}$) or $\text{Y}^{\text{III}}/\text{Ln}^{\text{III}}$ in **Y-1a** – **Lu-1m**.^{4,10} It is evident that the novel POM subclass of noble metalates offers not only new and exciting structures and compositions, but also interesting electronic and potentially functional properties.

3.3 3d Transition Metal-containing Polyoxopalladates

with Phenylarsonate Capping Groups

On the way of systematically investigation which transition metals could possibly be placed in the centre of the $\{\text{Pd}_{12}\text{L}_8\}$ structure type we obtained a novel family of polyoxopalladates, $\text{Na}_n[\text{MPd}^{\text{II}}_{12}(\text{AsPh})_8\text{O}_{32}] \cdot y\text{H}_2\text{O}$ ($\text{M} = \text{Sc}^{\text{III}}$ (**Sc-2a**), Mn^{II} (**Mn-2b**), Fe^{III} (**Fe-2c**), Co^{II} (**Co-2d**), Ni^{II} (**Ni-2e**), Cu^{II} (**Cu-2f**), Zn^{II} (**Zn-2g**); $y = 19 - 37$). These polyanions have been prepared in a simple one pot self-assembly reaction of $\text{Pd}_3(\text{CH}_3\text{COO})_6$, phenylarsonic acid and the salt of the respective $\text{M}^{\text{n}+}$ ion in 1.0 M aqueous sodium acetate solution (pH 6.9 – 7.0) in yields ranging from 7% (for **Sc-2a**) to 34% (for **Co-2d**). The compounds were characterized in the solid state by single-crystal XRD, elemental analysis, FT-IR spectroscopy, TGA. Moreover diamagnetic Sc^{III} (**Sc-2a**) and Zn^{II} (**Zn-2g**) derivatives were studied in solution by ^1H and ^{13}C NMR spectroscopy. It was shown that different 3d transition metal ions M can be incorporated in the center of the polyoxopalladate $[\text{MPd}^{\text{II}}_{12}(\text{AsPh})_8\text{O}_{32}]^{\text{n-}}$.

3.3.1 Synthetic Procedures

$\text{Na}_5[\text{Sc}^{\text{III}}\text{Pd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}] \cdot 21\text{H}_2\text{O}$ (Sc-2a**):** $\text{Pd}_3(\text{CH}_3\text{COO})_6$ (0.140 g, 0.208 mmol), PhAsO_3H_2 (0.125 g, 0.619 mmol) and $\text{Sc}(\text{CSF}_3\text{O}_3)_3$ (0.154 g, 0.313 mmol) were dissolved in

5 ml of sodium acetate solution 1.0 M (pH 6.9). While stirring, the solution was heated to 80°C for 90 min. Then it was cooled to room temperature, filtered and allowed to crystallize at room temperature. Dark red-brown crystals were obtained after several days, filtered off and air dried. Yield: 0.030 g (7 % based on {Pd}). Elemental analysis (%) calcd: Na 3.24, Sc 1.27, As 16.91, C 16.27, H 2.33; found: Na 4.17, Sc 1.11, As 16.17, C 16.90, H 2.52. IR (2% KBr pellet, ν/cm^{-1}): 1623 (m), 1479 (w), 1438 (m), 1178 (w), 1094 (m), 1026 (w), 804 (s), 742 (s), 695 (s), 629 (s), 538 (s), 502 (sh), 435 (s).

$\text{Na}_6[\text{Mn}^{\text{II}}\text{Pd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}]\cdot 27\text{H}_2\text{O}$ (Mn-2b): The compound was prepared by exactly the same procedure as **Sc-2a**, but with $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ (0.031 g, 0.157 mmol). Dark red-brown crystals were obtained. Yield: 0.060 g (15 % based on {Pd}). Elemental analysis (%) calcd: Na 3.74, Mn 1.49, Pd 34.66, As 16.27, C 15.65, H 2.57; found: Na 3.62, Mn 1.45, Pd 33.75, As 15.90, C 16.27, H 2.02. IR (2% KBr pellet, ν/cm^{-1}): 1626 (m), 1478 (w), 1438 (m), 1177 (w), 1094 (m), 1026 (w), 805 (s), 744 (s), 695 (s), 627 (s), 532 (s), 502 (sh), 435 (sh).

$\text{Na}_5[\text{Fe}^{\text{III}}\text{Pd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}]\cdot 23\text{H}_2\text{O}$ (Fe-2c): The compound was prepared by exactly the same procedure as **Sc-2a**, but with $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (0.063 g, 0.156 mmol). Dark red-brown crystals were obtained. Yield: 0.120 g (32 % based on {Pd}). Elemental analysis (%) calcd: Na 3.20, Fe 1.56, Pd 35.57, As 16.69, C 16.06, H 2.41; found: Na 3.22, Fe 1.52, Pd 34.61, As 16.62, C 16.53, H 2.11. IR (2% KBr pellet, ν/cm^{-1}): 1626 (m), 1479 (w), 1438 (m), 1176 (w), 1095 (m), 1022 (w), 804 (s), 744 (s), 693 (s), 641 (s), 538 (s), 499 (sh), 434 (s).

$\text{Na}_6[\text{Co}^{\text{II}}\text{Pd}^{\text{II}}_{12}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}]\cdot 26\text{H}_2\text{O}$ (Co-2d): The compound was prepared by exactly the same procedure as **Sc-2a**, but with $\text{Co}(\text{NO})_3\cdot 6\text{H}_2\text{O}$ (0.058 g, 0.156 mmol). Dark red-brown crystals were obtained. Yield: 0.130 g (34 % based on {Pd}). Elemental analysis (%) calcd: Na 3.76, Co 1.61, Pd 34.79, As 16.33, C 15.71, H 2.53; found: Na 3.55, Co 1.50, Pd 33.96, As 16.08, C 16.44, H 2.02. IR (2% KBr pellet, ν/cm^{-1}): 1626 (m), 1479 (w),

1438 (m), 1176 (w), 1094 (m), 1022 (w), 807 (s), 743 (s), 695 (s), 638 (s), 613 (sh), 531 (s), 431 (sh).

Na₆[Ni^{II}Pd^{II}₁₂(As^VPh)₈O₃₂]₃₀H₂O (Ni-2e): The compound was prepared by exactly the same procedure as **Sc-2a**, but with NiSO₄·6H₂O (0.055 g, 0.156 mmol). Dark red-brown crystals were obtained. Yield: 0.125 g (31 % based on {Pd}). Elemental analysis (%) calcd: Na 3.69, Ni 1.57, Pd 34.12, As 16.02, C 15.41, H 2.69; found: Na 3.82, Ni 1.56, Pd 33.20, As 15.78, C 16.69, H 2.04. IR (2% KBr pellet, ν/cm^{-1}): 1624 (m), 1480 (w), 1438 (m), 1178 (w), 1093(m), 1024(w), 806(s), 741(s), 692(s), 679(sh), 626 (s), 592 (sh), 529(s), 493(sh), 435(sh).

Na₆[Cu^{II}Pd^{II}₁₂(As^VPh)₈O₃₂]₁₉H₂O (Cu-2f): The compound was prepared by exactly the same procedure as **Sc-2a**, but with Cu(CH₃COO)₂·H₂O (0.059 g, 0.156 mmol). Dark red-brown crystals were obtained. Yield: 0.095 g (24 % based on {Pd}). Elemental analysis (%) calcd: Na 4.01, Cu 1.85, As 17.42, C 16.76, H 1.93; found: Na 3.89, Cu 2.37, As 16.89, C 16.85, H 2.30. IR (2% KBr pellet, ν/cm^{-1}): 1622 (m), 1478 (w), 1437 (m), 1176(w), 1091(m), 1022(w), 804(s), 744(s), 694(s), 647(s), 630(sh), 531(s), 501(sh), 448 (sh).

Na₆[Zn^{II}Pd^{II}₁₂(As^VPh)₈O₃₂]_yH₂O (Zn-2g): The compound was prepared by exactly the same procedure as **Sc-2a**, but with ZnCl₂ (0.021 g, 0.156 mmol). Dark red-brown crystals were obtained. Yield: 0.080 g (22 % based on {Pd}). Elemental analysis (%) calcd: Na 3.56, Zn 1.69, As 15.47, C 14.88, H 2.97; found: Na 3.68, Zn 1.65, As 15.66, C 13.88, H 2.09. IR (2% KBr pellet, ν/cm^{-1}): 1626 (m), 1482 (w), 1438 (m), 1180 (w), 1093 (m), 1024 (w), 803 (s), 744 (s), 696 (s), 641 (s), 529 (s), 431 (sh).

3.3.2 Single Crystal XRD

The compounds **Sc-2a** – **Zn-2g** are all isomorphous and crystallize in the tetragonal crystal system in the space group *I4/m*. The structure of the {MPd₁₂(AsPh)₈O₃₂} core is very

similar to that in the previously reported **Pd₁₃PhAs** and can be described in terms of Platonic and Archimedean solids.⁴ The main difference is that the central Pd^{II} ion in the latter has been replaced by a 3d transition metal ion (Fig. 3.5).

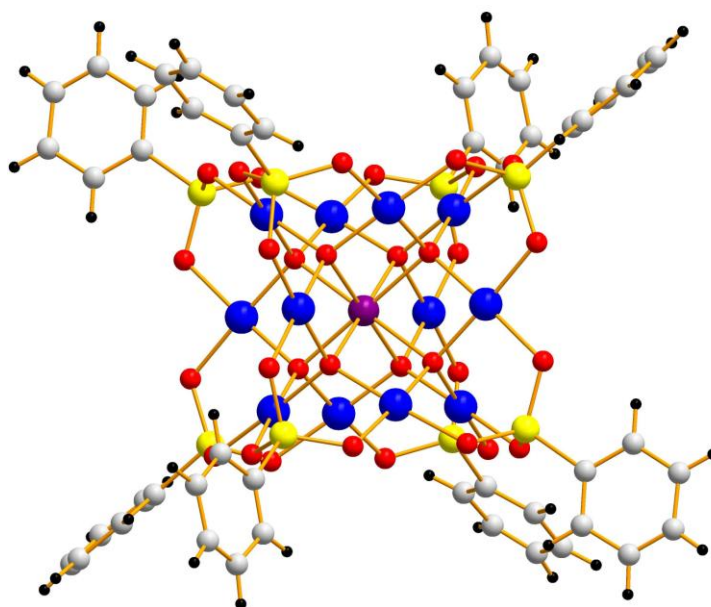


Figure 3.5 Ball-and-stick representation of $[\text{MPd}^{\text{II}}_{12}(\text{AsPh})_8\text{O}_{32}]^{n-}$.

Colour code: M violet, Pd blue, As yellow, O red, C grey, and H black.

As it was shown by single crystal XRD measurements the central transition metal ion in **Sc-2a – Zn-2g** is coordinated by eight oxygen atoms situated at the vertices of a cube. The twelve palladium(II) ions surrounding the central $\{\text{MO}_8\}$ fragment form a cuboctahedron. Each oxygen atom of the “inner” $\{\text{MO}_8\}$ cube ($\mu_4\text{-O}$) is coordinated by the transition metal ion and by three palladiums, situated on a trigonal face of the cuboctahedron. Each of the twelve Pd^{II} ions exhibits the expected square-planar coordination by two $\mu_4\text{-O}$ and two “outer” oxygen atoms ($\mu_2\text{-O}$). The 24 “outer” oxygen atoms form a truncated cube-shaped shell, which is capped by eight positively charged AsPh^{4+} groups. The eight As atoms possess

tetrahedral coordination geometry and form in fact an external, cube shaped shell. Selected bond distances for the polyanions in **Sc-2a** – **Zn-2g** are shown in Table 3.5.

Table 3.5 Selected bond lengths [Å] for the polyanions in **Sc-2a** – **Zn-2g**.

	M – (μ_4 -O)	Pd – (μ_4 -O) (mean)	Pd – (μ -O) (mean)	As – (μ -O) (mean)	As – C
Sc-2a	2.257(4)	1.980(4)	2.032(5)	1.686(5)	1.908(6)
Mn-2b	2.294(5)	1.971(5)	2.040(6)	1.669(7)	1.914(8)
Fe-2c	2.224(5)	1.973(5)	2.044(5)	1.675(6)	1.895(8)
Co-2d	2.259(6)	1.965(6)	2.040(7)	1.681(7)	1.910(9)
Ni-2e	2.277(7)	1.960(6)	2.040(7)	1.672(7)	1.917(10)
Cu-2f	2.270(4)	1.968(3)	2.045(4)	1.686(4)	1.903(4)
Zn-2g	2.269(7)	1.968(7)	2.043(8)	1.681(8)	1.892(11)

In the solid state the polyanions in **Sc-2a** – **Zn-2g** form the same hexagonal-packing framework as in **Y-1a** – **Lu-1m** (see § 3.2.2).

Tables 3.6 – 3.7 include further crystallographic data for **Sc-2a** – **Zn-2g**.

Table 3.6 Crystal data and structure refinement for **Sc-2a – Co-2d**.

	Sc-2a	Mn-2b	Fe-2c	Co-2d
empirical formula	C ₄₈ H ₈₂ As ₈ Na ₅ O ₅₃ Pd ₁₂ Sc	C ₄₈ H ₉₄ As ₈ Na ₆ O ₅₉ Pd ₁₂ Mn	C ₄₈ H ₈₆ As ₈ Na ₅ O ₅₅ Pd ₁₂ Fe	C ₄₈ H ₉₂ As ₈ Na ₆ O ₅₈ Pd ₁₂ Co
molecular weight [gmol ⁻¹]	3543.21	3684.27	3590.13	3670.25
crystal system	Tetragonal	Tetragonal	Tetragonal	Tetragonal
space group	I4/m	I4/m	I4/m	I4/m
<i>a</i> [Å]	15.8178(14)	16.109(3)	15.8607(13)	15.9271(4)
<i>b</i> [Å]	15.8178(14)	16.109(3)	15.8607(13)	15.9271(4)
<i>c</i> [Å]	24.962(3)	24.770(6)	24.9466(19)	25.1712(19)
<i>V</i> [Å ³]	6245.7(10)	6428(2)	6275.6(9)	6385.2(5)
<i>Z</i>	2	2	2	2
<i>T</i> [K]	100(2)	173(2)	100(2)	173(2)
ρ_{calcd} [Mgm ⁻³]	1.884	1.903	1.900	1.909
μ [mm ⁻¹]	3.924	3.868	3.969	3.924
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]				
<i>R</i> ₁ ^[a]	0.0467	0.0551	0.0508	0.0696
<i>wR</i> ₂ ^[b]	0.1486	0.1750	0.1538	0.2130
<i>R</i> indices (all data)				
<i>R</i> ₁ ^[a]	0.0635	0.0989	0.0866	0.1015
<i>wR</i> ₂ ^[b]	0.1594	0.2015	0.1807	0.2321

$$^{[a]} R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^{[b]} wR_2 = [\sum w (F_o^2 - F_c^2)^2 / \sum w (F_o^2)^2]^{1/2}$$

Table 3.7 Crystal data and structure refinement for **Ni-2e** – **Zn-2g**.

	Ni-2e	Cu-2f	Zn-2g
empirical formula	C ₄₈ H ₁₀₀ As ₈ Na ₆ O ₆₂ Pd ₁₂ Ni	C ₄₈ H ₆₄ As ₈ Na ₆ O ₄₄ Pd ₁₂ Cu	C ₄₈ H ₈₀ As ₈ Na ₆ O ₅₂ Pd ₁₂ Zn
molecular weight [gmol ⁻¹]	3742.09	3422.63	3653.3
crystal system	Tetragonal	Tetragonal	Tetragonal
space group	I4/m	I4/m	I4/m
<i>a</i> [Å]	16.1657(7)	15.8988(5)	15.8285(11)
<i>b</i> [Å]	16.1657(7)	15.8988(5)	15.8285(11)
<i>c</i> [Å]	24.744(3)	25.1299(11)	25.034(2)
<i>V</i> [Å ³]	6466.5(8)	6352.1(4)	6272.0(8)
<i>Z</i>	2	2	2
<i>T</i> [K]	173(2)	173(2)	100(2)
ρ_{calcd} [Mgm ⁻³]	1.922	1.789	1.873
μ [mm ⁻¹]	3.896	3.966	4.039
final <i>R</i> indices [<i>I</i> >2σ(<i>I</i>)]			
<i>R</i> ₁ ^[a]	0.0472	0.0549	0.0674
<i>wR</i> ₂ ^[b]	0.1509	0.1764	0.1984
<i>R</i> indices (all data)			
<i>R</i> ₁ ^[a]	0.0843	0.0689	0.1065
<i>wR</i> ₂ ^[b]	0.1723	0.2070	0.2250

$$^{[a]} R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^{[b]} wR_2 = [\sum w (F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$

3.3.3 FT-IR Spectroscopy

The polyoxopalladate salts **Sc-2a** – **Zn-2g** and the parent $\text{Na}_6[\text{Pd}^{\text{II}}_{13}(\text{PhAs})_8\text{O}_{32}]\cdot 24\text{H}_2\text{O}$ (**Na-Pd₁₃PhAs**) have similar FT-IR spectra showing only slight shifts in some band positions (see figures 3.6a – 3.6g).⁴ As an example, for **Sc-2a** the bands between 435 and 629 cm^{-1} correspond to the vibrational modes of the Pd–O groups, which could be superimposed with bands associated with the Sc–O vibrations. The strong band at 804 cm^{-1} is attributed to the vibrations of the $\{\text{AsO}_3\}$ fragments. The stretching and bending vibrations of the C–C and C–H bonds of the phenyl rings appear at 695, 742 and in the region between 1094–1479 cm^{-1} . The broad band at 1623 cm^{-1} belongs to asymmetric vibrations of the crystal waters.⁸

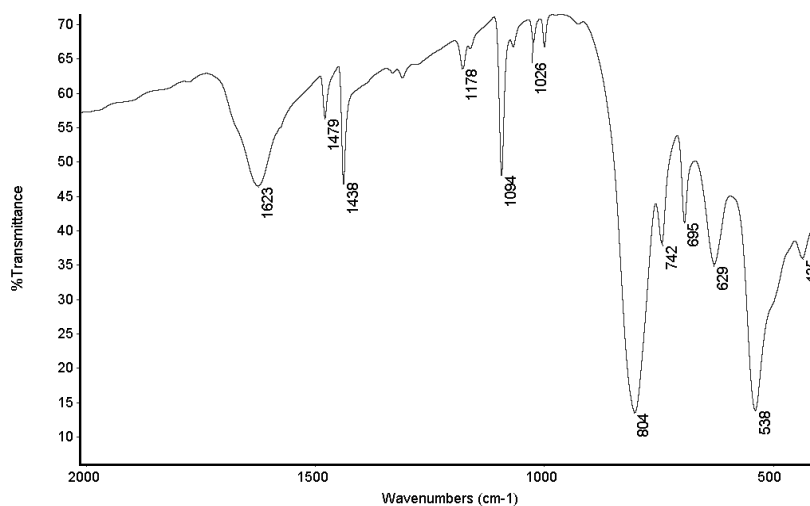


Figure 3.6a FT-IR spectrum of **Sc-2a**.

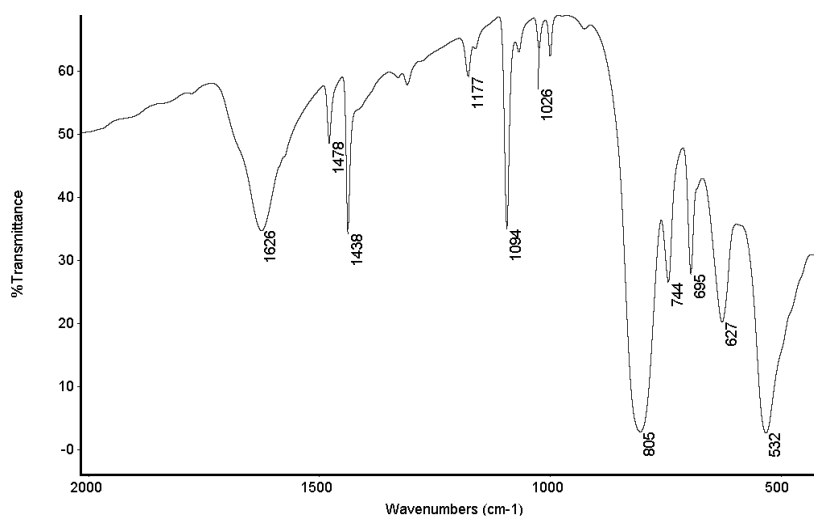


Figure 3.6b FT-IR spectrum of **Mn-2b**.

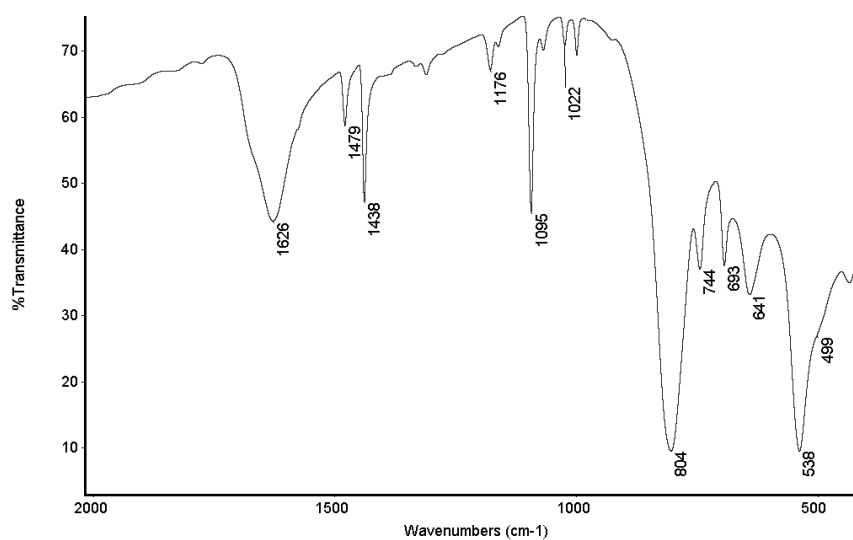


Figure 3.6c FT-IR spectrum of Fe-2c.

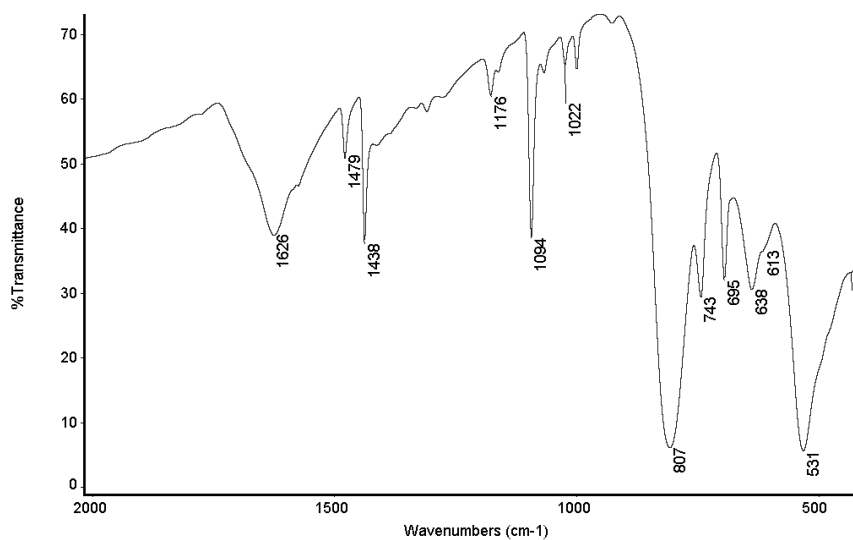


Figure 3.6d FT-IR spectrum of Co-2d.

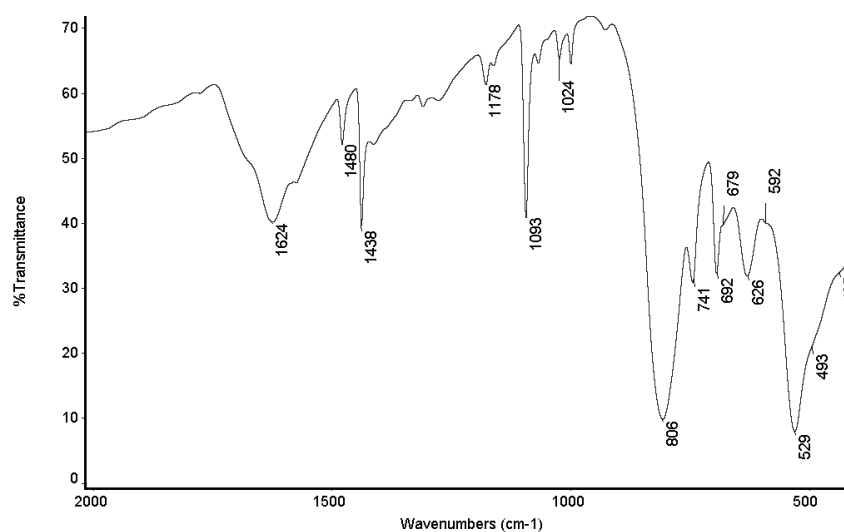


Figure 3.6e FT-IR spectrum of Ni-2e.

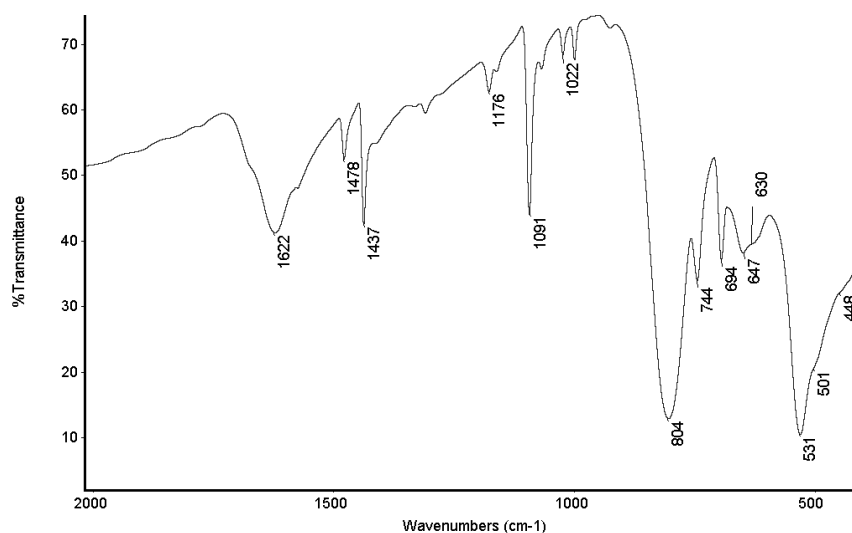


Figure 3.6f FT-IR spectrum of Cu-2f.

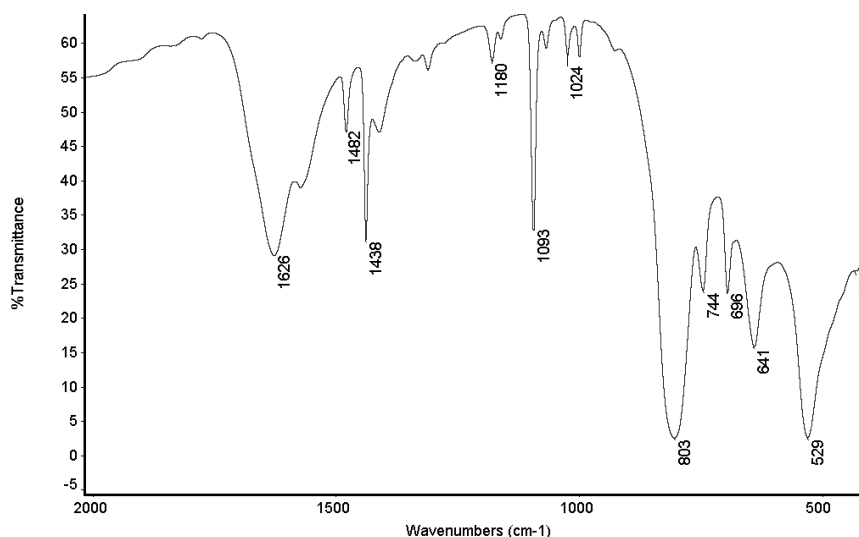


Figure 3.6g FT-IR spectrum of Zn-2g.

3.3.4 Thermogravimetric Analysis

The thermogravimetric processes of **Sc-2a** – **Zn-2g** are very similar and reveal several weight-loss steps (see Fig. 3.7a–3.7g). For example, for **Sc-2a** (Fig. 3.7a) the first step occurs between 25 and 222 °C and corresponds to the loss of 18 water molecules per formula unit. The combustion of eight phenyl groups per formula unit proceeds in the temperature range of 222 – 473 °C. The additional smooth weight loss before 525 °C is assigned to the removal of oxygen associated with the decomposition of As_2O_5 with formation of As_2O_3 and O_2 . Several

consecutive weight-loss steps covering the temperature range of 525 – 835 °C are attributed to arsenic volatility, most likely in the form of As_4O_6 .^{4,9}

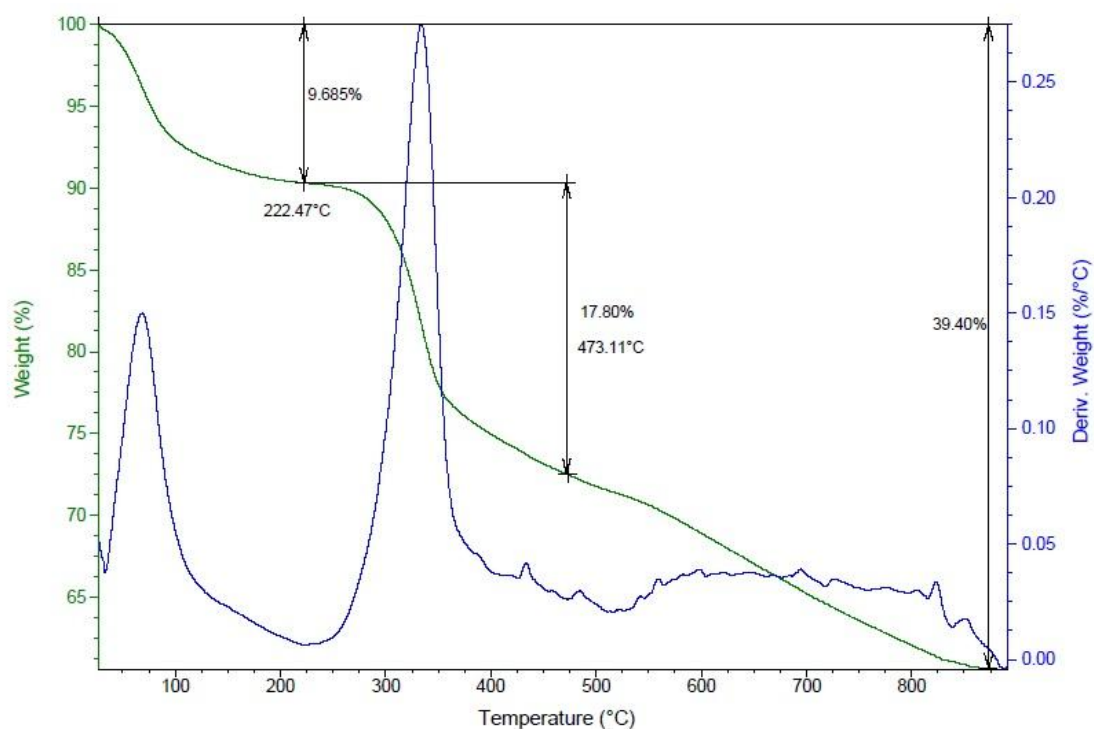


Figure 3.7a Thermogram of Sc-2a.

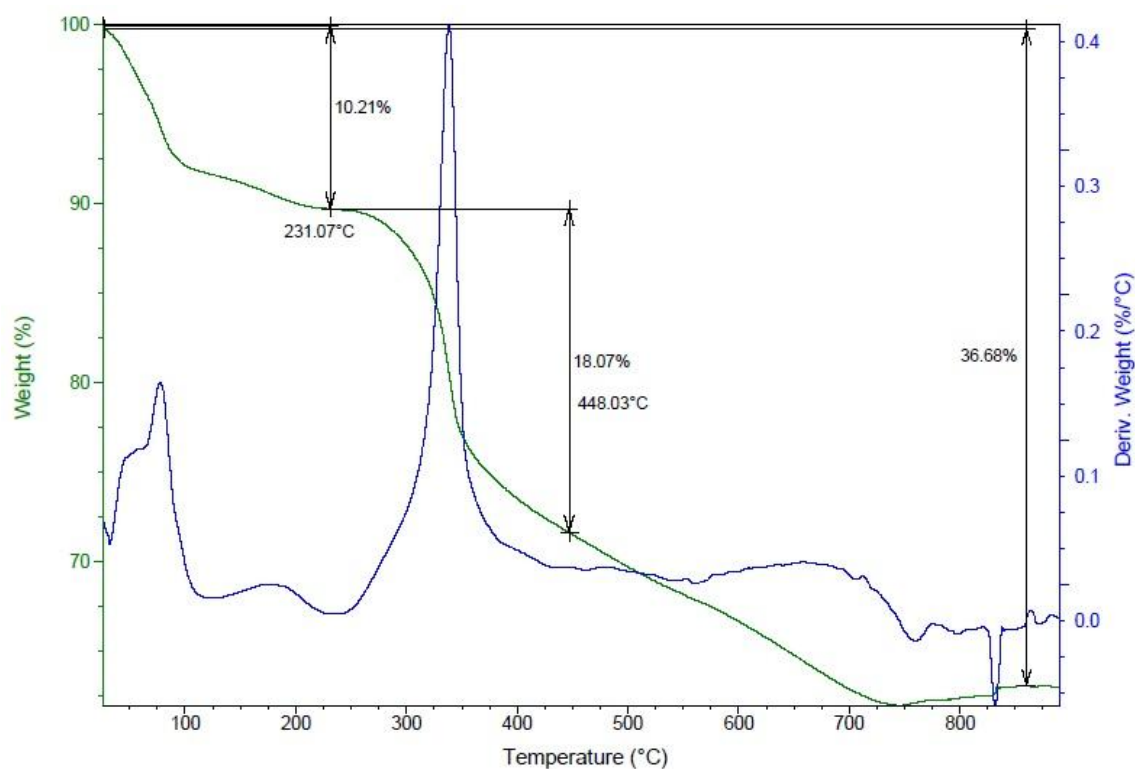


Figure 3.7b Thermogram of Mn-2b.

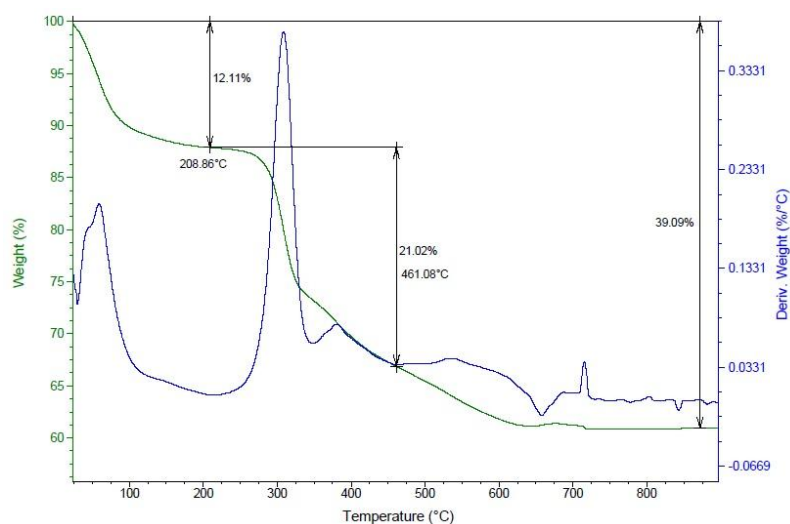


Figure 3.7c Thermogram of Fe-2c.

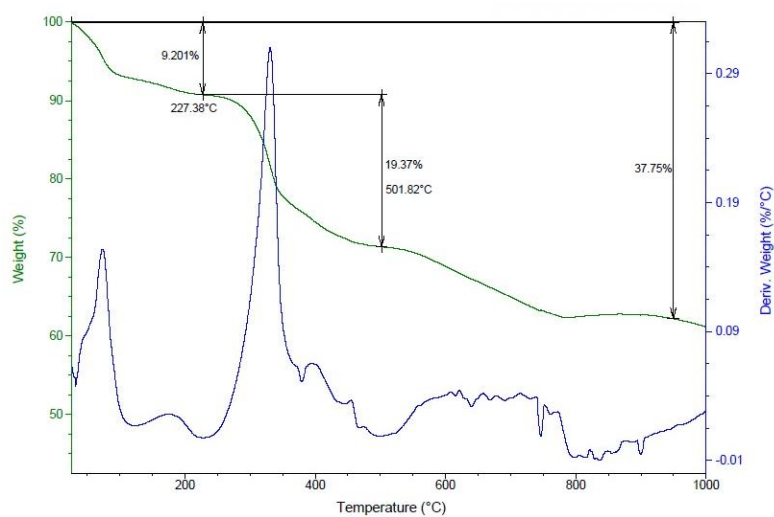


Figure 3.7d Thermogram of Co-2d.

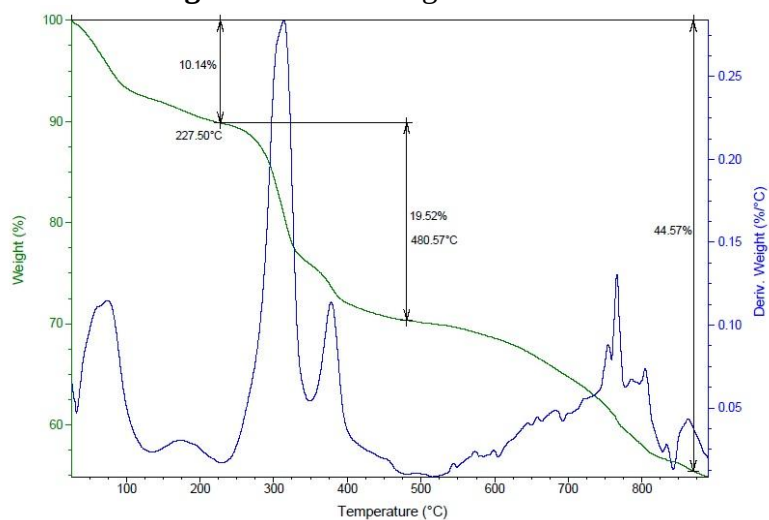


Figure 3.7e Thermogram of Ni-2e.

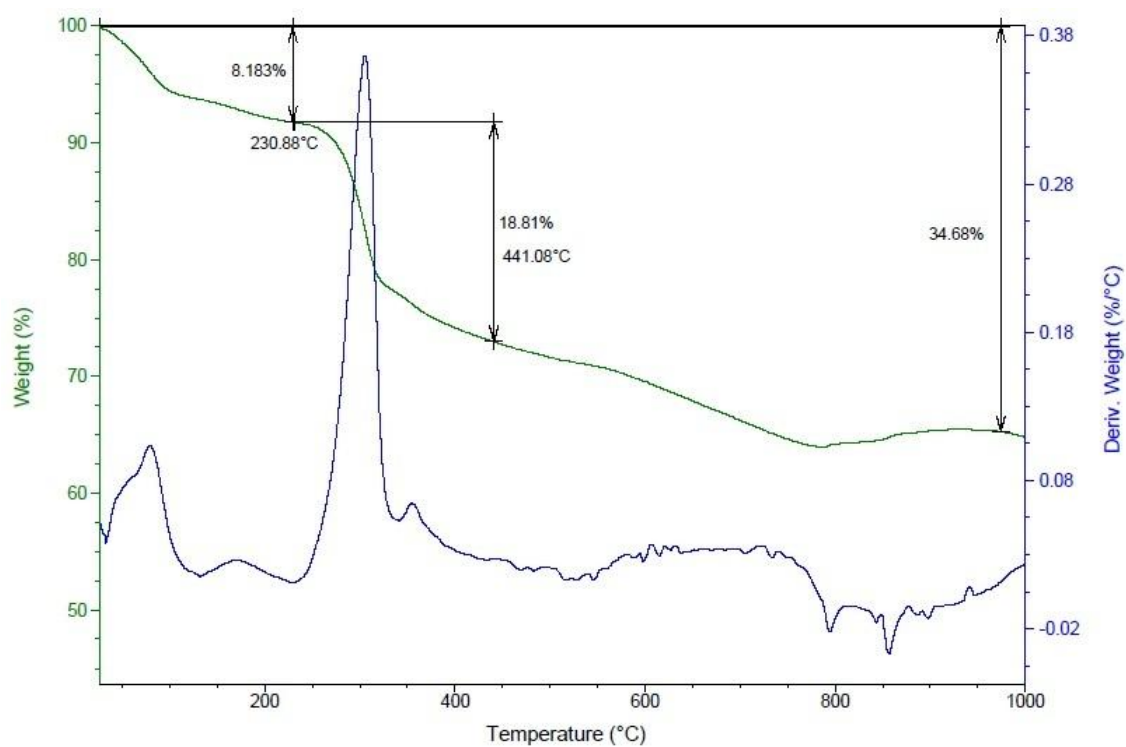


Figure 3.7f Thermogram of Cu-2f.

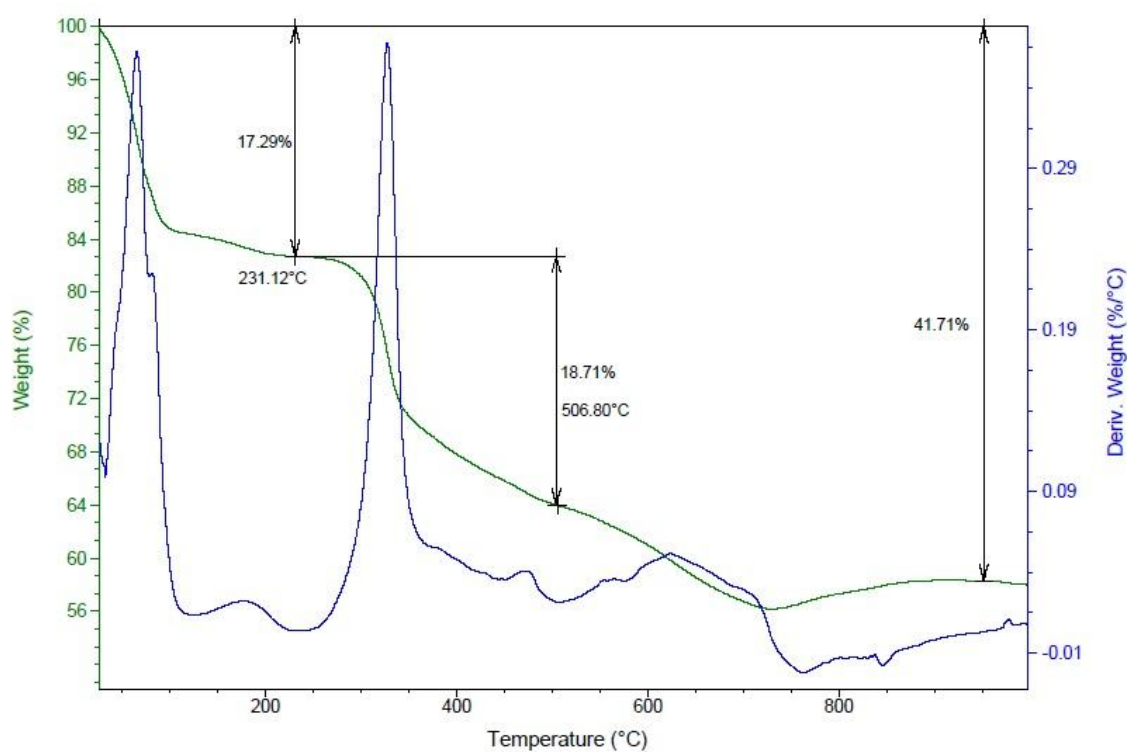


Figure 3.7g Thermogram of Zn-2g.

3.3.5 NMR Spectroscopy

We also performed ^{13}C and ^1H NMR studies on solution of **Sc-2a** and **Zn-2g** in D_2O .

^{13}C and ^1H NMR spectra are as expected for phenyl groups (Fig. 3.8-3.9).

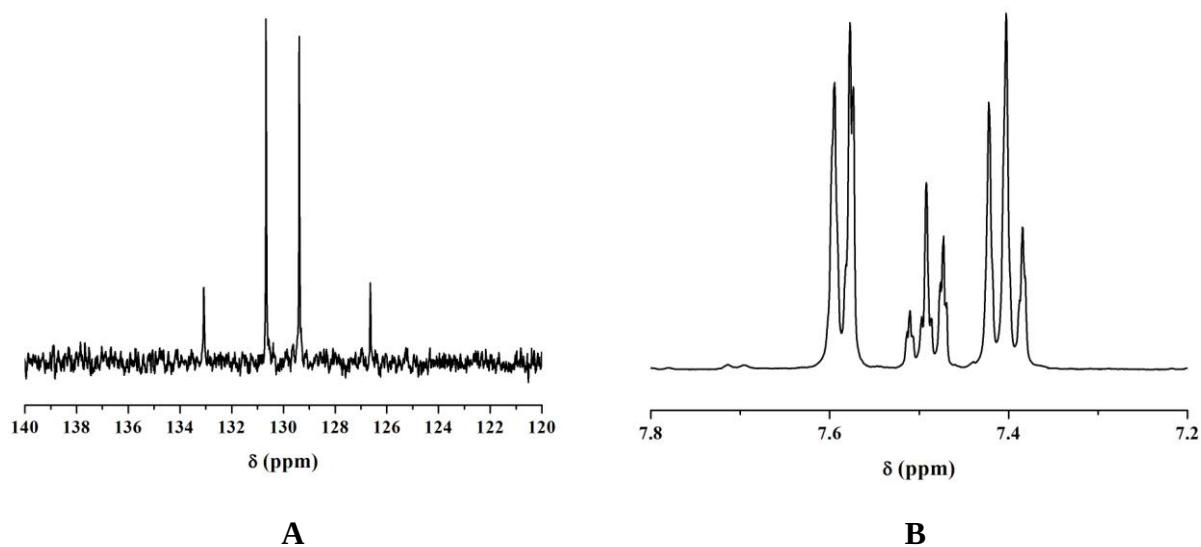


Figure 3.8 ^{13}C NMR spectrum (A) and ^1H NMR spectrum (B) of **Sc-2a**.

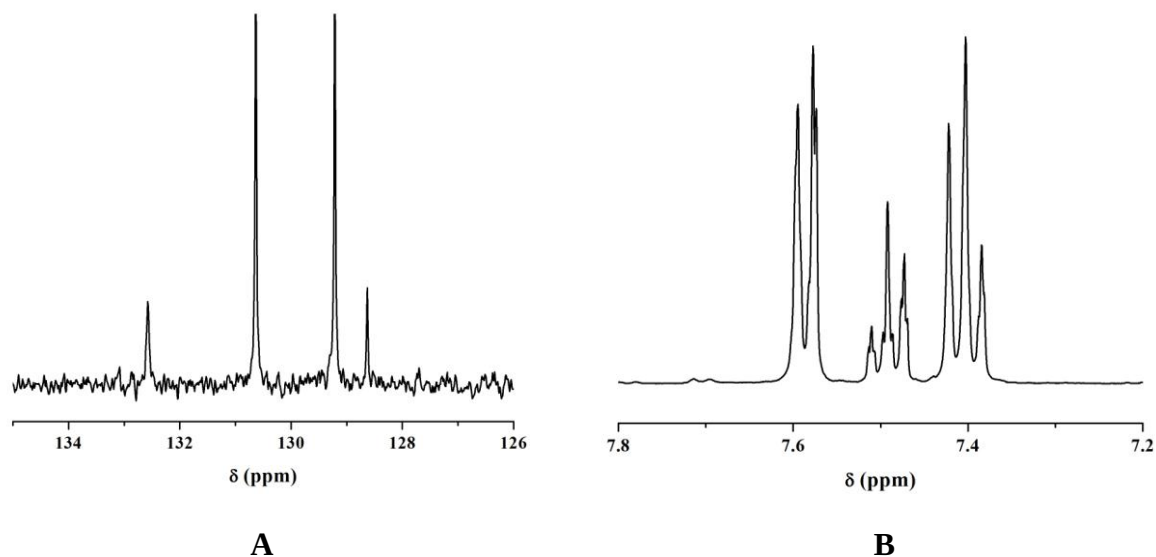


Figure 3.9 ^{13}C NMR spectrum (A) and ^1H NMR spectrum (B) of **Zn-2g**.

3.3.6 Conclusions

We have expanded the class of noble metalates by the discovery of a novel family of 3d transition metal-containing heteropolyoxopalladates, $[\text{MPd}^{\text{II}}_{12}(\text{AsPh})_8\text{O}_{32}]^{n-}$ ($\text{M} = \text{Sc}^{\text{III}}, \text{Mn}^{\text{II}}, \text{Fe}^{\text{III}}, \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Cu}^{\text{II}}, \text{Zn}^{\text{II}}$). These polyanions have all been prepared by reaction of $\text{Pd}_3(\text{CH}_3\text{COO})_6$, phenylarsonic acid and a salt of the respective M^{n+} ion in neutral aqueous medium by using conventional open-beaker synthetic techniques. This work extends our earlier studies on heteropoly-13-palladates, in particular $[\text{Pd}^{\text{II}}_{13}(\text{As}^{\text{V}}\text{Ph})_8\text{O}_{32}]^{6-}$ (**Pd₁₃PhAs**) which contains an eight-coordinated central Pd^{II} ion.⁴ The 7 polyanions have similar structure as **Pd₁₃PhAs**, but the central, eight-coordinated Pd^{II} has now been replaced by the 3d transition metal ions for which eight-coordination is also unusual.

3.4 Selenite (IV)-capped Lutetium- and 3d Transition Metal-containing

Polyoxopalladates

As it was previously showed the $\{\text{Pd}^{\text{II}}_{12}\text{Se}_8\text{O}_{32}\}$ polyoxopalladate shell encapsulated quite unusual six coordinated Pd^{II} ion.⁴ That is why we suggested to systematically study the possibility to incorporate in the center of the $\{\text{Pd}_{12}\text{Se}_8\text{O}_{32}\}$ shell the ions with large coordination number, such as 3d transition metals and lanthanides.

A novel series of 3d transition metal- and lutetium-containing polyoxopalladates with general formula $\text{Na}_{n-x}\text{H}_x[\text{MPd}^{\text{II}}_{12}\text{Se}_8\text{O}_{32}]\cdot y\text{H}_2\text{O}$, where $\text{M} = \text{Mn}^{\text{II}}$ (**Mn-3a**), Fe^{III} (**Fe-3b**), Co^{II} (**Co-3c**), Cu^{II} (**Cu-3d**), Zn^{II} (**Zn-3e**), Lu^{III} (**Lu-3f**), has resulted the investigation. The compounds **Mn-3a** – **Lu-3f** have been synthesized by reaction of $\text{Pd}_3(\text{CH}_3\text{COO})_6$, selenium dioxide and a salt of the respective 3d metal ion in 0.5 M aqueous sodium acetate solution (pH 6.9) in yields ranging from 9% (for **Fe-3b**) to 34% (for **Zn-3e**), and characterized in the solid state by FT-IR spectroscopy, TGA, single-crystal XRD and elemental analysis. The

diamagnetic Zn^{II} (**Zn-2e**) and Lu^{III} (**Lu-3f**) derivatives were studied in $\text{H}_2\text{O}/\text{D}_2\text{O}$ solution by ^{77}Se NMR spectroscopy. It was shown that ions of different 3d transition metals and lutetium can be incorporated in the center of the polyoxopalladate $[\text{MPd}^{\text{II}}_{12}\text{Se}_8\text{O}_{32}]^{\text{n-}}$. Interestingly, the XRD measurements showed that the coordination number of the central 3d transition metal or lutetium ions is eight in comparison with the six-coordinated palladium(II) center in $\{\text{Pd}^{\text{II}}_{12}\text{Se}_8\text{O}_{32}\}$ shell. These compounds are stable towards air and light in the solid state and can be successfully recrystallized several times from water.

3.4.1 Synthetic Procedures

$\text{Na}_{6-x}\text{H}_x[\text{MnPd}_{12}\text{Se}_8\text{O}_{32}]\cdot y\text{H}_2\text{O}$ (Mn-3a**):** $\text{Pd}_3(\text{CH}_3\text{COO})_6$ (0.140 g, 0.208 mmol), SeO_2 (0.070 g, 0.630 mmol) and $\text{MnSO}_4\cdot\text{H}_2\text{O}$ (0.009 g, 0.052 mmol) were dissolved in 5 ml of 0.5 M NaOAc solution (pH 6.9), while stirring and heating to 80°C . After 30 min of heating the pH was adjusted to 6.4 by adding several drops of 1 M NaOH. Then the reaction mixture was heated with stirring for 1 h. The solution was cooled to room temperature and filtrated. The filtrate was kept at room temperature for several days to produce red crystals, which were isolated by filtration, and air-dried. Yield: 0.040 g (15 %based on Pd). IR (2% KBr pellet, v/cm^{-1}): 1632(m), 797(s), 734(s), 645(s), 613(sh), 548(s), 501(sh).

$\text{Na}_{5-x}\text{H}_x[\text{FePd}_{12}\text{Se}_8\text{O}_{32}]\cdot y\text{H}_2\text{O}$ (Fe-3b**):** The compound was prepared by exactly the same procedure as **Mn-3a**, but with $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (0.022 g, 0.052 mmol). Dark-red crystals were obtained. Yield: 0.030 g (9% based on Pd). IR (2% KBr pellet, v/cm^{-1}): 1630 (m), 797 (s), 726 (s), 654 (s), 615 (sh), 551 (s), 501 (sh).

$\text{Na}_{6-x}\text{H}_x[\text{CoPd}_{12}\text{Se}_8\text{O}_{32}]\cdot y\text{H}_2\text{O}$ (Co-3c**):** The compound was prepared by exactly the same procedure as **Mn-3a**, but with $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.016 g, 0.052 mmol). Yield: 0.096 g (30 % based on Pd). IR (2% KBr pellet, v/cm^{-1}): 1628 (m), 799 (s), 738 (s), 658 (s), 624 (sh), 548 (s), 505 (sh).

Na₆[CuPd₁₂Se₈O₃₂]·12H₂O (Cu-3d): The compound was prepared by exactly the same procedure as **Mn-3a**, but with Cu(CH₃COO)₂·H₂O (0.011 g, 0.052 mmol). Yield: 0.100 g (30% based on Pd). IR (2% KBr pellet, ν/cm⁻¹): 1617 (m), 797 (s), 725 (s), 666 (sh), 611 (sh), 546 (s). Elemental analysis (%) calcd: Cu 2.24, Na 4.86, Pd 45.0, Se 22.26; found: Cu 2.15, Na 4.78, Pd 44.6, Se 22.40.

Na₆[ZnPd₁₂Se₈O₃₂]·13H₂O (Zn-3e): The compound was prepared by exactly the same procedure as **Mn-3a**, but with ZnCl₂ (0.007 g, 0.052 mmol). Yield: 0.113 g (34 % based on Pd). IR (2% KBr pellet, ν/cm⁻¹): 1628 (m), 797 (s), 737 (s), 656 (s), 624 (sh), 547 (s), 506 (sh). Elemental analysis (%) calcd: Zn 2.29, Na 4.83, Pd 44.7, Se 22.10; found: Zn 2.78, Na 5.09, Pd 44.4, Se 22.51.

Na_{5-x}H_x[LuPd₁₂Se₈O₃₂]·yH₂O (Lu-3f): The compound was prepared by exactly the same procedure as **Mn-3a**, but with LuCl₃·6H₂O (0.020 g, 0.052 mmol). Yield: 0.078 g (23 % based on Pd). IR (2% KBr pellet, ν/cm⁻¹): 1628 (m), 793 (s), 723 (s), 629 (s), 552(s), 435 (m).

3.4.2 Single Crystal XRD

The structure of the {MPd₁₂Se₈O₃₂} core in the compounds **Mn-3a** – **Lu-3f** is very similar to that in the previously reported [Pd^{II}₁₃Se₈O₃₂]⁶⁻ (**Pd₁₃Se**).⁴ The main difference is that the central six-coordinated Pd^{II} ion in the latter has been replaced by a 3d transition metal or lutetium ion (see Fig. 3.10). Single crystal X-ray analysis showed that the central ion in **Mn-3a** – **Lu-3f** is coordinated by eight oxygen atoms, so high coordination number is rather unusual for 3d transition metal ions.

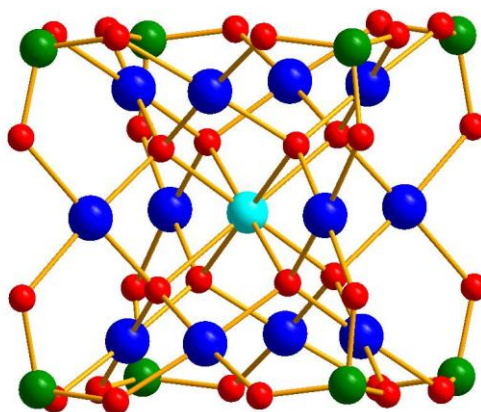


Figure 3.10 Ball-and-stick representation of $[\text{MPd}^{\text{II}}_{12}\text{Se}_8\text{O}_{32}]^{n-}$.

Color code: M turquoise, Pd blue, Se green, O red.

The twelve palladium(II) ions surrounding the central $\{\text{MO}_8\}$ fragment form a cuboctahedron. Each oxygen atom of the “inner” $\{\text{MO}_8\}$ cube ($\mu_4\text{-O}$) is coordinated by the central ion and by three palladiums, situated on a trigonal face of the cuboctahedron. Each of the twelve Pd^{II} ions exhibits the expected square-planar coordination by two $\mu_4\text{-O}$ and two “outer” oxygen atoms ($\mu_2\text{-O}$). The 24 “outer” oxygen atoms form a truncated cube-shaped shell, which is capped by eight Se^{4+} ions which exhibit a trigonal-pyramidal geometry with a stereochemically active, outward-facing lone pair. The eight selenium(IV) ions form in fact an external, distorted cube-shaped shell. Selected bond distances for the polyanions in **Mn-3a** – **Zn-3e** are shown in Table 3.8.

Table 3.8 Selected bond lengths [$\text{\AA}$] for the polyanions in **Mn-3a** – **Zn-3e**.

	M – ($\mu_4\text{-O}$)	Pd – ($\mu_4\text{-O}$)	Pd – ($\mu\text{-O}$)	Se – ($\mu\text{-O}$)
Mn-3a	2.219(14)–2.261(14)	1.936(14)–2.010(20)	2.017(16)–2.090(30)	1.670(20)–1.746(13)
Fe-3b	2.149(16)–2.236 (17)	1.890(16)–1.983(9)	2.021(12)–2.061(18)	1.659(19)–1.724(13)
Co-3c	2.190(20)–2.260(20)	1.927(16)–1.980(16)	2.012(17)–2.080(30)	1.665(19)–1.740(17)
Cu-3d	2.113(14)–2.319(12)	1.912(12)–1.989(7)	2.017(10)–2.079(15)	1.663(11)–1.714(10)
Zn-3e	2.180(20)–2.250(20)	1.941(19)–1.990(20)	2.033(17)–2.077(18)	1.665(18)–1.720(30)

In the solid state polyanions in **Mn-3a** – **Zn-3e** linked by sodium ions and form layers along the *b* axis (Fig. 3.11), stabilized by extensive hydrogen bonding between crystal waters and oxygen atoms of the polyanions.

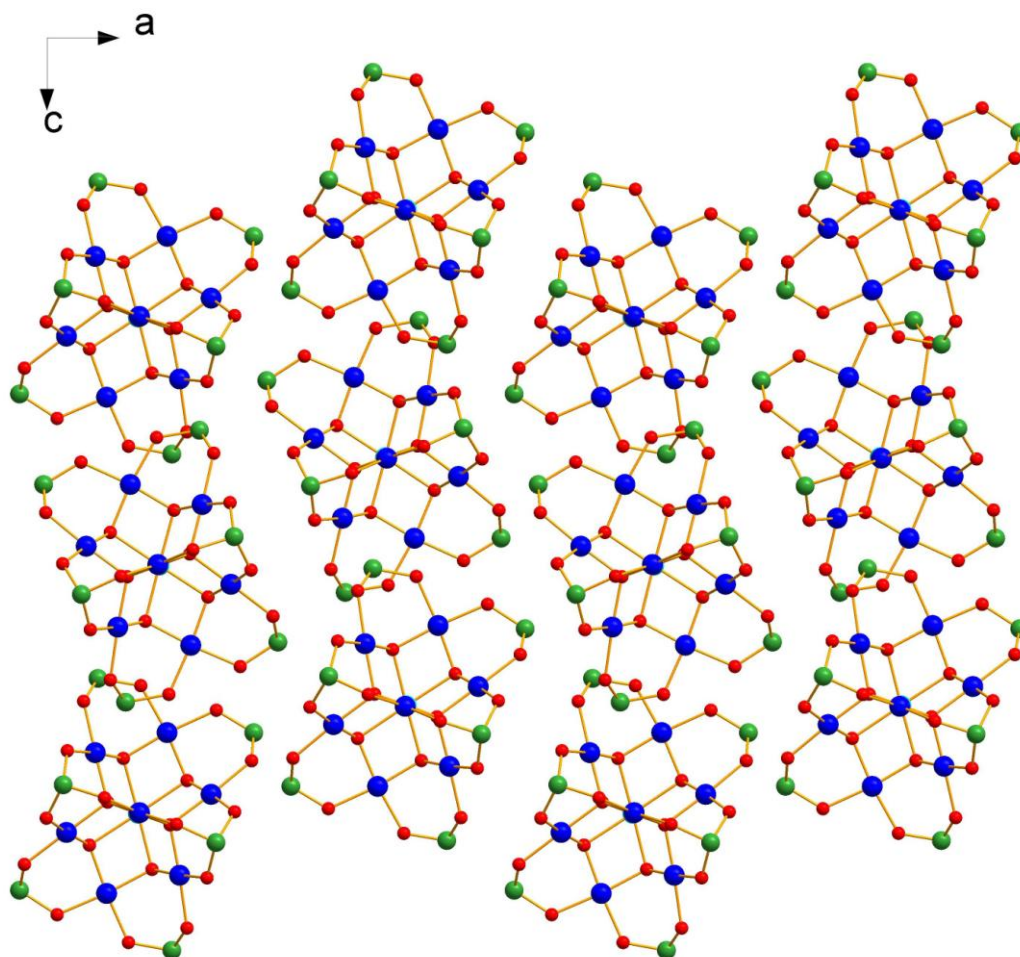


Figure 3.11 The packing arrangement of $[\text{MPd}^{\text{II}}_{12}\text{Se}_8\text{O}_{32}]^n$ along the *b* axis.

Color code: M turquoise, Pd blue, Se green, O red.

Tables 3.9 – 3.10 include further crystallographic data for **Mn-3a – Zn-3e**.

Table 3.9 Crystal data and structure refinement for **Mn-3a – Co-3c**.

	Mn-3a	Fe-3b	Co-3c
empirical formula	H ₁₈ Na ₆ O ₄₁ Pd ₁₂ Se ₈ Mn	H ₁₀ Na ₃ O ₃₆ Pd ₁₂ Se ₈ Fe	H ₁₀₅ Na _{4.5} O ₈₃ Pd ₁₂ Se ₈ Co
molecular weight [gmol ⁻¹]	2775.50	2619.38	3504.71
crystal system	Monoclinic	Orthorhombic	Orthorhombic
space group	P2(1)/n	Pnma	Pnma
<i>a</i> [Å]	18.826(3)	19.0338(9)	18.866(6)
<i>b</i> [Å]	12.951(2)	12.9678(8)	12.886(4)
<i>c</i> [Å]	18.860(3)	18.5027(8)	18.703(7)
α [°]	90.00	90.00	90.00
β [°]	90.00	90.00	90.00
γ [°]	90.00	90.00	90.00
<i>V</i> [Å ³]	4598.4(13)	4567.0(4)	4547(3)
<i>Z</i>	4	4	2
<i>T</i> [K]	293(2)	296(2)	100(2)
ρ_{calcd} [Mgm ⁻³]	4.009	3.810	2.560
μ [mm ⁻¹]	11.331	11.405	5.828
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]			
<i>R</i> ₁ ^[a]	0.0617	0.0439	0.0538
<i>wR</i> ₂ ^[b]	0.1406	0.0923	0.1508
<i>R</i> indices (all data)			
<i>R</i> ₁ ^[a]	0.1013	0.1063	0.0948
<i>wR</i> ₂ ^[b]	0.1522	0.1053	0.2184

$$^{[a]} R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^{[b]} wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$

Table 3.10 Crystal data and structure refinement for **Cu-3d** – **Zn-3e**.

	Cu-3d	Zn-3e
empirical formula	H ₂₄ Na ₆ O ₄₄ Pd ₁₂ Se ₈ Cu	H ₂₆ Na ₆ O ₄₅ Pd ₁₂ Se ₈ Zn
molecular weight [gmol ⁻¹]	2838.15	2858.00
crystal system	Monoclinic	Orthorhombic
space group	C2/m	Pnma
<i>a</i> [Å]	22.2989(9)	18.9183(11)
<i>b</i> [Å]	13.0548(5)	12.9759(7)
<i>c</i> [Å]	21.6390(13)	18.9534(11)
<i>α</i> [°]	90.00	90.00
<i>β</i> [°]	119.377(2)	90.00
<i>γ</i> [°]	90.00	90.00
<i>V</i> [Å ³]	5489.3(4)	4652.7(5)
<i>Z</i>	4	4
<i>T</i> [K]	173(2)	296(2)
ρ_{calcd} [Mgm ⁻³]	3.434	4.080
μ [mm ⁻¹]	9.657	11.454
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]		
<i>R</i> ₁ ^[a]	0.0498	0.0759
<i>wR</i> ₂ ^[b]	0.1634	0.1644
<i>R</i> indices (all data)		
<i>R</i> ₁ ^[a]	0.0758	0.1123
<i>wR</i> ₂ ^[b]	0.1749	0.1807

$$^{[a]} R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^{[b]} wR_2 = [\sum w (F_o^2 - F_c^2)^2 / \sum w (F_o^2)^2]^{1/2}$$

3.4.3 FT-IR Spectroscopy

The polyoxopalladate salts **Mn-3a** – **Lu-3f** and the parent $\text{Na}_6[\text{Pd}_{13}\text{Se}_8\text{O}_{32}]\cdot 10\text{H}_2\text{O}$ (**Na-Pd₁₃Se**) have similar FT-IR spectra showing only slight shifts in some band positions (see figures 3.12a – 3.12f).⁴ As an example, for **Mn-3a** the bands between 501 and 645 cm^{-1} correspond to the vibrational modes of the Pd–O groups, which could be superimposed with bands associated with the Mn–O vibrations. The strong bands at 734 and 797 cm^{-1} are attributed to the vibrations of the SeO_3^{2-} groups. The broad band at 1632 cm^{-1} belongs to asymmetric vibrations of the crystal waters.⁸

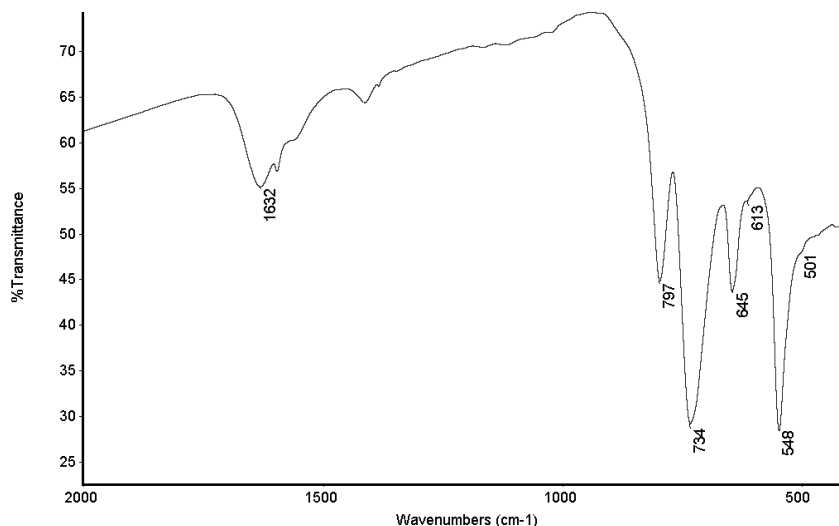


Figure 3.12a FT-IR spectrum of **Mn-3a**.

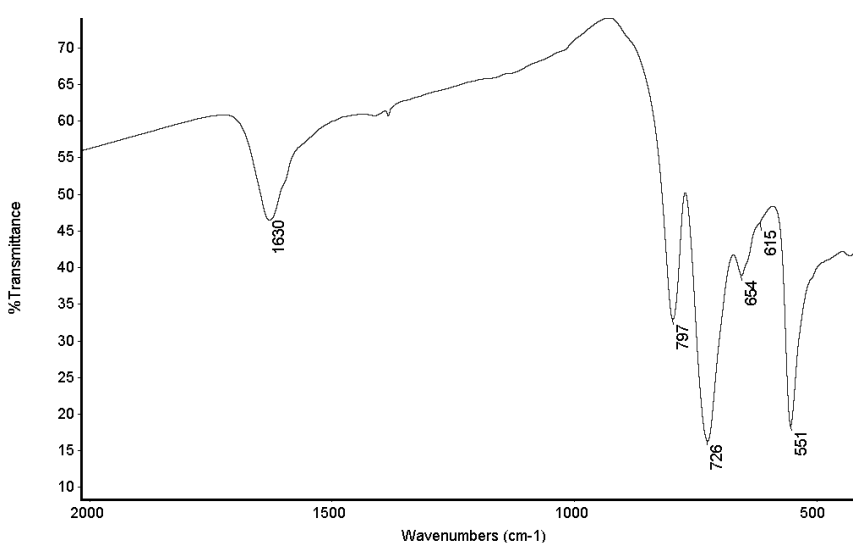


Figure 3.12b FT-IR spectrum of **Fe-3b**.

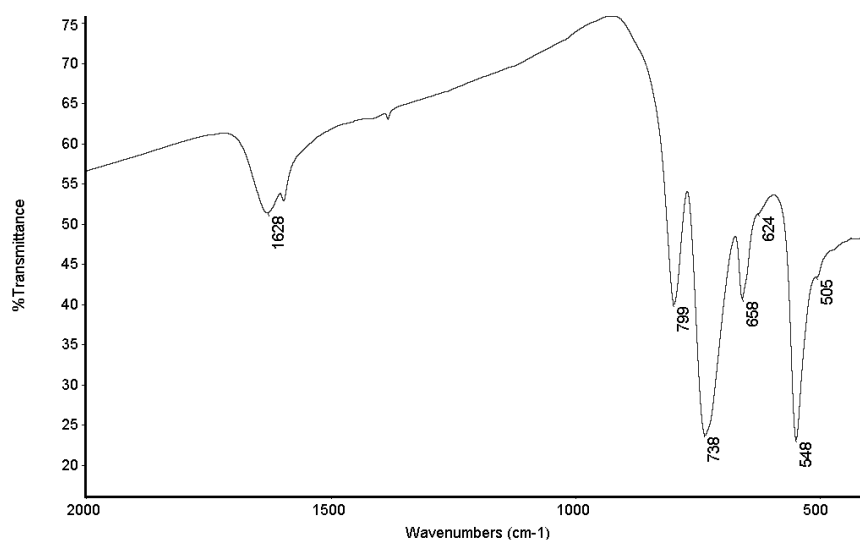


Figure 3.12c FT-IR spectrum of Co-3c.

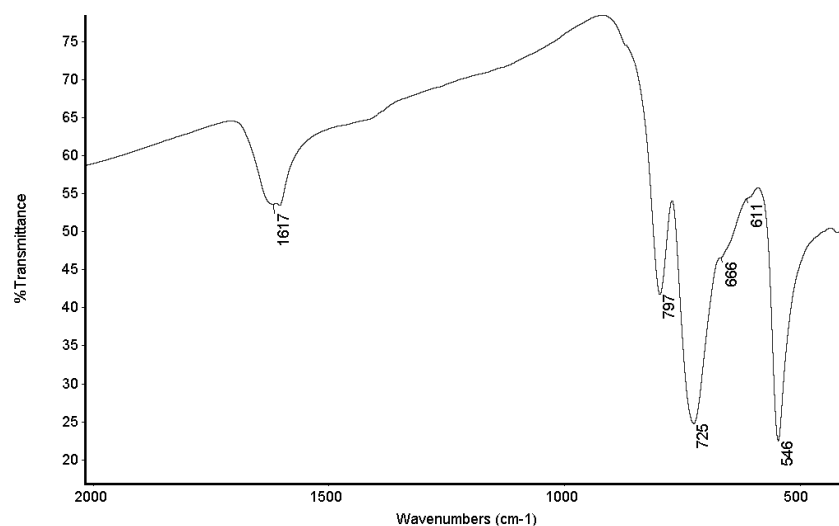


Figure 3.12d FT-IR spectrum of Cu-3d.

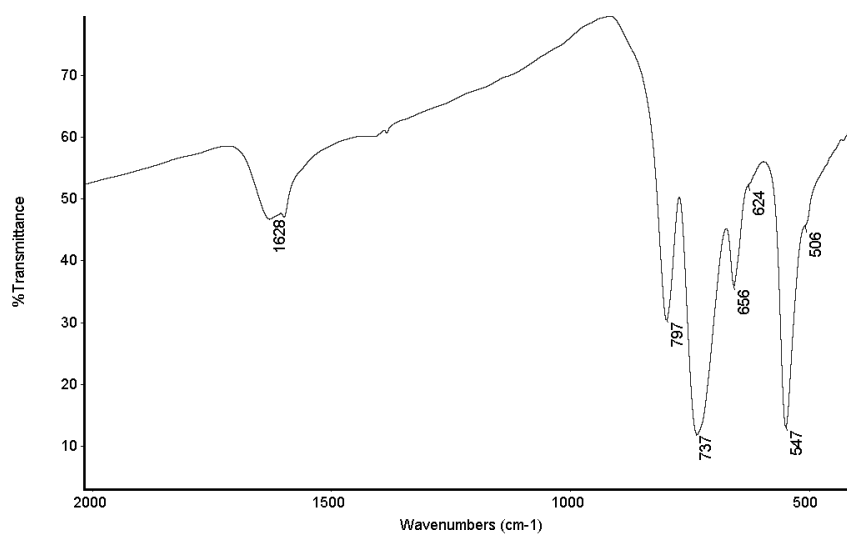


Figure 3.12e FT-IR spectrum of Zn-3e.

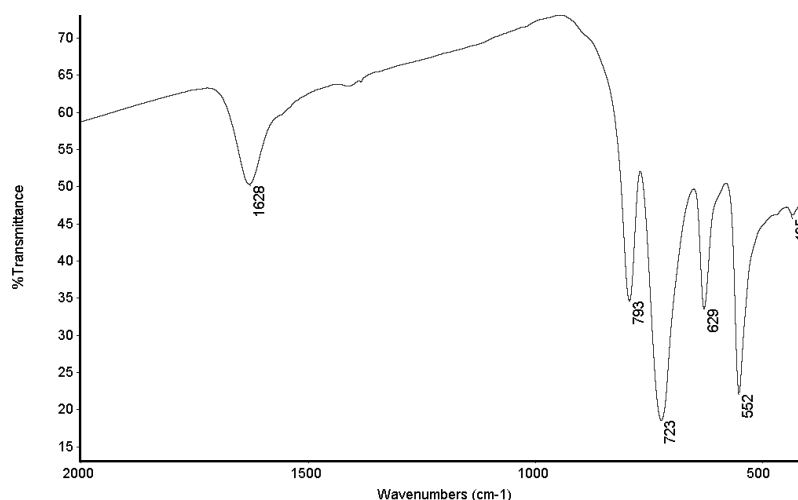


Figure 3.12f FT-IR spectrum of **Lu-3f**.

3.4.4 Thermogravimetric Analysis

The thermogravimetric processes of **Mn-3a** – **Lu-3f** are very similar and reveal several weight-loss steps (see Fig. 3.13a–3.13f). For example, for **Mn-3a** (Fig. 3.13a) the first weight loss step in the TGA curve is between 25 - 101°C and corresponds to the loss of the 8 water molecules per formula unit. The several consecutive weight loss steps covering the temperature range 195 – 776 °C are attributed to the release of 8 SeO₂ molecules per formula unit. The total observed weight loss for **Mn-3a** at 1200 °C is 47.18 %.

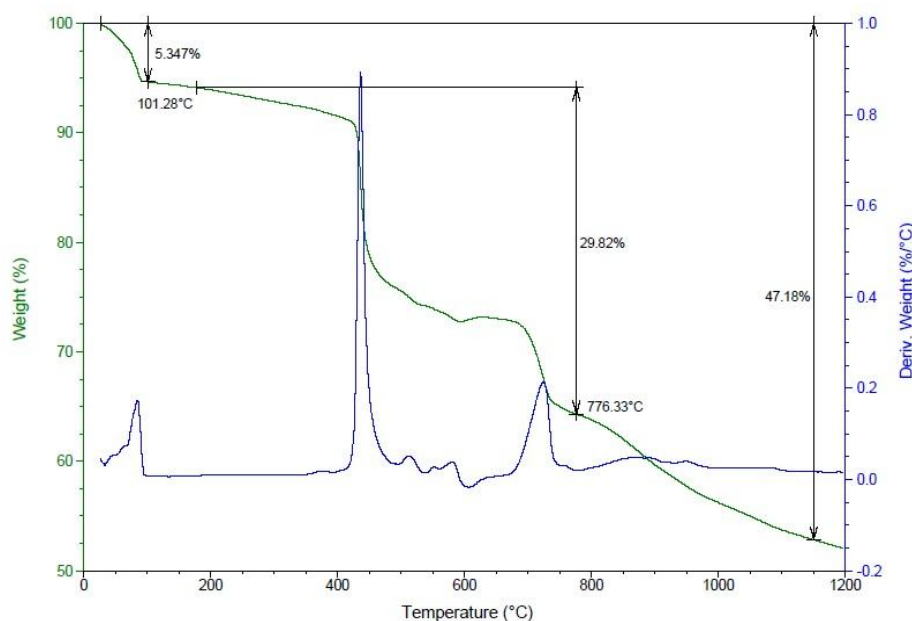


Figure 3.13a Thermogram of **Mn-3a**.

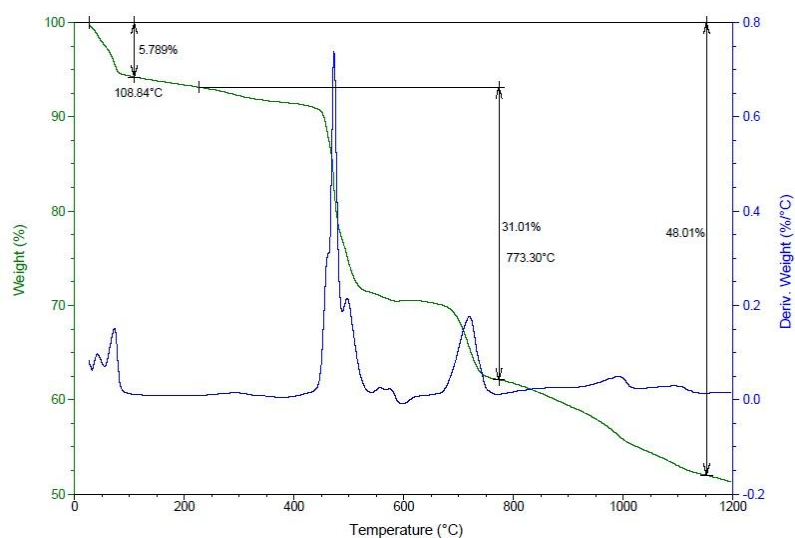


Figure 3.13b Thermogram of Fe-3b.

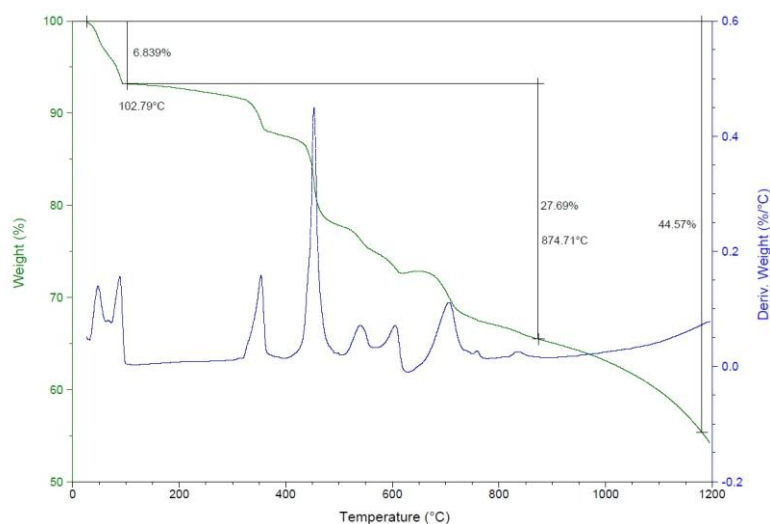


Figure 3.13c Thermogram of Co-3c.

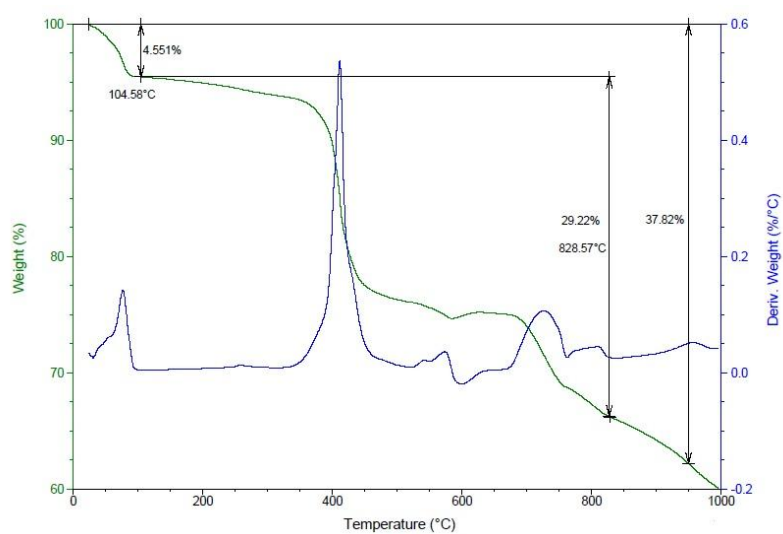
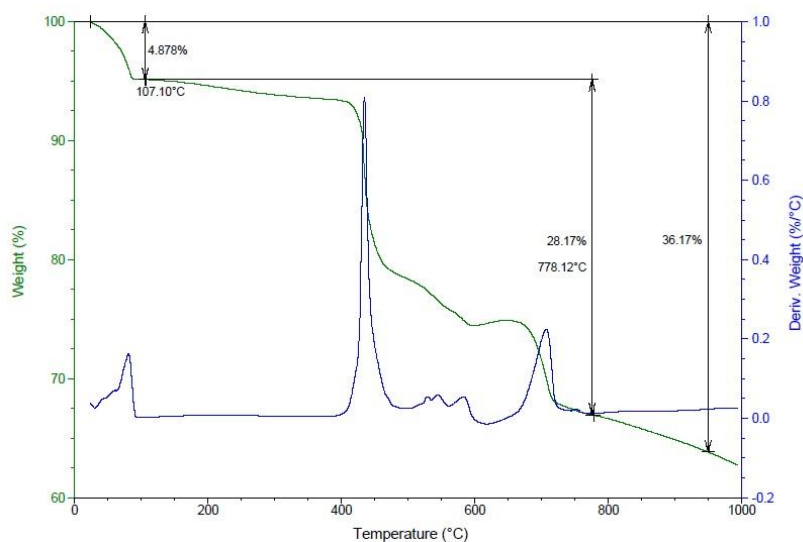
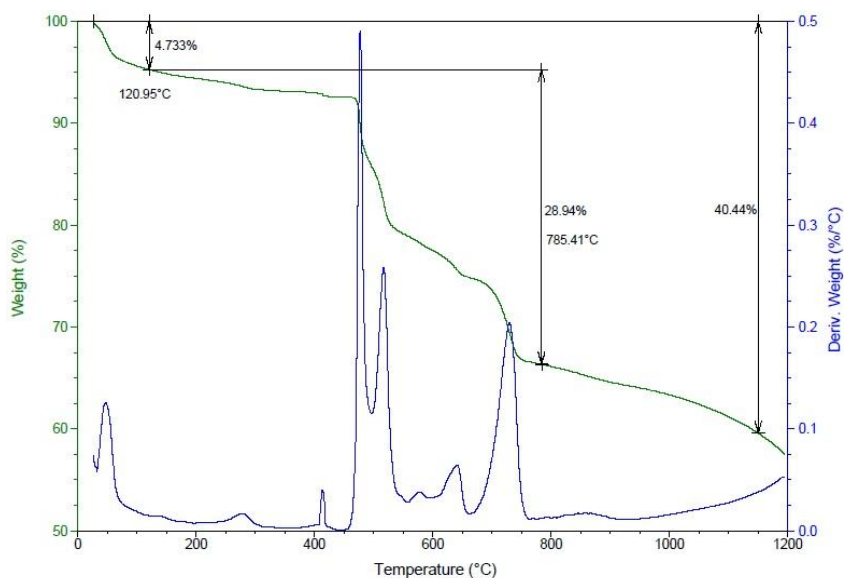


Figure 3.13d Thermogram of Cu-3d.

Figure 3.13e Thermogram of **Zn-3e**.Figure 3.13f Thermogram of **Lu-3f**.

3.4.5 NMR Spectroscopy

We performed ^{77}Se NMR study on solutions of **Zn-3e** and **Lu-3f** in $\text{H}_2\text{O}/\text{D}_2\text{O}$. The ^{77}Se NMR spectra (Fig. 3.14) revealed the expected one signal (at 1222.5 ppm for **Zn-3e** and at 1223.8 ppm for **Lu-3f**) fully consistent with the crystal structure and thus with the solution stability of the polyanions.

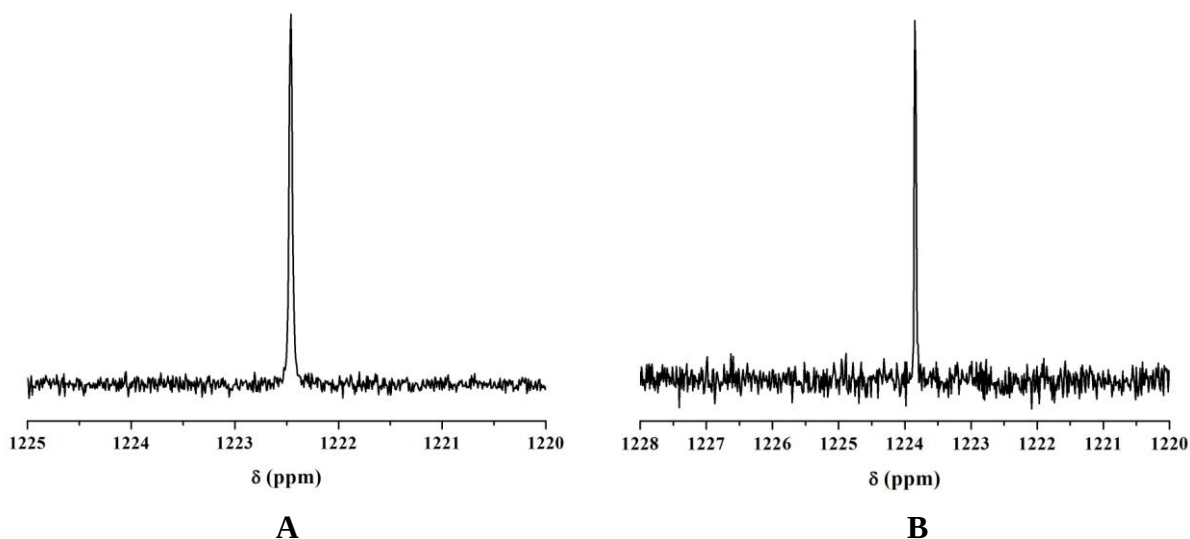


Figure 3.14 ^{77}Se NMR spectra of **Zn-3e** (A) and **Lu-3f** (B).

3.4.6 Conclusions

We have expanded the class of noble metalates by the discovery of a novel family of 3d transition metal and lutetium-containing heteropolyoxopalladates, $[\text{MPd}^{\text{II}}_{12}\text{Se}_8\text{O}_{32}]^{n-}$ ($\text{M} = \text{Mn}^{\text{II}}, \text{Fe}^{\text{III}}, \text{Co}^{\text{II}}, \text{Cu}^{\text{II}}, \text{Zn}^{\text{II}}, \text{Lu}^{\text{III}}$). These polyanions have all been prepared in simple open-beaker reactions of $\text{Pd}_3(\text{CH}_3\text{COO})_6$, selenium dioxide and the salt of the respective M^{n+} ion in aqueous medium. This work extends our earlier studies on polyoxo-13-palladates, in particular $[\text{Pd}_{13}\text{Se}_8\text{O}_{32}]^{6-}$ (**Pd₁₃Se**).⁴ The 6 polyanions have the similar structure as **Pd₁₃Se**, but the central, six-coordinated Pd^{II} ion has now been replaced by the 3d transition metal or lutetium ions. ^{77}Se NMR study performed on solutions of the diamagnetic **Zn-3e** and **Lu-3f** in $\text{H}_2\text{O}/\text{D}_2\text{O}$ showed that the polyanions are stable in aqueous medium.

3.5 Phenylphosphonate-capped 3d Transition Metal-containing

Polyoxopalladates

We have succeeded in the preparation of $\text{MPd}_{12}\text{L}_8$ derivatives by synthesis of two compounds with general formula $\text{Na}_6[\text{M}^{\text{II}}\text{Pd}^{\text{II}}_{12}(\text{P}^{\text{V}}\text{Ph})_8\text{O}_{32}]\cdot y\text{H}_2\text{O}$, where $\text{M} = \text{Cu}$ (**Cu-4a**) or Zn (**Zn-4b**), $y=35\text{--}36$. The compounds have been obtained by reaction of $\text{Pd}_3(\text{CH}_3\text{COO})_6$, phenylphosphoric acid and the respective salt of the M^{2+} ion in 2.0 M aqueous sodium acetate solution (pH 8.0) and characterized in the solid state by FT-IR spectroscopy, TGA, single crystal XRD and elemental analysis. The diamagnetic Zn^{II} derivative (**Zn-4b**) was studied in $\text{H}_2\text{O}/\text{D}_2\text{O}$ solution by ^{31}P and ^{13}C NMR spectroscopy.

3.5.1 Synthetic Procedures

$\text{Na}_6[\text{Cu}^{\text{II}}\text{Pd}^{\text{II}}_{12}(\text{PPh})_8\text{O}_{32}]\cdot 35\text{H}_2\text{O}$ (Cu-4a): $\text{Pd}_3(\text{CH}_3\text{COO})_6$ (0.140 g, 0.208 mmol), PhPO_3H_2 (0.100 g, 0.633 mmol) and $\text{Cu}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}$ (0.010 g, 0.052 mmol) were dissolved in 5 ml of 2.0 M sodium acetate solution (pH 8.0). The resulting solution was stirred and heated to 80°C for 1 hour. During the first 30 minutes the pH value of the reaction mixture was controlled and adjusted in the range 7.9 – 8.1 by adding 1 M NaOH. Then it was cooled to room temperature, filtered and allowed to crystallize at room temperature. Red crystals were obtained after several days, filtered off and air dried. Yield: 0.030 g (9 % based on {Pd}). Elemental analysis (%) calcd: Na 3.96, Cu 1.82, Pd 36.64, P 7.11, C 16.54; found: Na 4.09, Cu 1.86, Pd 37.26, P 7.23, C 15.85. IR (2% KBr pellet, v/cm^{-1}): 1630 (m), 1482(w), 1436 (m), 1130 (m), 1039(s), 940 (s), 759 (m), 718 (s), 702 (m), 659 (sh), 606 (s), 549 (m).

$\text{Na}_6[\text{Zn}^{\text{II}}\text{Pd}^{\text{II}}_{12}(\text{PPh})_8\text{O}_{32}]\cdot 36\text{H}_2\text{O}$ (Zn-4b): $\text{Pd}_3(\text{CH}_3\text{COO})_6$ (0.140 g, 0.208 mmol), PhPO_3H_2 (0.100 g, 0.633 mmol) and ZnCl_2 (0.0071 g, 0.052 mmol) were dissolved in 5 ml of sodium acetate solution 2.0 M (pH 8.0). The resulting solution was stirred and heated to 80°C for 1 hour. During the first 30 minutes the pH value of the reaction mixture was

controlled and adjusted in the range 7.9 – 8.1 by adding 1 M NaOH. Then it was cooled to room temperature, filtered and allowed to crystallize at room temperature. Red crystals were obtained after several days, filtered off and air dried. Yield: 0.030 g (9 % based on {Pd}). Elemental analysis (%) calcd: Na 3.93, Zn 1.87, Pd 36.43, P 7.07, C 16.45; found: Na 3.93, Zn 1.86, Pd 35.79, P 6.88, C 16.25. IR (2% KBr pellet, ν/cm^{-1}): 1629(m), 1484(w), 1436(m), 1129(m), 1035(s), 939(s), 816(w), 760(m), 720 (m), 701(m), 657(m), 607(s), 550(m), 445(m).

3.5.2 Single Crystal XRD

The compounds **Cu-4a** and **Zn-4b** are isomorphous and crystallize in the tetragonal crystal system in the space group $I4/m$. The structure of the $\{\text{MPd}_{12}(\text{PPh})_8\text{O}_{32}\}$ core is very similar to that in the previously reported **Pd₁₃PhAs** and can be described in terms of Platonic and Archimedean solids.⁴ The main difference is that the central Pd^{II} ion in the latter has been replaced by a Cu^{II} or Zn^{II} ion and the eight PhAsO_3^{2-} capping groups are replaced by PhPO_3^{2-} (see Fig. 3.15).

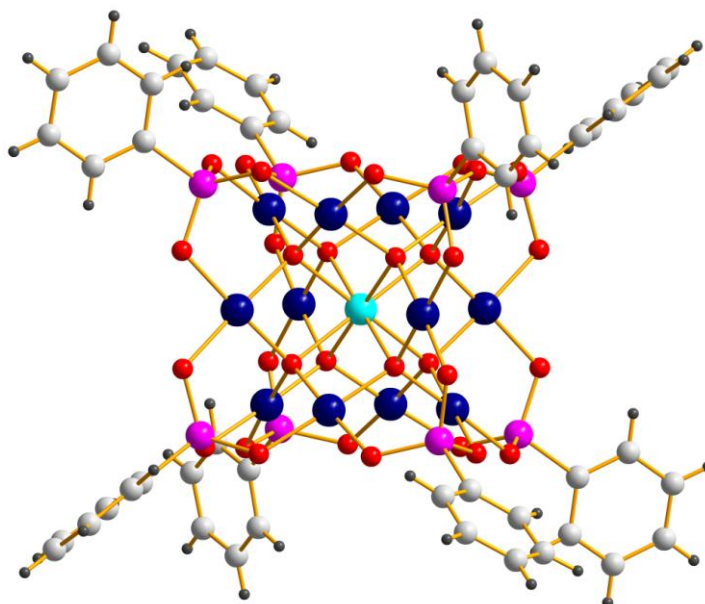


Figure 3.15 Ball-and-stick representation of $[\text{M}^{\text{II}}\text{Pd}^{\text{II}}_{12}(\text{PPh})_8\text{O}_{32}]^{6-}$.

Color code: M turquoise, Pd blue, P pink, O red, C grey, and H dark grey.

The central transition metal ion in **Cu-4a** and **Zn-4b** is coordinated by eight oxygen atoms situated at the vertices of a cube. The twelve palladium(II) ions surrounding the central {MO₈} fragment form a cuboctahedron. Each oxygen atom of the “inner” {MO₈} cube (μ_4 -O) is coordinated by the central ion and three palladiums, situated on a trigonal face of the cuboctahedron. Each of the twelve Pd^{II} ions exhibits the expected square-planar coordination by two μ_4 -O and two “outer” oxygen atoms (μ_2 -O). The 24 “outer” oxygen atoms form a truncated cube-shaped shell, which is capped by eight positively charged PPh⁴⁺ groups. The eight phosphorous ions possess tetrahedral coordination geometry and form in fact an external, cube-shaped shell. Selected bond distances for **Cu-4a** and **Zn-4b** are shown in Table 3.11.

Table 3.11 Selected bond lengths [Å] for the polyanions in **Cu-4a** and **Zn-4b**.

	M – (μ_4 -O)	Pd – (μ_4 -O) (mean)	Pd – (μ_2 -O) (mean)	P – (μ_2 -O) (mean)	P – C
Cu-4a	2.242(8)	1.956(7)	2.051(8)	1.532(9)	1.801(13)
Zn-4b	2.239(5)	1.960(5)	2.063(5)	1.537(5)	1.793(7)

Table 3.12 includes further crystallographic data for **Cu-4a** and **Zn-4b**.

Table 3.12 Crystal data and structure refinement for **Cu-4a** and **Zn-4b**.

	Cu-4a	Zn-4b
empirical formula	C ₄₈ H ₉₂ P ₈ Na ₆ O ₅₈ Pd ₁₂ Cu	C ₄₈ H ₁₄₀ P ₈ Na ₆ O ₈₂ Pd ₁₂ Zn
molecular weight [gmol ⁻¹]	3323.26	3707.07
crystal system	Tetragonal	Tetragonal
space group	I4/m	I4/m
<i>a</i> [Å]	15.928(3)	15.6887(9)
<i>b</i> [Å]	15.928(3)	15.6887(9)
<i>c</i> [Å]	24.313(5)	24.6896(16)
<i>V</i> [Å ³]	6168(2)	6077.0(6)
<i>Z</i>	2	2
<i>T</i> [K]	100(2)	100(2)
ρ_{calcd} [Mgm ⁻³]	1.789	2.026
μ [mm ⁻¹]	2.074	2.153
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]		
<i>R</i> ₁ ^[a]	0.0774	0.0472
<i>wR</i> ₂ ^[b]	0.2257	0.1224
<i>R</i> indices (all data)		
<i>R</i> ₁ ^[a]	0.1184	0.0670
<i>wR</i> ₂ ^[b]	0.2624	0.1332

$$^{[a]} R_1 = \sum | |F_o| - |F_c| | / \sum |F_o|, \quad ^{[b]} wR_2 = [\sum w (F_o^2 - F_c^2)^2 / \sum w (F_o^2)^2]^{1/2}$$

3.5.3 FT-IR Spectroscopy

The polyoxopalladates **Cu-4a** and **Zn-4b** have similar FT-IR spectra showing only slight shifts in some band positions relative to each other (Fig. 3.16a–3.16b). As an example, for **Cu-4a** (Fig. 3.16a) the bands at 549, 606 and 659 cm^{-1} can correspond to Pd–O as well as to Cu–O vibrations. The strong bands at 940, 1039 and 1130 cm^{-1} are attributed to the P–O vibrations. The stretching and bending vibrations of the C–C and C–H bonds of the phenyl rings appear in the region 702–759 cm^{-1} and at 1436 and 1482 cm^{-1} . The broad band at 1631 cm^{-1} belongs to asymmetric vibrations of crystal water.⁸

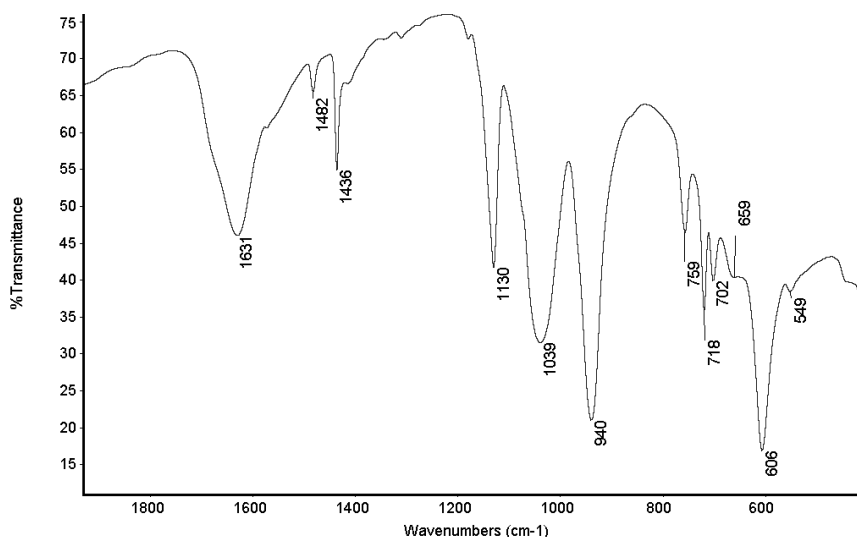


Figure 3.16a FT-IR spectrum of **Cu-4a**.

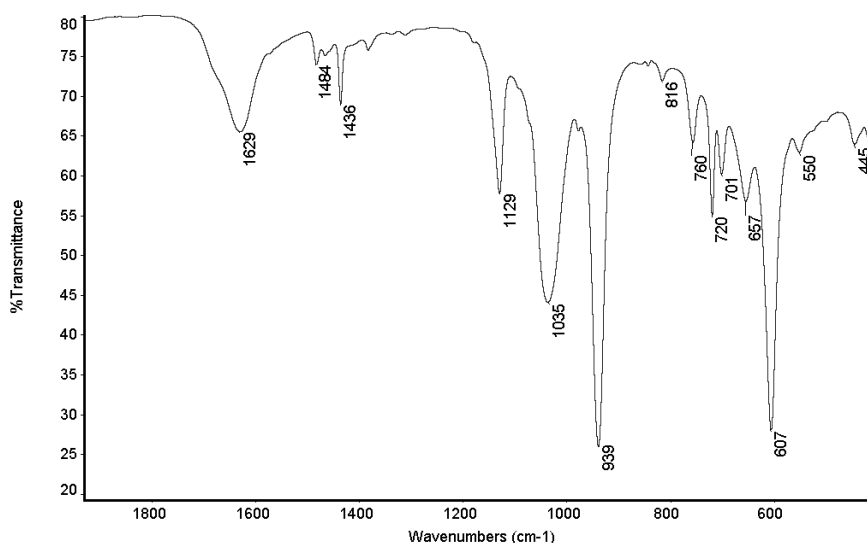


Figure 3.16b FT-IR spectrum of **Zn-4b**.

3.5.4 Thermogravimetric Analysis

The thermogravimetric processes of **Cu-4a** and **Zn-4b** are very similar and reveal several weight-loss steps (see Fig. 3.17a-3.17b). For example, for **Cu-4a** (Fig. 3.17a) the first step occurs between 25 and 144°C and corresponds to the loss of 26 water molecules per formula unit. The combustion of eight phenyl groups per formula unit of **Cu-4a** proceeds in the temperature range of 144–550°C. The total weight loss for **Cu-4a** at 1000°C is 39%.

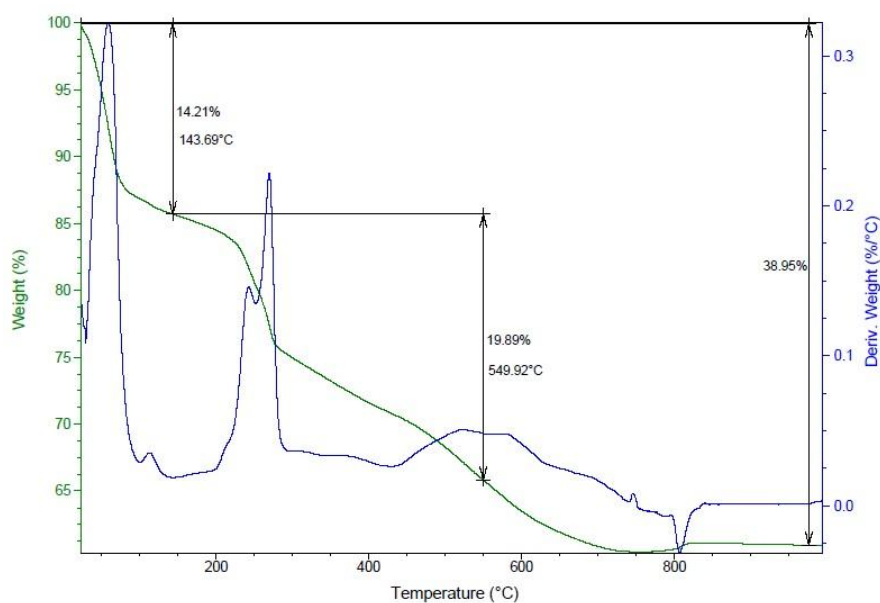


Figure 3.17a Thermogram of **Cu-4a**.

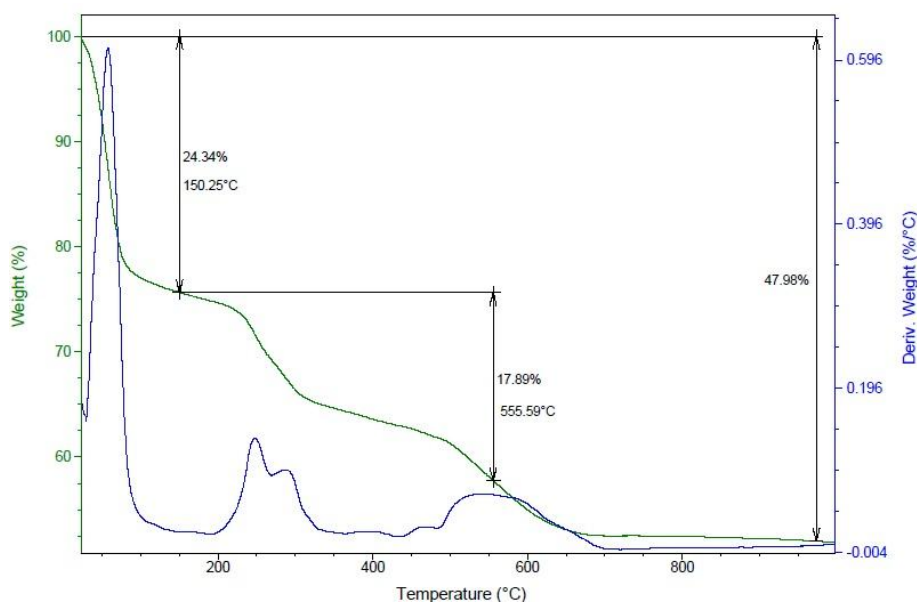


Figure 3.17b Thermogram of **Zn-4b**.

3.5.5 NMR Spectroscopy

We performed ^{31}P and ^{13}C NMR studies on solution of **Zn-4b** in $\text{H}_2\text{O}/\text{D}_2\text{O}$. ^{13}C NMR spectrum is as expected for phenyl groups (Fig. 3.18). The ^{31}P NMR spectrum (Fig. 3.19) revealed the expected one signal at 29.5 ppm fully consistent with the crystal structure and thus with the solution stability of the polyanion.

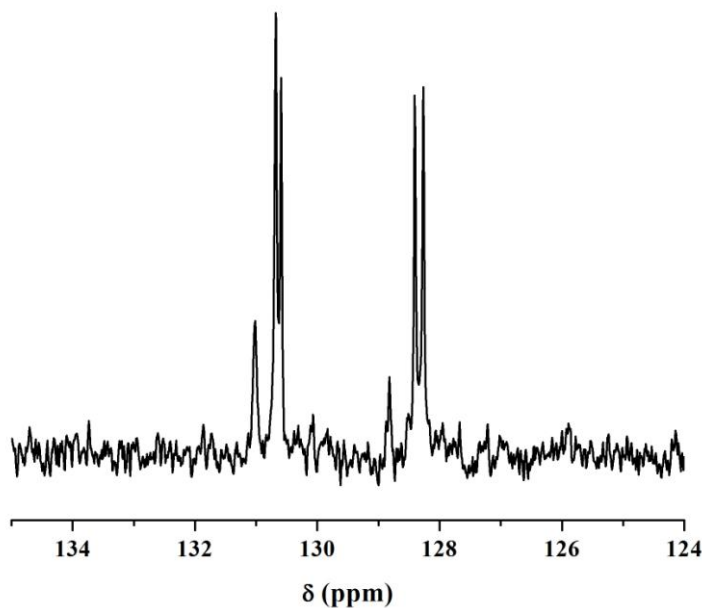


Figure 3.18 ^{13}C NMR spectrum of **Zn-4b**.

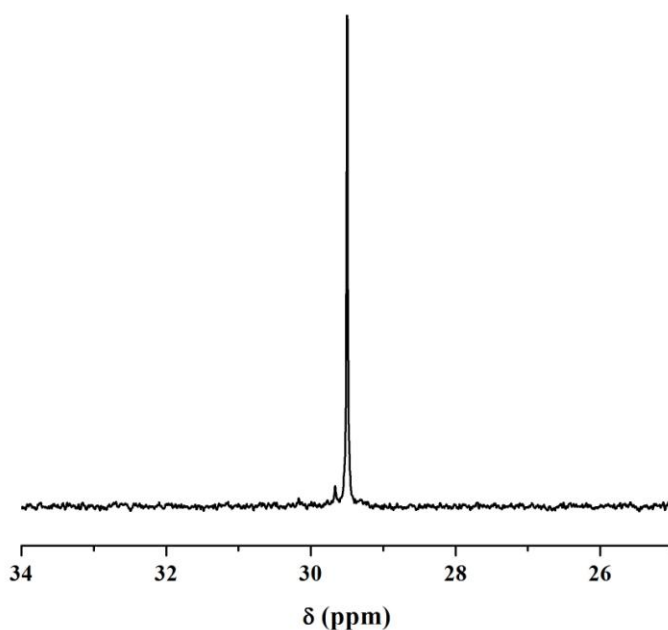


Figure 3.19 ^{31}P NMR spectrum of **Zn-4b**.

3.5.6 Conclusions

We have shown that the phenylphosphonate group PhPO_3^{2-} can play the role of the capping unit L in $\{\text{Pd}_{12}\text{L}_8\}$ polyoxopalladate shell. Two novel compounds with the general formula $\text{Na}_6[\text{M}^{\text{II}}\text{Pd}^{\text{II}}_{12}(\text{P}^{\text{V}}\text{Ph})_8\text{O}_{32}]\cdot y\text{H}_2\text{O}$ ($\text{M} = \text{Cu}, \text{Zn}; y = 35\text{--}36$) have been isolated and characterized by single crystal XRD, elemental analysis, TGA and IR spectroscopy. Multinuclear NMR spectroscopy (^{31}P , ^{13}C) study was done on solution of the diamagnetic Zn^{II} derivative (**Zn-4b**) in $\text{H}_2\text{O}/\text{D}_2\text{O}$, and showed that the polyanion $[\text{Zn}^{\text{II}}\text{Pd}^{\text{II}}_{12}(\text{P}^{\text{V}}\text{Ph})_8\text{O}_{32}]^{6-}$ is solution stable. It should be noted that till now we were not able to incorporate palladium(II) ion in the center of $\{\text{Pd}^{\text{II}}_{12}(\text{PPh})_8\text{O}_{32}\}$ shell.

3.6 Phosphate-capped 3d Transition Metal-containing Polyoxopalladates

On the way of systematic investigation of the $\text{M}^{n+}/\text{Pd}^{2+}/\text{PO}_4^{3-}$ system (where $\text{M}^{n+} = 3\text{d}$ transition metal ions) we obtained a novel family of polyoxopalladates, $\text{Na}_{16-n-z}[\text{M}^n\text{Pd}^{\text{II}}_{12}\text{P}_8\text{O}_{40}\text{H}_z]\cdot y\text{H}_2\text{O}$ ($\text{M} = \text{Mn}^{\text{II}}$ (**Mn-5a**), Fe^{III} (**Fe-5b**), Co^{II} (**Co-5c**), Cu^{II} (**Cu-5d**), Zn^{II} (**Zn-5e**); $y = 16 - 37$). The compounds were characterized by single-crystal XRD, elemental analysis, IR spectroscopy, TGA. The diamagnetic Zn^{II} derivative (**Zn-5e**) was studied in solution by ^{31}P NMR spectroscopy.

A series of novel 3d transition metal-containing polyoxopalladatophosphates have been prepared in a simple one pot self-assembly reaction of $\text{Pd}_3(\text{CH}_3\text{COO})_6$ and a salt of the respective 3d metal ion in a sodium phosphate buffer at pH 6.0–6.7, and isolated as hydrated sodium salts in yields ranging from 21% (for **Mn-5a** and **Co-5c**) to 43% (for **Fe-5b**). The compounds **Mn-5a** – **Zn-5e** are stable towards air and light in the solid state and can be successfully recrystallized several times from a sodium phosphate buffer (pH 6.0 – 6.7). It should be noted that during the synthesis and crystallization of **Mn-5a** – **Zn-5e** the pH value

of the reaction mixture is important, and it is particularly crucial for the copper(II)-containing derivative **Cu-5d**. Thus, while a pure sample of **Cu-5d** can be isolated at pH values of 6.0–6.2, formation of a mixture of **Cu-5d** and a hydrated sodium salt of $[\text{Cu}^{\text{II}}_2\text{Pd}^{\text{II}}_{22}\text{P}^{\text{V}}_{12}\text{O}_{60}(\text{OH})_8]^{20-}$ (**NaPd₂₂-6**, see Chapter IV) was observed in the pH range 6.2–6.9.¹¹ Pure compound **Cu-5d** could also be obtained by dissolving **NaPd₂₂-6** in 0.25 M sodium phosphate solution at pH 6.0–6.2 and adding one equivalent of Pd^{2+} ions.

3.6.1 Synthetic Procedures

Na₉[Mn^{II}Pd^{II}₁₂P₈O₃₅(OH)₅].32H₂O (Mn-5a): $\text{Pd}_3(\text{CH}_3\text{COO})_6$ (0.084 g, 0.125 mmol) and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (0.005 g, 0.031 mmol) were dissolved in 9 ml of 0.25 M sodium phosphate buffer (pH 6.9). While stirring, the solution was heated to 80°C. During the first 30 minutes the pH of the solution was adjusted in the range 6.6 – 6.7 by adding 1 M NaOH. The resulting solution was heated to 80°C for 1 hour. Then it was cooled to room temperature, filtered and allowed to crystallize at room temperature. Red crystals were obtained after several days, filtered off and air dried. Yield: 0.020 g (21 % based on {Pd}). Elemental analysis (%) calcd: Na 6.88, Mn 1.83, Pd 42.4, P 8.24; found: Na 6.66, Mn 1.84, Pd 41.7, P 8.70. IR (2% KBr pellet, ν/cm^{-1}): 1630 (m), 1116 (m), 1062 (m), 964 (s), 653 (m), 610 (s), 548 (m), 443 (m).

Na₉[Fe^{III}Pd^{II}₁₂P₈O₃₆(OH)₄].16H₂O (Fe-5b): $\text{Pd}_3(\text{CH}_3\text{COO})_6$ (0.084 g, 0.125 mmol) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.013 g, 0.031 mmol) were dissolved in 3 ml of 0.5 M sodium phosphate buffer (pH 6.9). While stirring, the solution was heated to 80°C. During the first 30 minutes the pH of the solution was adjusted in the range 6.6 – 6.7 by adding 1 M NaOH. The resulting solution was heated to 80°C for 1 hour. Then it was cooled to room temperature, filtered and allowed to crystallize at room temperature. Black crystals were obtained after several days, filtered off and air dried. Yield: 0.036 g (43 % based on {Pd}). Elemental analysis (%) calcd:

Na 7.61, Fe 2.05, Pd 47.0, P 9.11; found: Na 7.37, Fe 1.84, Pd 47.3, P 8.65. IR (2% KBr pellet, ν/cm^{-1}): 1628 (m), 1123 (s), 956(s), 919 (s), 757(sh), 656(m), 617(s), 558 (m), 452 (m).

Na₁₀[Co^{II}Pd^{II}₁₂P₈O₃₆(OH)₄] $\cdot$ 30H₂O (Co-5c): The compound was prepared by exactly the same procedure as **Mn-5a**, but by using Co(NO₃)₂ $\cdot$ 6H₂O (0.009 g, 0.031 mmol) instead of MnSO₄ $\cdot$ H₂O. Red crystals were obtained. Yield: 0.020 g (21 % based on {Pd}). Elemental analysis (%) calcd: Na 7.67, Co 1.97, Pd 42.59, P 8.26; found: Na 7.66, Co 1.92, Pd 42.45, P 8.18. IR (2% KBr pellet, ν/cm^{-1}): 1630 (m), 1067 (m), 972 (s), 901 (m), 665 (m), 607 (s), 552 (sh), 443 (m).

Na₁₀[Cu^{II}Pd^{II}₁₂P₈O₃₆(OH)₄] $\cdot$ 31H₂O (Cu-5d): Pd₃(CH₃COO)₆ (0.084 g, 0.125 mmol) and Cu(CH₃COO)₂ $\cdot$ H₂O (0.013 g, 0.062 mmol) were dissolved in 3 ml of 0.5 M sodium phosphate buffer (pH 6.9). The solution was heated to 80°C with stirring. After 10 minutes the pH of the solution was adjusted in the range 6.5 – 6.6 using 1 M NaOH. The reaction mixture was then heated to 80°C for 1 hour with continuous stirring. During this time the pH value of the solution decreased, and was maintained in the range of 6.0-6.2 by using 0.5 M H₃PO₄. The resulting solution was then filtered and allowed to crystallize at room temperature. Red crystals were obtained after several days, filtered off and air dried. Yield: 0.031 g (33 % based on {Pd}). Elemental analysis (%) calcd: Na 7.61, Cu 2.10, Pd 42.28, P 8.20; found: Na 7.67, Cu 2.05, Pd 41.96, P 8.30. IR (2% KBr pellet, ν/cm^{-1}): 1630 (m), 1078 (s), 969 (s), 935 (sh), 670 (m), 609 (s), 549 (sh), 442 (m).

Na₉[Zn^{II}Pd^{II}₁₂P₈O₃₅(OH)₅] $\cdot$ 37H₂O (Zn-5e): The compound was prepared by exactly the same procedure as **Mn-5a**, but by using ZnCl₂ (0.004 g, 0.031 mmol) instead of MnSO₄ $\cdot$ H₂O. Red crystals were obtained. Yield: 0.025 g (26 % based on {Pd}). Elemental analysis (%) calcd: Na 6.66, Zn 2.10, Pd 41.1, P 7.97; found: Na 6.37, Zn 2.04, Pd 40.4,

P 8.46. IR (2% KBr pellet, ν/cm^{-1}): 1630 (m), 1072 (m), 970 (s), 905 (sh), 663 (m), 609 (s), 543 (sh), 445 (m).

3.6.2 Single Crystal XRD

The structure of polyanions in **Mn-5a** – **Zn-5e** comprises a central, 8-coordinated 3d metal ion (Mn^{II} , Fe^{III} , Co^{II} , Cu^{II} , Zn^{II}) surrounded by a shell of twelve square-planar $\text{Pd}^{\text{II}}\text{O}_4$ units, and eight tetrahedral phosphate capping groups (see Fig. 3.20). The structure hence resembles the cuboid-shaped Pd_{13}As .^{10a}

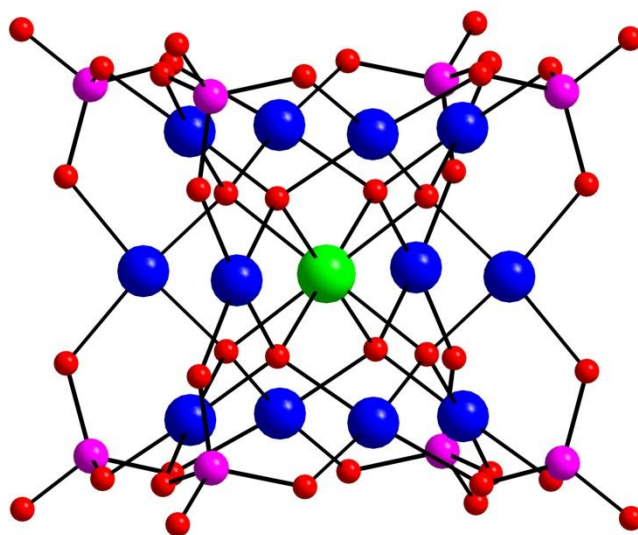


Figure 3.20 Ball-and-stick representation of $[\text{M}^n\text{Pd}^{\text{II}}_{12}\text{P}_8\text{O}_{40}]^{n-16}$.

Colour legend: M green, Pd blue, P pink, O red.

Single crystal XRD analysis showed that the central ion in **Mn-5a** – **Zn-5e** is coordinated by eight oxygen atoms, forming a regular cube in all of the compounds except **Cu-5d**, where the central $\{\text{Cu}^{\text{II}}\text{O}_8\}$ motif is a distorted rhombohedron. Such a high coordination number is rather unusual for 3d transition metal ions. A rare example is our 22-palladate (**NaPd₂₂-6**, see Chapter IV), where the two Cu^{II} ions are each encapsulated in a distorted cuboid $\{\text{O}_8\}$ coordination geometry.¹¹ The twelve palladium(II) ions surrounding the central $\{\text{MO}_8\}$ fragment form a closed cuboctahedral shell. All eight μ_4 -oxygens of the

“inner” $\{\text{MO}_8\}$ motif are coordinated by the transition metal ion and by three palladiums, which are situated on a trigonal face of the cuboctahedron. Each of the twelve Pd^{II} ions exhibits the expected square-planar coordination by two “inner” $\mu_4\text{-O}$ and two “outer” $\mu_2\text{-O}$ atoms. The 24 “outer” oxygens form a truncated-cuboid-shaped shell, which is capped by eight positively charged PO^{3+} groups. The eight P^{V} ions possess tetrahedral coordination geometry and in fact form an external, cuboid-shaped shell. Bond valence sum (BVS) calculations³ on **Mn-5a** – **Zn-5e** indicated partial protonation of the terminal oxygens. The exact number of protons for each polyanion was determined based on elemental analysis and charge-balance considerations. Selected bond distances for **Mn-5a** – **Zn-5e** are shown in Table 3.13.

Table 3.13 Selected bond distances/Å for **Mn-5a** – **Zn-5e**.

	M – ($\mu_4\text{-O}$)	Pd – ($\mu_4\text{-O}$)	Pd – ($\mu\text{-O}$)	P – ($\mu\text{-O}$)	P – O_{term}
Mn-5a	2.266(6)	1.951(6)-1.967(6)	2.043(7)-2.053(7)	1.537(9)-1.554(9)	1.560(8)
Fe-5b	2.206(8)	1.958(2)	2.043(5)	1.555(6)	1.509(9)
Co-5c	2.234(9)	1.941(9)-1.958(9)	2.030(11)-2.047(11)	1.533(14)-1.568(13)	1.569(12)
Cu-5d	2.078(12)- 2.369(10)	1.920(11)-1.993(10)	2.021(11)-2.090(11)	1.522(12)-1.567(12)	1.556(11)- 1.568(11)
Zn-5e	2.238(6)- 2.239(6)	1.945(7)-1.961(7)	2.051(8)-2.059(9)	1.520(10)-1.556(9)	1.557(9)

Table 3.14 includes further crystallographic data for **Mn-5a – Zn-5e**.

Table 3.14 Crystal data and structure refinement for **Mn-5a – Zn-5e**.

	Mn-5a	Fe-5b	Co-5c	Cu-5d	Zn-5e
empirical formula	H ₆₉ MnNa ₉ O ₇₂ P ₈ Pd ₁₂	H ₃₆ FeNa ₉ O ₅₆ P ₈ Pd ₁₂	H ₆₄ CoNa ₁₀ O ₇₀ P ₈ Pd ₁₂	H ₆₆ CuNa ₁₀ O ₇₁ P ₈ Pd ₁₂	H ₇₉ ZnNa ₉ O ₇₇ P ₈ Pd ₁₂
molecular weight [g·mol ⁻¹]	3007.96	2719.61	2997.90	3020.53	3108.47
crystal system	Tetragonal	Cubic	Tetragonal	Triclinic	Tetragonal
space group	P4/mnc	Fm-3m	P4/mnc	P-1	P4/mnc
<i>a</i> [Å]	14.9393(2)	20.1226(18)	14.857(2)	12.148(3)	14.9240(6)
<i>b</i> [Å]	14.9393(2)	20.1226(18)	14.857(2)	12.528(2)	14.9240(6)
<i>c</i> [Å]	20.1922(5)	20.1226(18)	20.153(3)	12.587(3)	20.1787(10)
<i>α</i> [°]	90.00	90.00	90.00	72.547(10)	90.00
<i>β</i> [°]	90.00	90.00	90.00	87.055(12)	90.00
<i>γ</i> [°]	90.00	90.00	90.00	85.191(11)	90.00
<i>V</i> [Å ³]	4506.55(14)	8148.0(13)	4448.5(10)	1820.5(6)	4494.3(3)
<i>Z</i>	2	4	2	1	2
<i>T</i> [K]	173(2)	296(2)	100(2)	100(2)	173(2)
<i>ρ</i> _{calcd} [Mg·m ⁻³]	2.217	2.217	2.238	2.755	2.297
<i>μ</i> [mm ⁻¹]	2.754	3.043	2.836	3.531	2.895
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]					
<i>R</i> ₁ ^[a]	0.0665	0.0599	0.0725	0.0691	0.0722
<i>wR</i> ₂ ^[b]	0.2099	0.1809	0.2308	0.1899	0.2077
<i>R</i> indices (all data)					
<i>R</i> ₁ ^[a]	0.0730	0.0751	0.0907	0.1100	0.0827
<i>wR</i> ₂ ^[b]	0.2165	0.2054	0.2417	0.2100	0.2165

$$^{[a]} R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^{[b]} wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$

3.6.3 FT-IR Spectroscopy

The polyoxopalladate salts **Mn-5a** – **Zn-5e** have similar FT-IR spectra showing only slight shifts in some band positions relative to each other (see Fig. 3.21a–3.21e). As an example, for **Mn-5a** (Figure 3.21a) the bands at 443, 548, 610, 653 cm^{-1} can correspond to Pd-O as well as to Mn-O vibrations. The bands at 1116, 1062 and 964 cm^{-1} are attributed to the phosphate heterogroups, and the broad band at 1630 cm^{-1} is due to crystal water.⁸

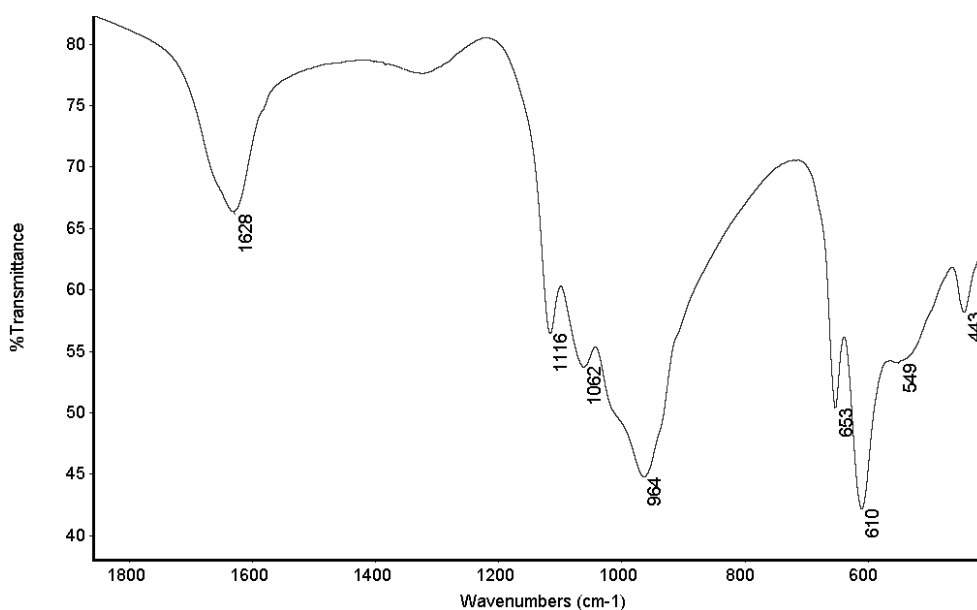


Figure 3.21a FT-IR spectrum of **Mn-5a**.

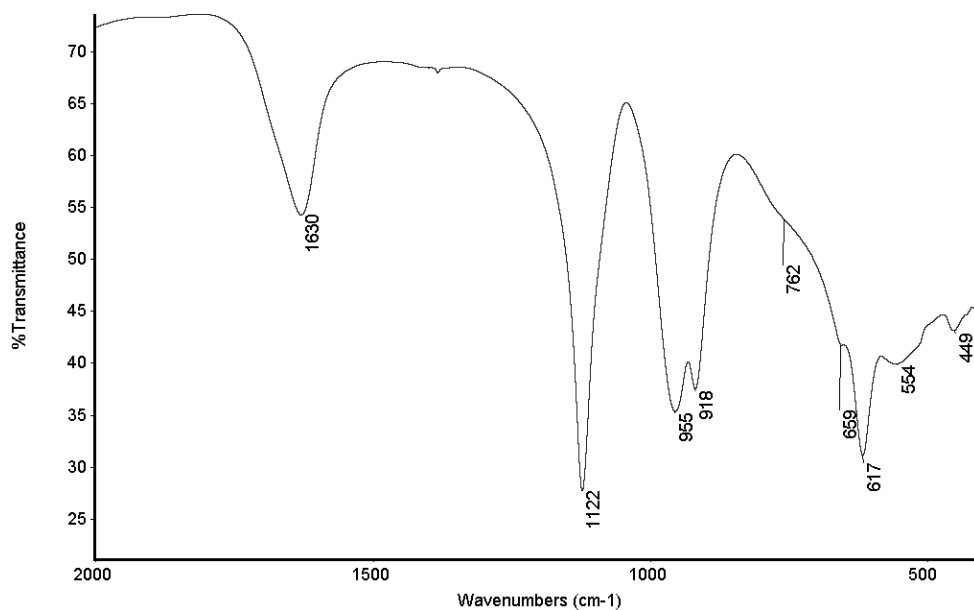


Figure 3.21b FT-IR spectrum of **Fe-5b**.

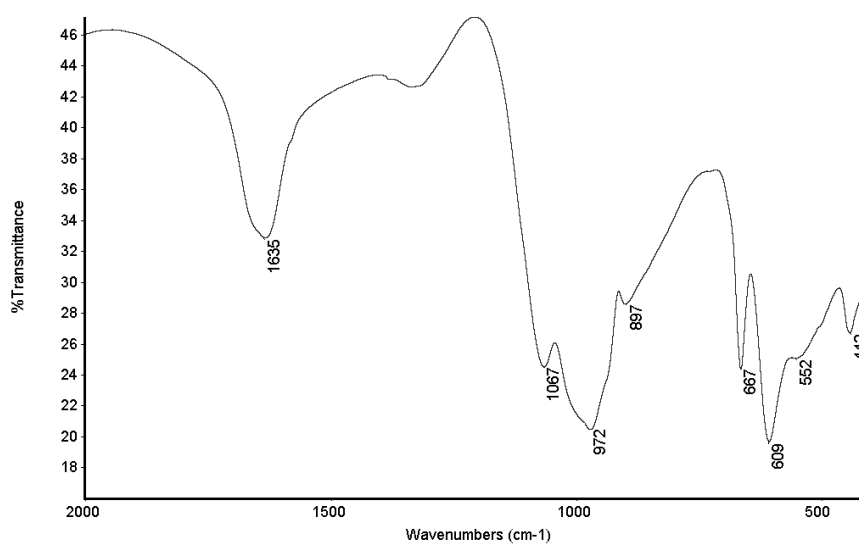


Figure 3.21c FT-IR spectrum of Co-5c.

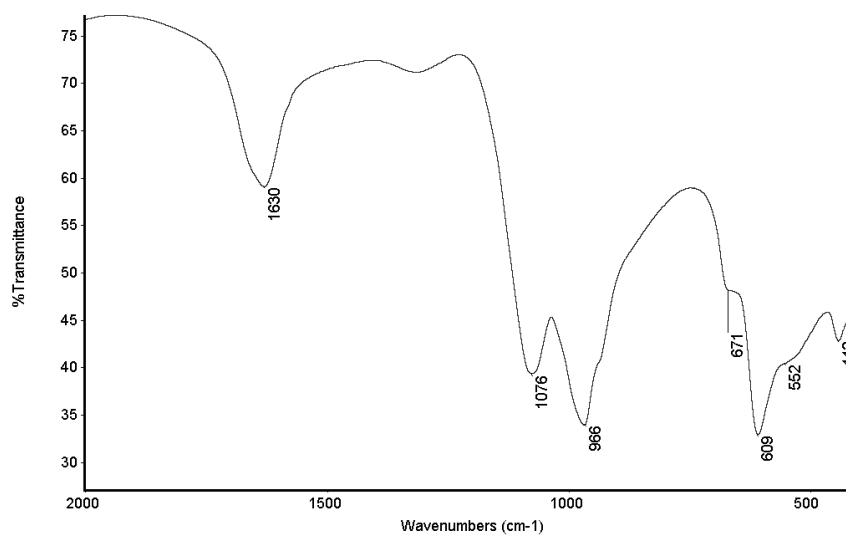


Figure 3.21d FT-IR spectrum of Cu-5d.

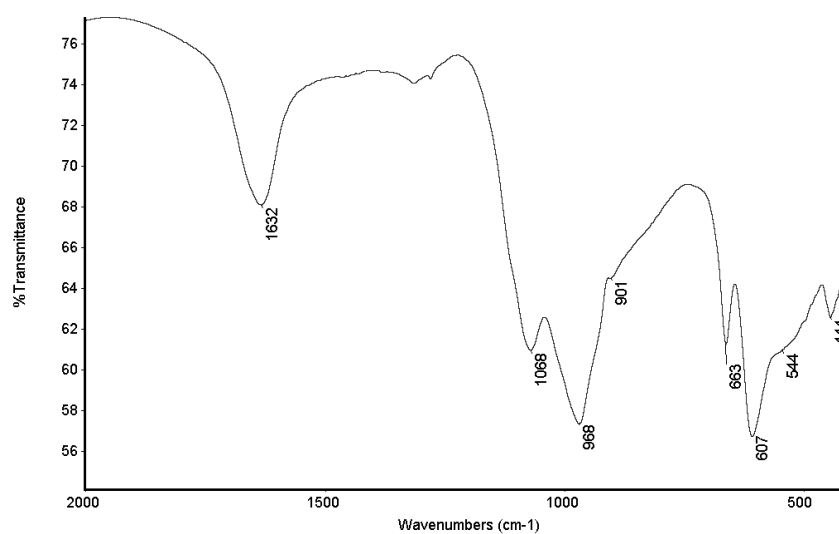


Figure 3.21e FT-IR spectrum of Zn-5e.

3.6.4 Thermogravimetric Analysis

The thermogravimetric processes of **Mn-5a** – **Zn-5e** are very similar and reveal two weight-loss steps (see Figures 3.22a–3.22e). For example, for **Mn-5a** the first step begins at 25 °C and is complete at 212 °C and corresponds to the loss of 27 water molecules. The number of water molecules determined by TGA is slightly lower than that obtained by crystallography (32 molecules). This fact can be easily explained by partial loss of crystal waters when drying the samples. Single crystals for XRD measurements were taken directly from the mother liquid, put in oil and frozen under nitrogen flow on the diffractometer, whereas the samples for TGA were air-dried for at least one day. The smooth weight loss in the temperature range of 212 – 363 °C corresponds to the loss of ~3 water molecules per formula unit **Mn-5a**, which must originate from $[\text{Mn}^{\text{II}}\text{Pd}^{\text{II}}_{12}\text{P}_8\text{O}_{35}(\text{OH})_5]^{9-}$. This implies that the polyanion is being decomposed. The total observed weight loss at 1200 °C is 25.8 %.

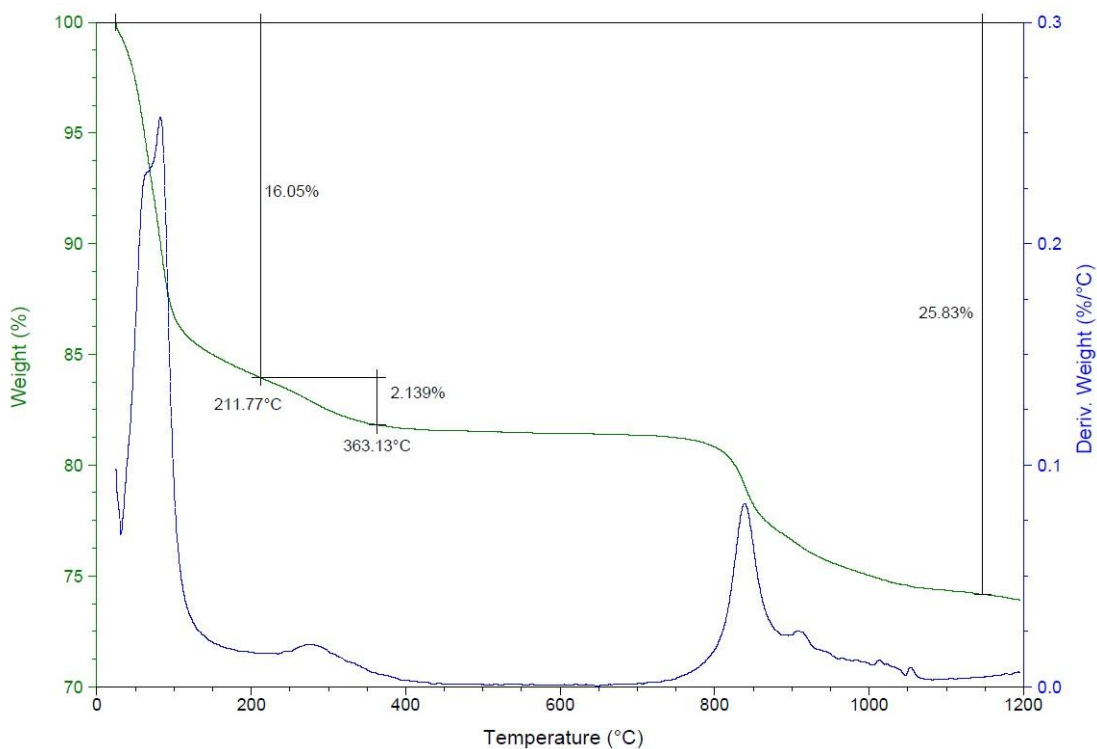


Figure 3.22a Thermogram of **Mn-5a**.

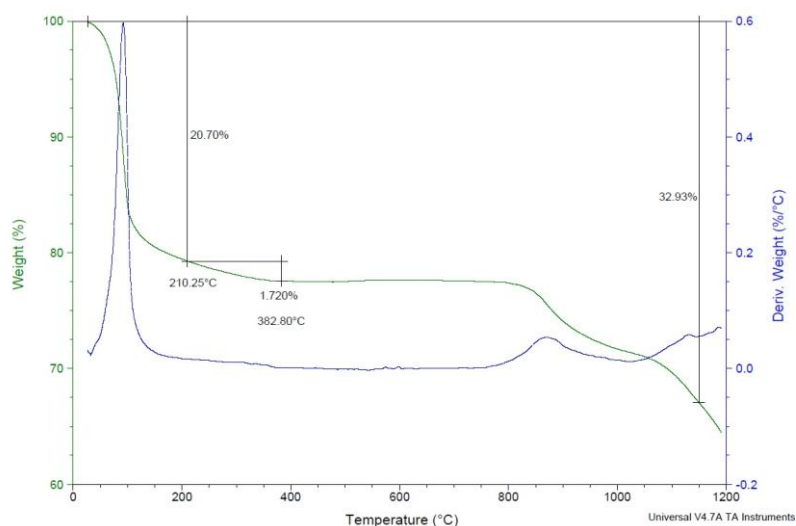


Figure 3.22b Thermogram of Fe-5b.

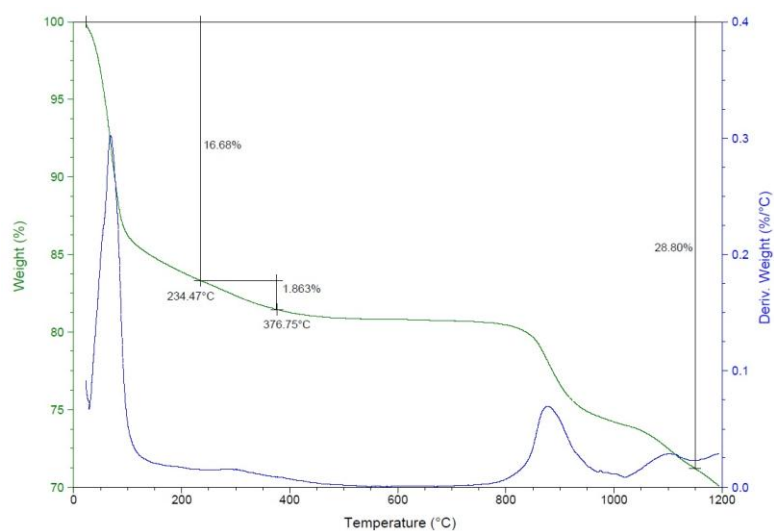


Figure 3.22c Thermogram of Co-5c.

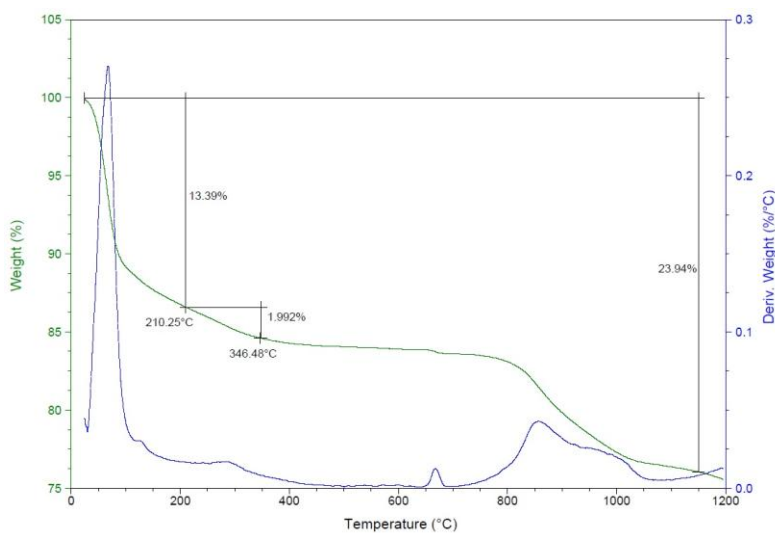


Figure 3.22d Thermogram of Cu-5d.

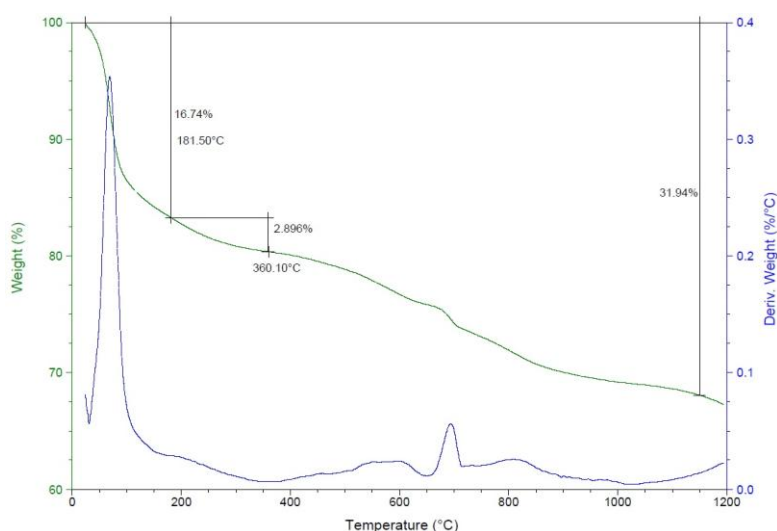


Figure 3.22e Thermogram of **Zn-5e**.

3.6.5 NMR Spectroscopy

We performed ^{31}P NMR study on the diamagnetic Zn^{II} derivative (**Zn-5e**) redissolved in $\text{H}_2\text{O}/\text{D}_2\text{O}$ at room temperature. The ^{31}P NMR spectrum (Fig. 3.23) revealed the expected singlet at 15.8 ppm, fully consistent with the solid state structure and hence demonstrating solution stability of the polyanion.

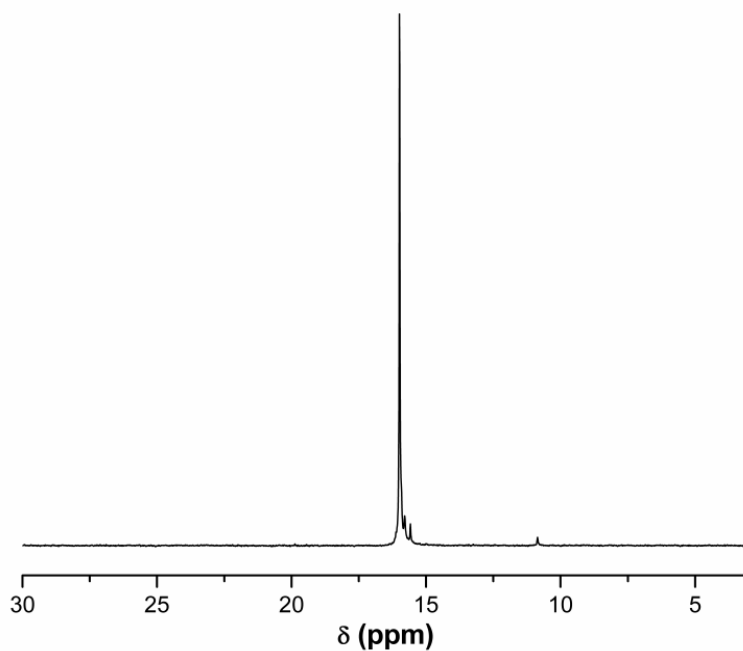


Figure 3.23 ^{31}P NMR spectrum of **Zn-5e** recorded at room temperature in $\text{H}_2\text{O}/\text{D}_2\text{O}$.

3.6.6 Conclusions

In summary, we have reported on the synthesis and characterization by single crystal XRD, elemental analysis, TGA and IR spectroscopy of the series of novel 3d transition metal-containing polyoxopalladatophosphates $\text{Na}_{16-n-z}[\text{M}^n\text{Pd}^{\text{II}}_{12}\text{P}_8\text{O}_{40}\text{H}_z]\cdot y\text{H}_2\text{O}$ ($\text{M} = \text{Mn}^{\text{II}}, \text{Fe}^{\text{III}}, \text{Co}^{\text{II}}, \text{Cu}^{\text{II}}, \text{Zn}^{\text{II}}$; $y = 16 - 37$). The solution stability of the diamagnetic compound (**Zn-5e**) was confirmed by ^{31}P NMR. Electrochemical studies of **Mn-5a** and **Fe-5b** were done by Dr. Bineta Keita from the group of Prof. Louis Nadjo (Université Paris-Sud, Orsay Cedex, France) and showed that owing to the high stability and electrochemical properties, the polyanions **Mn-5a** and **Fe-5b** are potentially new mixed-metal electrocatalysts. **Mn-5a** is expected to be interesting for catalyzing the water oxidation due to the higher-valent Mn^{3+} generated in positive potential domain. EPR measurements on **Mn-5a** and **Cu-5d** were carried out by the group of Prof. Naresh S. Dalal (Florida State University, USA). Preliminary catalytic studies performed on **Fe-5b** and **Cu-5d** by the group of Prof. Dr. Detlef Heller (Leibniz Institute for Catalysis at the University of Rostock (LIKAT), Germany) showed that these two POMs could be used as precatalysts for hydrogenation of olefins.

EPR measurements carried out on **Mn-5a** and **Cu-5d** revealed that the coordination of the transition metal centers incorporated in the $\{\text{Pd}_{12}\text{P}_8\text{O}_{40}\}$ shell is inherently distorted and dynamic, which contradicts to perfectly cubic $\{\text{MnO}_8\}$ unit in **Mn-5a** found by single crystal XRD. This indicates that the X-ray crystal structure taken is averaged and points to the complementary nature of the X-ray diffraction analysis and EPR spectroscopy on magnetic systems with the later showing an advantage of detecting the dynamic nature of the structure.

We also tried to incorporate palladium(II) and lanthanide(III) ions in the center of the cuboid-shaped polyoxopalladate family **MPd₁₂P₈**, but without success. This is in contrast to the isostructural polyanions with phenylarsonate capping groups (**MPd₁₂AsPh₈**, $\text{M} = \text{Pd}^{\text{II}}, \text{Ln}^{\text{III}}$), for which we isolated and characterized $[\text{Pd}^{\text{II}}_{13}\text{O}_{32}(\text{As}^{\text{V}}\text{Ph})]^{6-}$ and

$[\text{LnPd}^{\text{II}}_{12}\text{O}_{32}(\text{As}^{\text{V}}\text{Ph})_8]^{5-}$ (Ln = Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y).^{4,10b} This supports our earlier observation that, in addition to the size of the encapsulated guest ion, also the type of hetero group influences the detailed orientation of the eight donor oxygens surrounding the central cavity of the **MPd₁₂L₈** assembly.^{10b} Thus, the shorter $\text{P}^{\text{V}} - \text{O}(\text{Pd})$ bonds of the phosphate capping groups, compared to the longer $\text{As}^{\text{V}} - \text{O}(\text{Pd})$ bonds of the PhAsO_3^{2-} or AsO_4^{3-} capping groups, apparently lead to a decrease in size of the inner cavity of the **{Pd₁₂O₃₂}** shell, and as a result large metal ions such as lanthanides (and even Pd^{II} ions) cannot be incorporated. Hence, the **{Pd₁₂O₃₂}** assembly can be viewed as an anionic, inorganic host for cationic metal ion guests, and the selection of the capping group allows tuning the size, coordination number and geometry of the central cavity.

3.7 References

1. Sheldrick, G. M. *Acta Crystallogr.* **2007**, A64, 112-122.
2. Sheldrick, G. M. *SADABS, Program for empirical X-ray absorption correction*, Bruker-Nonius, **1990**.
3. Brown, I. D.; Altermatt, D. *Acta Crystallogr., Sect. B: Struct. Sci.*, **1985**, 41, 244-247.
4. Izarova, N. V.; Dickman, M. H.; Biboum, R. N.; Keita, B.; Nadjo, L.; Ramachandran, V.; Dalal, N. S.; Kortz, U. *Inorg. Chem.* **2009**, 48, 7504-7506.
5. a) Creaser, I.; Heckel, M. C.; Neitz, R. J.; Pope, M. T. *Inorg. Chem.* **1993**, 32, 1573-1578; b) Zhang, C.; Howell, R. C.; Scotland, K. B.; Perez, F. G.; Todaro, L.; Francesconi, L. C. *Inorg. Chem.* **2004**, 43, 7691-7701; c) Wang, Q.-M.; Yan, B. *Inorg. Chem. Commun.* **2004**, 7, 1124-1127; d) Boglio, C.; Lemièrè, G.; Hasenknopf, B.; Thorimbert, S.; Lacote, E.; Malacria, M. *Angew. Chem. Int. Ed.* **2006**, 45, 3324-3327; e) Boglio, C.; Lenoble, G.; Duhayon, C.; Hasenknopf, B.; Thouvenot, R.; Zhang, C.; Howell, R. C.; Burton-Pye, B. P.;

- Francesconi, L. C.; Lacôte, E.; Thorimbert, S.; Malacria, M.; Afonso, C.; Tabet, J.-C. *Inorg. Chem.* **2006**, *45*, 1389-1398; f) Huang, W.; Francesconi, L. C.; Polenova, T. *Inorg. Chem.* **2007**, *46*, 7861-7869; g) AlDamen, M. A.; Cardona-Serra, S.; Clemente-Juan, J. M.; Coronado, E.; Gaita-Ariño, A.; Martí-Gastaldo, C.; Luis, F.; Montero, O. *Inorg. Chem.* **2009**, *48*, 3467-3479.
6. a) Wassermann, K.; Dickman, M. H.; Pope, M. T. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1445-1448; b) Howell, R. C.; Perez, F. G.; Jain, S.; Horrocks, W. D. W. J.; Rheingold, A. L.; Francesconi, L. C. *Angew. Chem. Int. Ed. Engl.* **2001**, *40*, 4031-4034; c) Xue, G. L.; Vaissermann, J.; Gouzerh, P. *J. Clust. Sci.* **2002**, *13*, 409-421; d) Izarova, N. V.; Sokolov, M. N.; Samsonenko, D. G.; Rothenberger, A.; Naumov, D. Yu.; Fenske, D.; Fedin, V. P. *Eur. J. Inorg. Chem.* **2005**, 4985-4996; e) Izarova, N. V.; Sokolov, M. N.; Samsonenko, D. G.; Rothenberger, A.; Fenske, D.; Fedin, V. P. *Russ. Chem. Bull., Int. Ed.* **2008**, *57*, 78-82; f) Ismail, A. H.; Dickman, M. H.; Kortz, U. *Inorg. Chem.* **2009**, *48*, 1559-1565; g) Hussain, F.; Spingler, B.; Conrad, F.; Speldrich, M.; Kögerler, P.; Boskovic, C.; Patzke, G.R. *Dalton Trans.* **2009**, *23*, 4423-4425; h) Hussain, F.; Gable, R.W.; Speldrich, M.; Kögerler, P.; Boskovic, C. *Chem. Comm.* **2009**, 328-330; i) Hussain, F.; Conrad, F.; Patzke, G.R. *Angew. Chem. Int. Ed. Engl.* **2009**, *48*, 9088-9091.
7. a) Nishio, M. *CrystEngComm.* **2004**, *6*, 130-158; b) Nishio, M.; Hirota, M.; Umezawa, Y. *The CH/π Interaction. Evidence, Nature, and Consequences*, Wiley-VCH, **1998**.
8. Nakamoto K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds-Part A: Theory and Applications in Inorganic Chemistry*, 5th ed., Wiley and Sons, New York, **1997**.
9. Helsen, L.; Van den Bulck, E.; Van Bael, M. K.; Vanhoyland, G.; Mullens, J. *Thermochim. Acta.* **2004**, *414*, 145-153.

10. a) Chubarova, E. V.; Dickman, M. H.; Keita, B.; Nadjó, L.; Miserque, F.; Mifsud, M.; Arends, I. W. C. E.; Kortz, U. *Angew. Chem.* **2008**, *120*, 9685-9689; *Angew. Chem. Int. Ed. Engl.* **2008**, *47*, 9542-9546; b) Barsukova, M.; Izarova, N. V.; Biboum, R. N.; Keita, B.; Nadjó, L.; Ramachandran, V.; Dalal, N. S.; Antonova, N. S.; Carbó, J.J.; Poblet, J. M.; Kortz, U. *Chem. Eur. J.* **2010**, *16*, 9076-9085.
11. Barsukova-Stuckart, M.; Izarova, N. V.; Jameson, G. B.; Ramachandran, V.; Wang, Z.; van Tol, J.; Dalal, N. S.; Ngo Biboum, R.; Keita, B.; Nadjó, L.; Kortz, U. *Angew. Chem.* **2011**, *123*, 2688-2692; *Angew. Chem. Int. Ed. Engl.* **2011**, *50*, 2639-2642.
12. a) Izarova, N. V.; Biboum, R. N.; Keita, B.; Mifsud, M.; Arends, I.W.C.E.; Jameson, G. B.; Kortz, U. *Dalton Trans.* **2009**, *43*, 9385-9387; b) Xu, F.; Scullion, R. A.; Yan, J.; Miras, H. N.; Busche, C.; Scandurra, A.; Pignataro, B.; Long, D.; Cronin, L. *J. Am. Chem. Soc.* **2011**, *133*, 4684-4686.

Chapter IV Results

Synthesis and Characterization of Double-cuboid-shaped Copper(II)-containing Polyoxopalladate(II)

In this chapter we report a new structural type of noble metalates. In the course of studying the ability of the cubic $\{\text{Pd}_{12}\text{L}_8\}$ shell to incorporate different guest cations M and also heterogroups L we obtained a novel, double-cuboid-shaped copper(II)-containing polyoxo-22-palladate(II) $[\text{Cu}_2\text{Pd}_{22}\text{P}_{12}\text{O}_{60}(\text{OH})_8]^{20-}$ (**Pd₂₂-6**). This polyanion contains the largest number of palladium ions yet found in polyoxopalladate chemistry. The bonding of each Cu^{II} ion involves the very rare eight-fold oxo-coordination.

4.1 Synthetic Procedure

$\text{Na}_{20}[\text{Cu}^{\text{II}}_2\text{Pd}^{\text{II}}_{22}\text{P}^{\text{V}}_{12}\text{O}_{60}(\text{OH})_8] \cdot 58\text{H}_2\text{O}$ (**NaPd₂₂-6**): $\text{Pd}_3(\text{CH}_3\text{COO})_6$ (0.140 g, 0.208 mmol), and $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (0.021 g, 0.104 mmol) were dissolved in 5 mL of 0.5 M NaH_2PO_4 buffer (pH 6.9). While stirring, the solution was heated to 80 °C. After dissolution of all the components the pH of the reaction mixture was adjusted to 6.9 – 7.0 by addition of 1 M NaOH. The resulting solution was heated at 80 °C for 1 hour. Then it was cooled to room temperature, filtered and allowed to crystallize at room temperature in an open vial. Needle-like orange-red crystals were obtained after several days, which were filtered off and air dried. Yield: 0.033 g (21 % based on Pd). Elemental analysis calcd (%): Na 8.45, Cu 2.34, Pd 43.03, P 6.83; found: Na 8.53, Cu 2.29, Pd 42.45, P 6.99. IR (2% KBr pellet, v/cm^{-1}): 1634 (m), 1087 (s), 973 (s), 934 (s), 678 (sh), 614 (s), 580 (sh), 551(m), 444 (m). The title compound is stable in the solid state under air and light, soluble in water and can be repeatedly recrystallized from aqueous solution. In particular the pH value of the reaction

mixture is a crucial factor for the formation of **NaPd₂₂-6**. For example, at slightly lower pH (6.0 – 6.2), we observed the formation of dark-red, octahedral crystals of **Cu-5d** (see section 3.6). At the intermediate pH range 6.2 – 6.9, a mixture of these two compounds was obtained. In the absence of copper(II) ions, a similar synthetic procedure leads to the star-shaped polyoxo-15-palladate(II).¹

4.2 Single Crystal XRD

Single crystal XRD analysis showed that the polyanion **Pd₂₂-6** consists of two {CuPd₁₁P₆O₃₂} fragments, which are connected by four hydroxo bridges (Fig. 4.1).

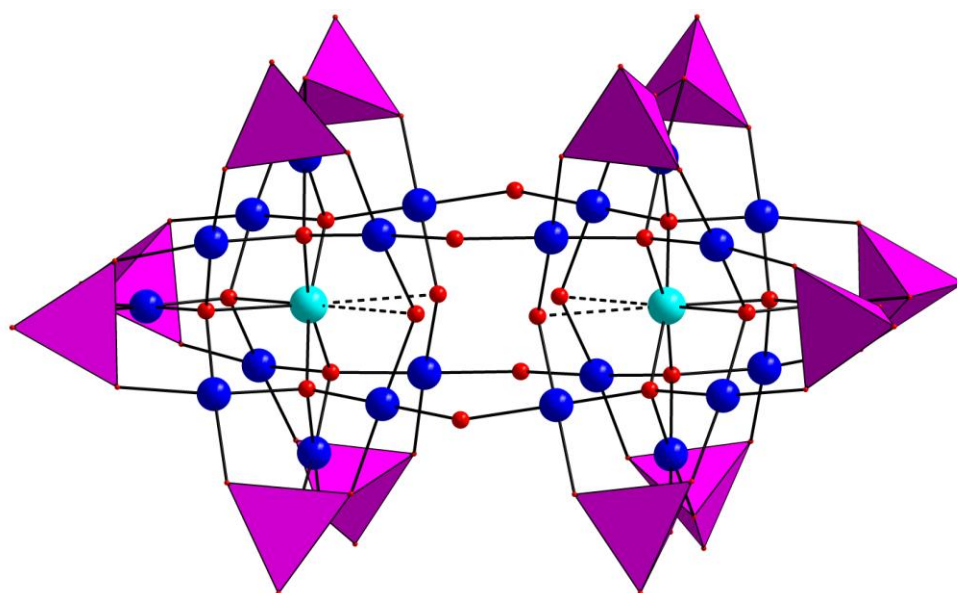


Figure 4.1 Combined ball-and-stick/polyhedral representation of **Pd₂₂-6**.

Color code: Cu turquoise, Pd blue, O red balls, {PO₄} purple tetrahedra. The very long Cu-O bonds (2.759(6) – 2.839(6) Å) are indicated by dotted lines (see text for details).

The structure of each {CuPd₁₁P₆O₃₂} building block is reminiscent of the parent **Pd₁₃L₈** structure, with the central Pd^{II} ion being replaced by Cu^{II} and a {PdP₂O₈} edge of the cube

missing. The structure of **Pd₂₂-6** can also be viewed as two fused ‘lacunary’ {CuPd₁₁P₆O₃₂} units. As found for the entire **Pd₁₃L₈** family, the two Cu^{II} ions in **Pd₂₂-6** are encapsulated in a distorted cubic {O₈} ligand field. Owing to the symmetry of the polyanion, the {O₈} cube is disproportionately stretched along one of its diagonal planes (the horizontal O₄ plane in Fig. 4.1). Thus the Cu–O distances are very long for the two *cis* oxygen atoms of this diagonal plane (Cu–O₈₉ and Cu–O₀₁₁, 2.759(6), 2.839(6) Å), somewhat elongated for the other two oxygen atoms in the same plane (2.274(6), 2.290(6) Å), and are in the usual range of 2.032(6) – 2.066(6) Å for the remaining four oxygen atoms of the {O₈} cuboid motif. The coordination sphere of the Cu^{II} ions in **Pd₂₂-6** can be described as a strongly distorted cube (with coordination number 8), or if the very long Cu–O bonds are ignored, as a trigonal prism (coordination number 6) with the Cu^{II} ions displaced towards one of the square faces (the distance Cu^{II} – {O₄ face} is 0.166(2) Å).

Regarding the linkage of the Pd^{II} ions to the oxygen atoms of the {O₈} cuboid, the oxygen atoms can be divided into two groups: six μ_4 -bridging oxygen atoms, each of which is coordinated by a Cu^{II} and three Pd^{II} ions (Pd–O 1.929(6) – 2.012(6) Å), and two μ_2 -bridging oxygen atoms coordinated by two Pd^{II} centers (Pd–O 2.008(6) – 2.034(6) Å). All Pd^{II} ions within the {CuPd₁₁P₆O₃₂} fragment have the expected square-planar coordination geometry and coordinate two oxygen atoms of the inner {O₈} motif. Seven of the eleven Pd^{II} ions in each {CuPd₁₁P₆O₃₂} half unit complete their square-planar coordination with oxygen atoms of two neighboring tetrahedral phosphate groups (Pd–O 2.015(6) – 2.070(6) Å; P–O 1.532(6) – 1.573(7) Å). The remaining four Pd^{II} centers complete their square-planar coordination geometry with an oxygen atom of a phosphate heterogroup (Pd–O 2.005(6) – 2.021(6) Å; P–O 1.547(6) – 1.568(7) Å) and a μ_2 -bridging oxygen atom of the hydroxo group (see below) linking the two {CuPd₁₁P₆O₃₂} fragments (Pd–O 2.026(6) – 2.035(6) Å).

In the solid state, individual polyanions of **NaPd₂₂-6** are surrounded by sodium counter-cations and water molecules linked together through a framework of strong hydrogen bonds as well as $\text{Na}^+ \cdots \text{OH}_2$ and $\text{Na}^+ \cdots \{\text{OPO}_3\}$ interactions. Both XRD and elemental analysis are consistent with the presence of a total of 20 Na^+ ions in **NaPd₂₂-6**. Eight additional protons are thus required to balance the negative charges of **NaPd₂₂-6**. By using bond valance sum (BVS) calculations² four of the eight protons in the structure of **NaPd₂₂-6** can be unambiguously associated with the four μ_2 -oxygen atoms linking the two $\{\text{CuPd}_{11}\text{P}_6\text{O}_{32}\}$ units of **Pd₂₂-6** (two symmetrically independent O810, O911) (see Fig. 4.1). One more proton is most likely located at the inversion center of **Pd₂₂-6**, being surrounded by a square of four oxygen atoms (O89, O011 and their inversion-related counterparts) separated from each other by 2.53 and 2.69 Å. This description is consistent with the observation of electron density at the inversion center in the difference Fourier map. The remaining three protons are disordered over the terminal oxygen atoms of ten of the twelve phosphate capping groups (P–O 1.513(6)– 1.533(7) Å). The calculated BVS values for the structurally inequivalent oxygens in **NaPd₂₂-6** are presented in Table 4.1.

The presence of bridging hydroxo groups in **Pd₂₂-6** supports the important role of pH value in the formation of this polyanion. The availability of OH^- ions appears to drive the dimerization of ‘lacunary’ $\{\text{CuPd}_{11}\text{P}_6\text{O}_{32}\}$ motifs derived from **Cu-5d** species (see section 3.6). We believe that the formally ‘monolacunary’ $\{\text{CuPd}_{11}\text{P}_6\text{O}_{32}\}$ ion may exhibit a chemistry as rich and diverse as that of the monolacunary $\{\text{XW}_{11}\}$ (X=P, Si, Ge, etc.) Keggin ions.

Table 4.1. Bond valence sum values for different structural types of oxygen atoms in **NaPd₂₂-6**.

μ_2 -O (Pd–O–Pd, between two {CuPd ₁₁ P ₆ } units)	BVS value	μ_2 -O (Pd–O–P)	BVS value
O810	1.028	O2P1	1.698
O911	1.032	O3P1	1.660
μ_2 -O (Pd–O–Pd, within {CuPd ₁₁ P ₆ } unit)	BVS value	O8P1	1.733
O89	1.087 (1.129)*	O1P2	1.706
O011	1.095 (1.150)*	O3P2	1.629 (1.739)**
Terminal oxygens	BVS value	O4P2	1.651 (1.762)**
O1P	1.321	O4P3	1.709
O2P	1.339 (1.474)**	O5P3	1.648 (1.829)**
O3P	1.293	O9P3	1.782
O4P	1.212	O5P4	1.697 (1.852)**
O5P	1.275	O6P4	1.759
O6P	1.317	O0P4	1.695
μ_4 -O (Cu, 3Pd)	BVS value	O1P5	1.732
O134	2.228	O6P5	1.647
O167	2.242	O7P5	1.668
O238	2.095	O1P6	1.698
O271	2.133	O2P6	1.729
O459	2.099	O7P6	1.738
O560	2.113		

* The values in brackets consider weak interaction of the respective oxygen ion with Cu^{II}.

** The values in brackets consider weak electrostatic bonds of the respective oxygen ion with Na⁺ countercations.

Table 4.2 include further crystallographic data for **NaPd₂₂-6**.

Table 4.2 Crystal data and structure refinement for **NaPd₂₂-6**.

NaPd₂₂-6	
empirical formula	H ₁₀₀ CuNa ₁₀ O ₈₂ P ₆ Pd ₁₁
molecular weight [gmol ⁻¹]	3062.46
crystal system	Triclinic
space group	<i>P</i> -1
<i>a</i> [Å]	14.7854(7)
<i>b</i> [Å]	15.5644(8)
<i>c</i> [Å]	20.2597(10)
α [°]	101.940(3)
β [°]	111.254(2)
γ [°]	96.890(3)
<i>V</i> [Å ³]	4152.8(4)
<i>Z</i>	2
<i>T</i> [K]	173(2)
ρ_{calcd} [Mgm ⁻³]	2.446
μ [mm ⁻¹]	2.865
final <i>R</i> indices [<i>I</i> >2 σ (<i>I</i>)]	
<i>R</i> ₁ ^[a]	0.0846
<i>wR</i> ₂ ^[b]	0.1855
<i>R</i> indices (all data)	
<i>R</i> ₁ ^[a]	0.1365
<i>wR</i> ₂ ^[b]	0.2135

$$^{[a]} R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^{[b]} wR_2 = [\sum w (F_o^2 - F_c^2)^2 / \sum w (F_o^2)^2]^{1/2}$$

4.3 FT-IR Spectroscopy

Figure 4.2 shows bands at 614, 580, 551 and 444 cm^{-1} which can be attributed to Pd-O as well as to Cu-O vibrations. The strong bands at 1087, 973 and 934 cm^{-1} are attributed to the phosphate heterogroups, and the broad band at 1634 cm^{-1} is due to crystal water.³

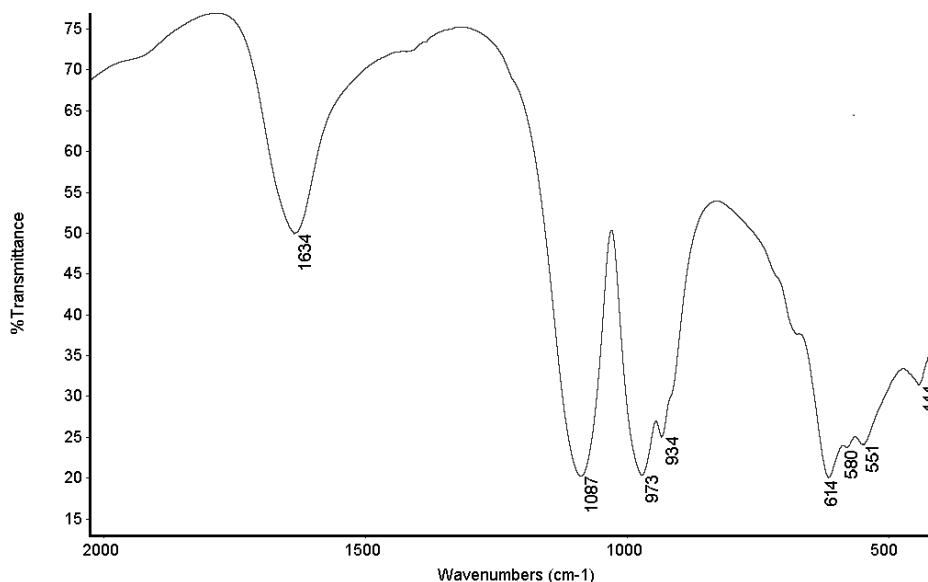


Figure 4.2 FT-IR spectrum of **NaPd₂₂-6**.

4.4 Thermogravimetric Analysis

The TGA curve of **NaPd₂₂-6** exhibits two weight-loss steps (Fig. 4.3). The first step begins at 25 °C (consistent with the discrepancy of crystal water content of air-dried crystals and a single crystal mounted under a nitrogen stream) and is complete at 156 °C, corresponding to the loss of all 58 water molecules per formula unit. The experimental weight loss of 19.2% is in excellent agreement with the calculated value of 19.2%. The total observed weight loss at 900 °C is 31.7 %.

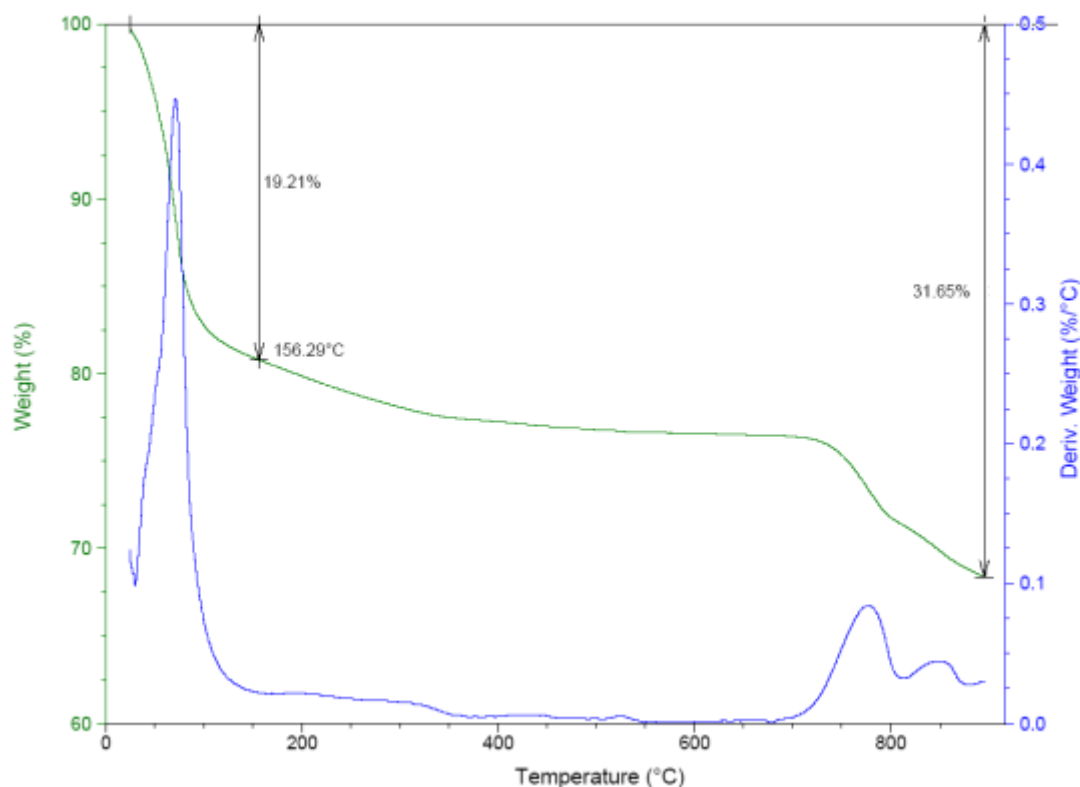


Figure 4.3 Thermogram of **NaPd₂₂₋₆**.

4.5 Conclusions

In conclusion, we have prepared a novel, discrete, solution-stable, double-cuboid-shaped copper(II)-containing polyoxo-22-palladate(II), $[\text{Cu}^{\text{II}}_2\text{Pd}^{\text{II}}_{22}\text{P}^{\text{V}}_{12}\text{O}_{60}(\text{OH})_8]^{20-}$ (**Pd₂₂₋₆**) using a simple, one pot procedure in aqueous solution and mild reaction conditions. The pH value and the presence of Cu^{II} ions play a key role in the formation of **Pd₂₂₋₆**. The salt $\text{Na}_{20}[\text{Cu}^{\text{II}}_2\text{Pd}^{\text{II}}_{22}\text{P}^{\text{V}}_{12}\text{O}_{60}(\text{OH})_8] \cdot 58\text{H}_2\text{O}$ (**NaPd₂₂₋₆**) was characterized by single crystal XRD, elemental analysis, IR and TGA. Electrochemical studies on **NaPd₂₂₋₆** were done by the group of Prof. Louis Nadjo (Université Paris-Sud, Orsay Cedex, France) and showed that the compound could be used for the preparation of electrocatalysts. EPR and magnetic susceptibility measurements on **NaPd₂₂₋₆** were carried out by the group of Prof. Naresh S. Dalal (Florida State University, USA). The bonding of each Cu^{II} ion in **Pd₂₂₋₆** involves the

very rare eight-fold oxo-coordination. **NaPd₂₂-6** has afforded, to our knowledge, the first detailed EPR measurements on Cu^{II} ions in this coordination geometry. In addition, the magnetic exchange interaction between the two Cu^{II} ions in **Pd₂₂-6** is found to be unexpectedly large, possibly opening up a new area for theoretical investigations of magnetic interactions on Cu^{II} and other complexes under controlled bonding parameters. **NaPd₂₂-6** contains the largest number of palladium ions yet found in the polyoxopalladate chemistry.⁴

4.6 References

1. Izarova, N. V.; Ngo Biboum, R.; Keita, B.; Mifsud, M.; Arends, I.W.C.E.; Jameson, G. B.; Kortz, U. *Dalton Trans.* **2009**, 43, 9385-9387;
2. Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, B41, 244-247.
3. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds - Part A: Theory and Applications in Inorganic Chemistry*, 5th ed., Wiley and Sons, New York, 1997.
4. Barsukova-Stuckart, M.; Izarova, N. V.; Jameson, G. B.; Ramachandran, V.; Wang, Z.; van Tol, J.; Dalal, N. S.; Ngo Biboum, R.; Keita, B.; Nadjo, L.; Kortz, U. *Angew. Chem.* **2011**, 123, 2688-2692; *Angew. Chem. Int. Ed. Engl.* **2011**, 50, 2639-2642.

Chapter V Results

Synthesis and Characterization of Yttrium-containing

Isopolytungstate $[YW_{10}O_{36}]^{9-}$

Commonly, POMs are based on the well-known Keggin ion $([XM_{12}O_{40}]^{n-})$ or lacunary fragments of that structure. In contrast, the structure of the $[MW_{10}O_{36}]^{n-}$ polyanions is based on two monolacunary $[W_5O_{18}]^{6-}$ Lindqvist fragments encapsulating a central metal ion in a square-antiprismatic fashion. M can be a variety of tri- and tetravalent metals and to date derivatives have been described for lanthanides $(Na_2(NH_4)_7[La(W_5O_{18})_2] \cdot 16H_2O)$,¹ $Na_6H_2[Ce(W_5O_{18})_2] \cdot 30H_2O$,^{2,3} $Na_8[Ce(W_5O_{18})_2] \cdot 30H_2O$,⁴ $Na_9[Ce(W_5O_{18})_2] \cdot NaCl \cdot 30H_2O$,⁵ $K_3Na_4H_2[Pr(W_5O_{18})_2] \cdot 22H_2O$, $K_3Na_4H_2[Nd(W_5O_{18})_2] \cdot 22H_2O$, $K_3Na_4H_2[Dy(W_5O_{18})_2] \cdot 21H_2O$,⁶ $K_3Na_4H_2[Sm(W_5O_{18})_2] \cdot 22H_2O$,⁷ $Na_6H_3[Sm(W_5O_{18})_2] \cdot 28H_2O$,⁸ $NaSr_4[Eu(W_5O_{18})_2] \cdot 34.5H_2O$,⁹ $K_3Na_4H_2[Gd(W_5O_{18})_2] \cdot 21H_2O$,¹⁰ $Na_8H[Gd(W_5O_{18})_2] \cdot 30H_2O$,¹¹ $K_3Na_4H_2[Tb(W_5O_{18})_2] \cdot 20H_2O$ ¹²) and some actinides $(Na_8[Th(W_5O_{18})_2] \cdot 28H_2O)$,¹³ $Na_8[U(W_5O_{18})_2] \cdot 30H_2O$ ¹⁴). A polyanion with the formula $[PtW_{10}O_{36}]^{8-}$ has been predicted by Gibbs¹⁵ but not yet obtained. The structure of $[Pd_2W_{10}O_{36}]^{8-}$ containing two four-coordinate, square-planar Pd^{2+} hetero atoms between two $[W_5O_{18}]^{6-}$ anionic fragments is also known.¹⁶

Salts of the anion $[YW_{10}O_{36}]^{9-}$ were first reported by Peacock and Weakley.² Subsequently the compound was characterized by ^{89}Y -, ^{17}O - and ^{183}W -NMR spectroscopy.^{17,18} The application of salts of $[YW_{10}O_{36}]^{9-}$ as catalysts with H_2O_2 for alcohol oxidations and alkene epoxidations has been studied.¹³ However, the structure of the $[MW_{10}O_{36}]^{n-}$ anion containing Y^{3+} has not yet been published. As the result of our work in this area we obtained $Na_9[YW_{10}O_{36}] \cdot 35H_2O$ (**Na-7**) and conducted its characterization by single crystal XRD, TGA, elemental analysis, FT-IR and NMR (^{183}W , ^{89}Y) spectroscopy.

5.1 Synthetic Procedure

Compound **Na-7** was synthesized by a modification of the method described by *Peacock and Weakley*²: Na₂WO₄·2H₂O (2.45 g, 7.42 mmol) was dissolved in distilled water (10 ml), the pH was adjusted to 7.2 with 2 M HCl, heated to 45°C, and YCl₃·6H₂O (0.225 g, 0.742 mmol), dissolved in 4 ml of water, was added dropwise. The pH was set to 6.6 – 6.8 by addition of a 2 M solution of NaOH. The resulting solution was stirred and heated to 60 °C for 3 h and then cooled to room temperature. After several days colorless, needle-shaped crystals suitable for X-ray diffraction were obtained. Yield: 1.6 g, 60% (based on {W}). Elemental analysis for **Na-7**, calculated (found): Na 6.2 (6.8), W 55.0 (56.1), Y 2.7 (2.9) %.

5.2 Single Crystal XRD

The single-crystal X-ray analysis shows that the anion [YW₁₀O₃₆]⁹⁻ consists of a central square-antiprismatic yttrium(III) atom sandwiched between two monolacunary Lindqvist units [W₅O₁₈]⁶⁻ (Fig.5.1).

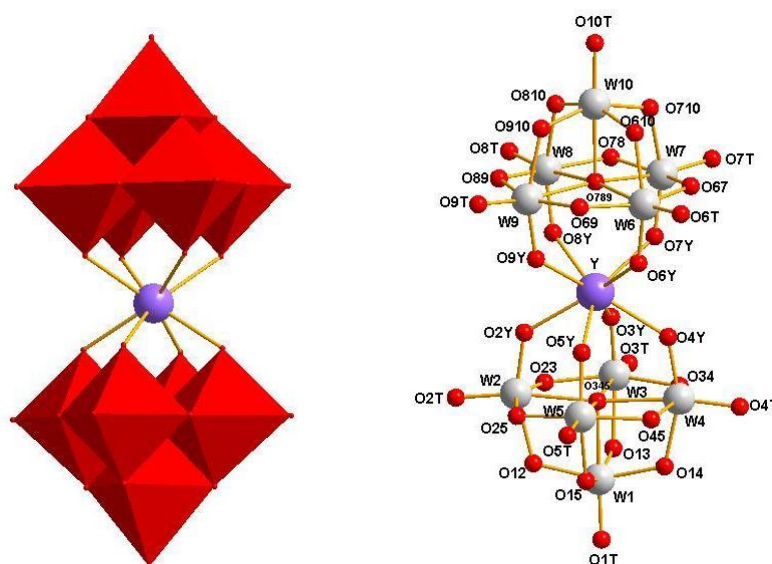


Figure 5.1 Polyhedral (left) and ball-and-stick (right) representations of [YW₁₀O₃₆]⁹⁻.

The WO₆ octahedra are shown in red, and the balls represent Y(purple), O (red), W (grey).

Thus the structure of the polyanion is essentially that of similar, previously-reported $[\text{MW}_{10}\text{O}_{36}]^{n-}$ anions. The eight Y–O(Y) bond distances range from 2.353(8) to 2.394(7) Å. In comparison with the mean Ln–O(Ln) distances for the compounds with the central lanthanides La^{3+} (2.525(6) Å)¹ and Ce^{3+} (2.510(3) Å)⁵ the average Y–O(Y) of 2.373(7) Å is shorter. The O(Y)–Y–O(Y) angles are in the range 73.1(3) – 144.6(2)° (see Table 5.1), which can be separated into four groups, depending on whether the oxygen atoms lie in the same square plane of the square antiprismatic coordination geometry, or in different planes: O–Y–O “cis” (same plane) are in the range 73.1(3) – 75.6(3)°; O–Y–O “trans” (same plane) are in the range 115.3(3) – 118.0(2)°; O–Y–O “cis” (different planes) are in the range 73.4(2)–79.0(2)°; O–Y–O “trans” (different planes) are in the range 139.2(2) – 144.6(2)°.

Table 5.1 Selected bond angles [°] for **Na-7**.

O3Y – Y – O5Y	117.1(3)	O4Y – Y – O9Y	139.2(3)
O3Y – Y – O2Y	75.6(3)	O8Y – Y – O9Y	73.1(3)
O5Y – Y – O2Y	73.5(2)	O6Y – Y – O9Y	74.0(2)
O3Y – Y – O4Y	74.7(2)	O3Y – Y – O7Y	75.6(3)
O5Y – Y – O4Y	73.9(2)	O5Y – Y – O7Y	143.2(2)
O2Y – Y – O4Y	118.0(2)	O2Y – Y – O7Y	141.8(3)
O3Y – Y – O8Y	79.0(2)	O4Y – Y – O7Y	77.1(2)
O5Y – Y – O8Y	140.6(2)	O8Y – Y – O7Y	73.4(2)
O2Y – Y – O8Y	77.0(2)	O6Y – Y – O7Y	73.1(3)
O4Y – Y – O8Y	144.4(2)	O9Y – Y – O7Y	115.4(3)
O3Y – Y – O6Y	139.2(2)	W2 – O2Y – Y	129.6(4)
O5Y – Y – O6Y	77.1(2)	W3 – O3Y – Y	131.5(4)
O2Y – Y – O6Y	143.0(3)	W4 – O4Y – Y	129.7(4)
O4Y – Y – O6Y	73.4(2)	W5 – O5Y – Y	131.9(4)
O8Y – Y – O6Y	115.3(3)	W6 – O6Y – Y	131.7(4)
O3Y – Y – O9Y	144.6(2)	W7 – O7Y – Y	131.2(4)
O5Y – Y – O9Y	75.4(2)	W8 – O8Y – Y	132.8(4)
O2Y – Y – O9Y	77.2(3)	W9 – O9Y – Y	131.4(4)

The W–O distances are typical and lie in the range 1.716(7) – 2.369(7) Å. These can be divided into the following four groups: W–O (t), representing terminal groups, are in the range 1.716(7) – 1.749(8) Å; W–O (μ_2), where O (μ_2) is a bridging oxygen atom between two tungsten atoms, are in the range 1.870(7) – 2.046(7) Å; W–O (μ_5), representing tungsten bonds to the central oxygen atom of each $\{W_5O_{18}\}$ unit, are in the range 2.248(7) – 2.369(7) Å; and W–O (Y), tungsten-oxygen bonds to those oxygen atoms which are coordinated to yttrium, are in the range 1.771(7) – 1.797(7) Å. The O–W–O angles are in the range 72.4(3) – 178.9(3)°, which can be classified into several groups (see Table 5.2). Other bond angles are typical of the $[MW_{10}O_{36}]^{n-}$ anion.

Table 5.2 O–W–O angles groups [°] for Na-7.

Group	Range	Average
O(t)–W–O(Y)	102.7(3) – 105.8(3)	104.3
O(t)–W–O(W)	96.6(3) – 104.8(3)	100.7
O(t)–W–O(μ_5)	170.5(3) – 178.9(3)	174.7
“cis” O(Y)–W–O(W)	91.1(3) – 93.0(3)	92.1
“trans” O(Y)–W–O(W)	156.1(3) – 159.1(3)	157.6
O(Y)–W–O(μ_5)	83.0(3) – 85.0(3)	84.0
O(W)–W–O(μ_5)	72.4(3) – 79.2(3)	75.8
“cis” O(W)–W–O(W)	82.5(3) – 89.8(3)	86.2
“trans” O(W)–W–O(W)	152.4(3) – 155.8(3)	154.1

In the solid state, the polyanions $[YW_{10}O_{36}]^{9-}$ form rows along the *a* direction which alternate with rows of cations to form sheets in the *ac* plane (Fig. 5.2). The title polyanions are connected through infinite zig-zag chains of hydrated sodium ions, of the formula $[Na_9O_4(H_2O)_{32}]_{\infty}$ (Fig. 5.3). The Na–O_{water} contact distances range from 2.269(9) to 2.537(9) Å. There are additionally three water molecules hydrogen-bonded to the anion-cation cluster. In contrast, the Na⁺ cations of $Na_2(NH_4)_7[La(W_5O_{18})_2] \cdot 16H_2O$ form

$\{\text{Na}_2(\text{H}_2\text{O})_{10}\}^{2+}$ fragments,¹ and in the Ce^{3+} analog $\text{Na}_9[\text{Ce}(\text{W}_5\text{O}_{18})_2]\cdot\text{NaCl}\cdot 30\text{H}_2\text{O}$, the $[\text{Ce}(\text{W}_5\text{O}_{18})_2]^{9-}$ anions are connected through pairs of $\{\text{Na}(\text{H}_2\text{O})_4\}^+$ groups, which also results in an infinite chain.⁵

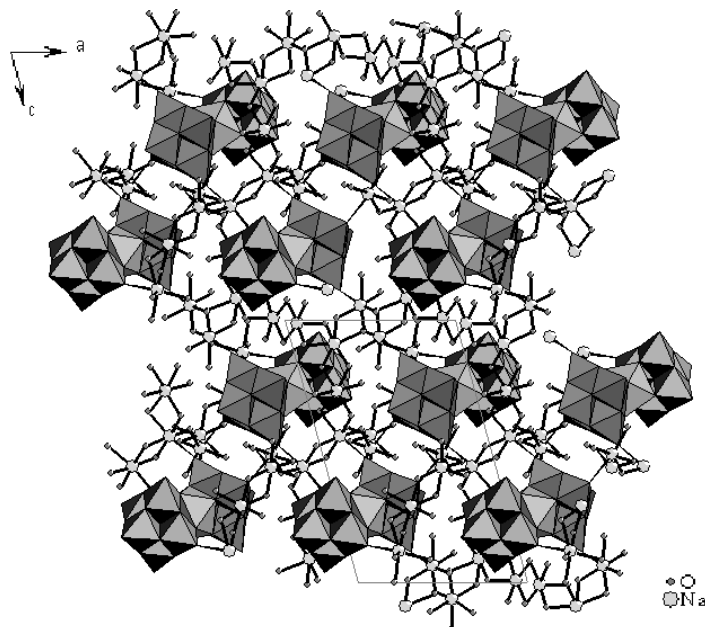


Figure 5.2 Combined polyhedral/ball-and-stick representation of the crystal packing of **Na-7**, viewed along the *b* axis.

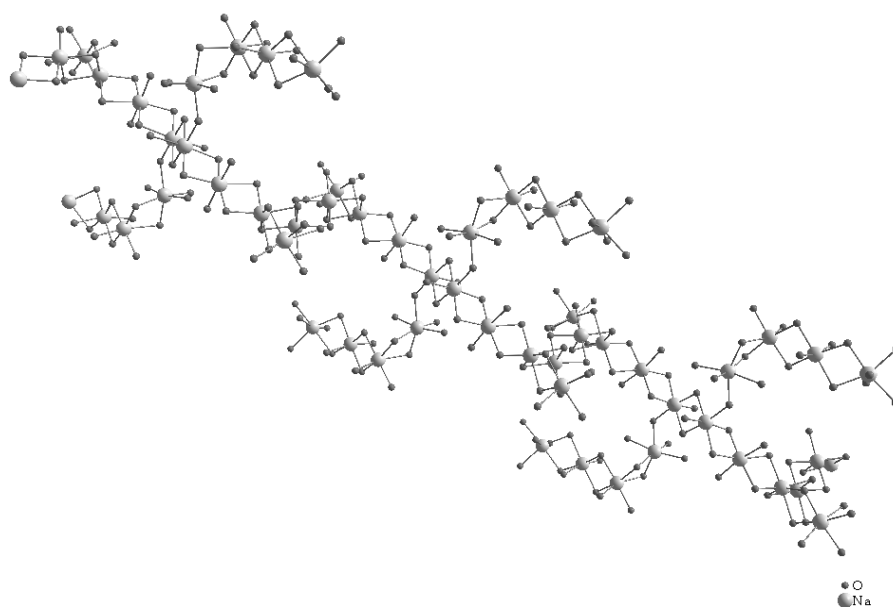


Figure 5.3 Ball-and-stick representation of the chain $\{\text{Na}_9\text{O}_4(\text{H}_2\text{O})_{32}\}_\infty$ in **Na-7**.

Additional crystallographic data for Na-7 are summarized in Table 5.3.

Table 5.3 Crystal data and structure refinement for **Na-7**.

empirical formula	H ₇₀ Na ₉ O ₇₁ W ₁₀ Y
molecular weight [g mol ⁻¹]	3340.9
crystal system	Triclinic
space group	$P\bar{1}$
crystal size, mm	0.41×0.04×0.02
<i>a</i> [Å]	12.7625(9)
<i>b</i> [Å]	13.0825(10)
<i>c</i> [Å]	20.4959(17)
α [°]	82.856(5)
β [°]	74.520(4)
γ [°]	88.822(4)
<i>V</i> [Å ³]	3272.1(4)
<i>Z</i>	2
<i>T</i> [K]	173(2)
ρ_{calcd} [Mg m ⁻³]	3.391
μ [mm ⁻¹]	18.563
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	
<i>R</i> ₁ ^[a]	0.0403
<i>wR</i> ₂ ^[b]	0.0810
<i>R</i> indices (all data)	
<i>R</i> ₁ ^[a]	0.0718
<i>wR</i> ₂ ^[b]	0.0922

$$^{[a]} R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^{[b]} wR_2 = [\sum w (F_o^2 - F_c^2)^2 / \sum w (F_o^2)^2]^{1/2}$$

5.3 FT-IR Spectroscopy

The IR spectrum of **Na-7** (Fig. 5.4) shows characteristic bands at 940, 896, 845, 782, 707, 615, 580, 547, 490 and 422 cm^{-1} that conforms to the reported data for $[\text{MW}_{10}\text{O}_{36}]^{n-}$ anions containing compounds.^{19,20} The band at 940 cm^{-1} is attributed to the $\nu(\text{W}-\text{O}_t)$ vibration modes; at 896 and 707 cm^{-1} to $\nu(\text{Y}-\text{O}-\text{W})$; and at 845 and 782 cm^{-1} to $\nu(\text{W}-\text{O}-\text{W})$ modes.

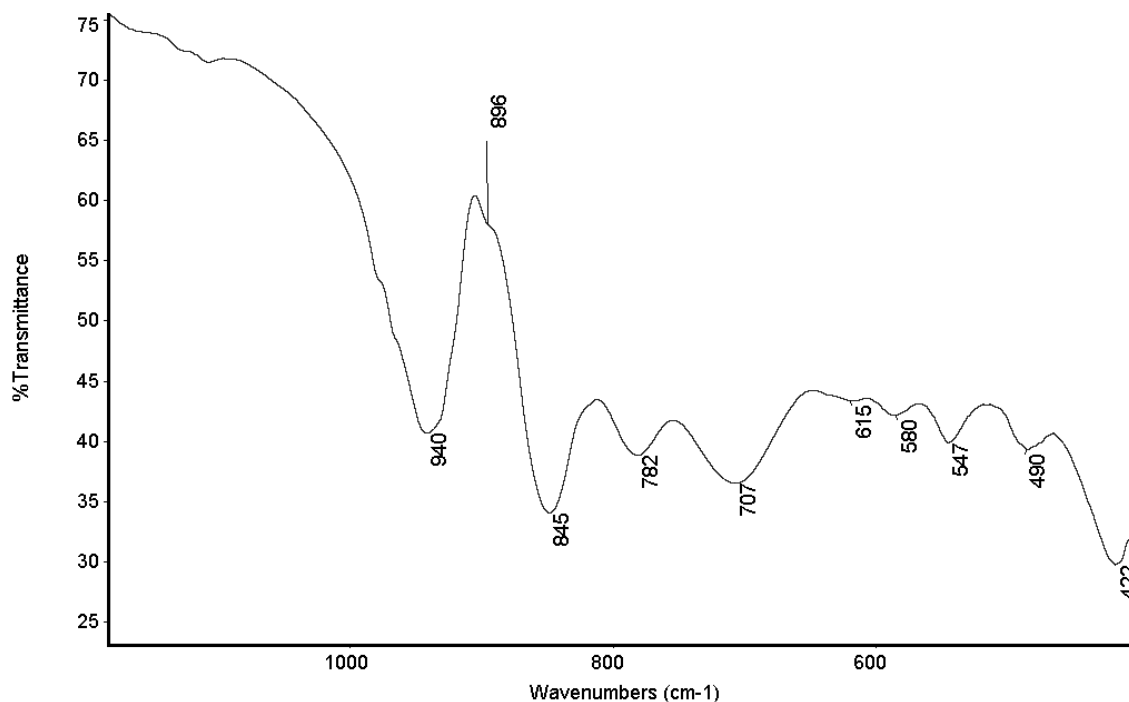


Figure 5.4 FT-IR spectrum of **Na-7**.

5.4 Thermogravimetric Analysis

TGA of **Na-7** (Fig. 5.5) indicates one weight-loss step, which occurs between 20 $^{\circ}\text{C}$ and 172 $^{\circ}\text{C}$ and corresponds to the removal of about 33 lattice water molecules; this result is very close to the 35 water molecules determined by single crystal XRD analysis. The small discrepancy may be due to rapid loss of water during air-dry of **Na-7** sample before TGA.

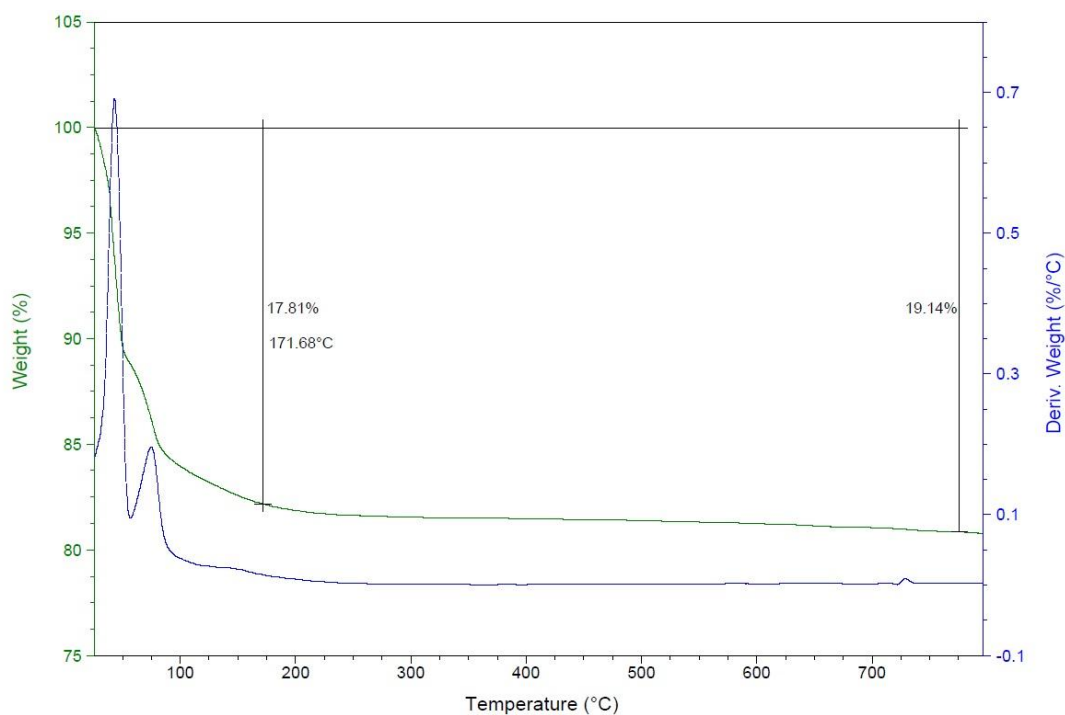


Figure 5.5 Thermogram of **Na-7**.

5.5 NMR Spectroscopy

The solution properties of **Na-7** were investigated by ^{183}W and ^{89}Y NMR spectroscopy. The experiments were carried out on **Na-7** redissolved in $\text{H}_2\text{O}/\text{D}_2\text{O}$. For ^{183}W NMR the expected two peaks are seen at -1.3 ppm ($\omega = 5$ Hz) and -14.3 ppm ($\omega = 20$ Hz), respectively, with an intensity ratio of 1:4 (Fig. 5.6). The more intense, upfield signal is assigned to the 8 equivalent central tungstens of two lacunary Lindqvist anions, while the small, downfield signal corresponds to the two capping tungstens (see Fig. 5.1).

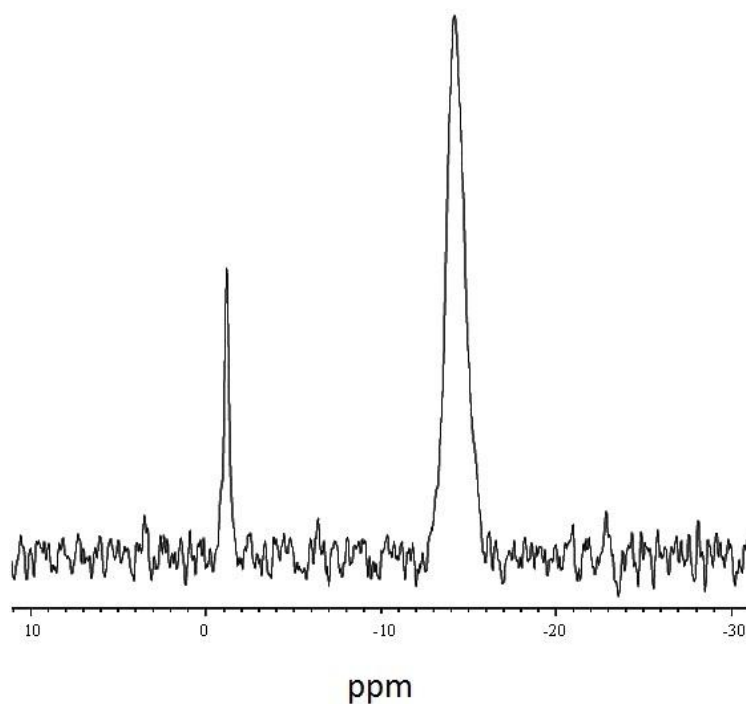


Figure 5.6 ^{183}W -NMR spectrum of **Na-7** redissolved in $\text{H}_2\text{O}/\text{D}_2\text{O}$.

On the other hand, the ^{89}Y NMR spectrum showed the expected singlet at -12.9 ppm ($\omega = 14$ Hz), Fig. 5.7.

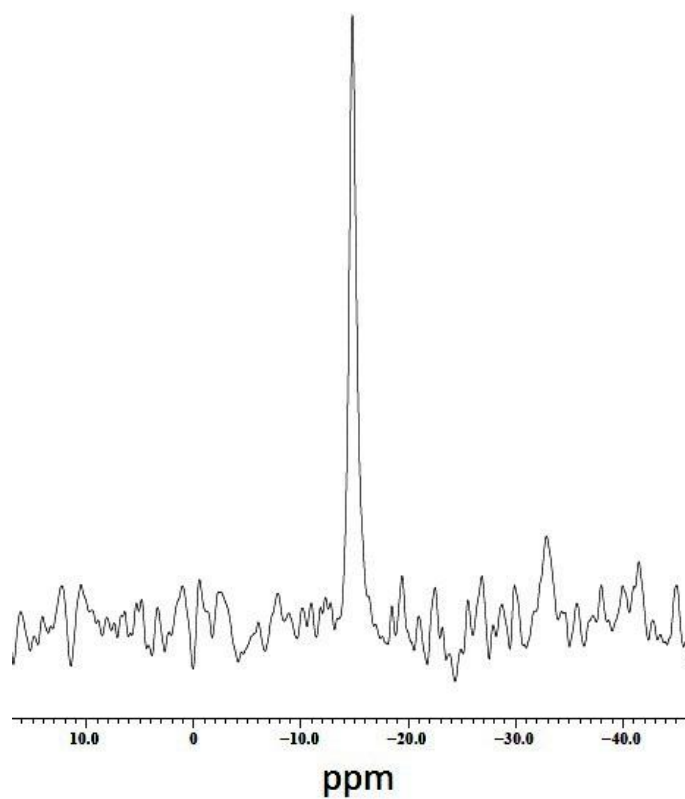


Figure 5.7 ^{89}Y -NMR spectrum of **Na-7** redissolved in $\text{H}_2\text{O}/\text{D}_2\text{O}$.

These results are fully consistent with the observed solid-state structure of the polyanion $[\text{YW}_{10}\text{O}_{36}]^{9-}$ being maintained in aqueous solution. It should be noted that Fedotov et al.¹⁸ reported two peaks with a 4:1 ratio for the ^{183}W -NMR spectrum of $\text{K}_9[\text{YW}_{10}\text{O}_{36}]\cdot n\text{H}_2\text{O}$. However, in their case the more intense line apparently (spectra not shown) appeared at -11 ppm ($\omega=15$ Hz) and the other one at -28 ppm ($\omega=15$ Hz). It is not clear to us why their results are different from ours. Fedotov et al.¹⁷ also reported a ^{89}Y NMR peak at -19 ppm ($\omega=2$ Hz).

5.6 Conclusions

In summary, we have synthesized the nonasodium decatungstoyttrate 35-hydrate, $\text{Na}_9[\text{YW}_{10}\text{O}_{36}]\cdot 35\text{H}_2\text{O}$ (**Na-7**). The compound was characterized in the solid state by a variety of analytical techniques such as X-ray crystallography, IR spectroscopy and TGA. The ^{183}W and ^{89}Y NMR studies of **Na-7** redissolved in $\text{H}_2\text{O}/\text{D}_2\text{O}$ reveal that the solid-state structure of the diamagnetic polyanion $[\text{YW}_{10}\text{O}_{36}]^{9-}$ is maintained in solution.

5.7 References

1. Paz, F. A. A.; Balula, M. S. S.; Cavaleiro, A. M. V.; Klinowski, J.; Nogueira, H. I. S. *Acta Crystallogr. E*. **2005**, *61*, i28-i31.
2. Peacock, R. D.; Weakley, T. J. R. *J. Chem. Soc. A*. **1971**, 1836-1839.
3. Iball, J.; Low, J. N.; Weakley, T. J. R. *J. Chem. Soc. Dalton Trans.* **1974**, 2021-2024.
4. Rosu, C.; Weakley, T. J. R. *Acta Crystallogr. C*. **1998**, *54*, IUC9800047.
5. Xue, G.; Vaissermann, J.; Gouzerh, P. *J. Cluster Sci.* **2002**, *13*, 409-421.
6. Ozeki, T.; Yamase, T. *Acta Crystallogr. B*. **1994**, *50*, 128-134.
7. Ozeki, T.; Yamase, T. *Acta Crystallogr. C*. **1993**, *49*, 1574-1577.

8. Ozeki, T.; Yamase, T. *Acta Crystallogr. C.* **1994**, 50, 327-330.
9. Yamase, T.; Ozeki, T.; Ueda, K. *Acta Crystallogr. C.* **1993**, 49, 1572-1574.
10. Yamase, T.; Ozeki, T. *Acta Crystallogr. C.* **1993**, 49, 1577-1580.
11. Yamase, T.; Ozeki, T.; Tosaka, M. *Acta Crystallogr. C.* **1994**, 50, 1849-1852.
12. Ozeki, T.; Takahashi, M.; Yamase, T. *Acta Crystallogr. C.* **1992**, 48, 1370-1374.
13. Griffith, W. P.; Morley-Smith, N.; Nogueira, H. I. S.; Shoair, A. G. F.; Suriaatmaja, M.; White, A. J. P.; Williams, D. J. *J. Organomet. Chem.* **2000**, 607, 146-155.
14. Golubev, A. M.; Kazanskii, L. P.; Torchenkova, E. A.; Simonov, V. I.; Spitsyn, V. I. *Dokl. Acad. Nauk.* **1975**, 221, 351-352.
15. Gibbs, W. *Chem. Ber.* **1877**, 10, 1384-1388.
16. Angus-Dunne, S. J.; Burns, R. C.; Craig, D. C.; Lawrance, G. A. *J. Chem. Soc., Chem. Commun.* **1994**, 523-524.
17. Fedotov, M. A.; Samokhvalova, E. P.; Maksimov, G. M.; Torchenkova, E. A. *Zh. Strukt. Khim.* **1989**, 30, 174.
18. Fedotov, M. A.; Samokhvalova, E. P.; Kazansky L. P.; Maksimov, G. M.; Torchenkova, E. A. *Polyhedron.* **1996**, 15, 3341-3351.
19. Kazanskii, L. P.; Golubev, A. M.; Baburina, I. I.; Torchenkova, E. A.; Spitsyn, V. I. *Izv. Acad. Nauk, Ser. Khim.* **1978**, 2215-2219.
20. Shiozaki, R.; Inagaki, A.; Nishino, A.; Nishio, E.; Maekawa, M.; Kominami, H.; Kera, Y. *J. Alloys Compds.* **1996**, 234, 193-198.

Chapter VI Results

Synthesis and Characterization of Organoantimony-containing Heteropolytungstates

The organically-derivatized POMs are of particular interest nowadays due to the combination of features of both the incorporated organic units and polyoxoanions. The functionalization of POMs with organometallic moieties allows tuning the redox and acid–base properties, solubility, biological activity and toxicity of POMs, might improve their stability.¹ Moreover hybrid organic-inorganic POMs can combine several interesting features, e.g. chirality,² magnetic, electrical³ and catalytic properties.⁴

In particular, organotin species have been widely studied as derivatizing agents because of the stability of the Sn–C bond and also the fact that Sn^{IV} can substitute the addenda metals in POM skeletons. Thus, several examples of monomeric and dimeric monoorganotin-containing heteropolytungstates have been reported.^{5,6} In the Kortz group such complexes with organotin as $(\{C_6H_5Sn\}_2As_2W_{19}O_{67}(H_2O))^{8-}$,^{6b} $[\{Sn(CH_3)_2(H_2O)\}_{24}\{Sn(CH_3)_2\}_{12}(A-\alpha-XW_9O_{34})_{12}]^{36-}$ ($X = P^V, As^V$),^{6d} $([\{(CH_3)_2Sn\}_2(W_6O_{22})]^{4-})_{\infty}$,^{6f} $[\{(Sn(CH_3)_2)(Sn(CH_3)_2O)(A-\alpha-PW_9O_{34})\}_3]^{21-}$,^{6g} $[\{(CH_3)_2Sn(H_2O)\}_3(A-\alpha-PW_9O_{34})]^{3-}$,^{6m} have been obtained. Compared to that of organotin, POMs functionalized by organoantimony fragments are quite scarce. In 1989, the group of Liu reported on the solid state structure of $[(Ph_2Sb)_2(\mu-O)_2(\mu-MoO_4)_2]^{2-}$, in which two separated MoO₄ tetrahedra bridge two octahedrally coordinated antimony ions.⁷ A few years later, Krebs and co-workers prepared the isostructural tungsten analogue.⁸ Recently, Winpenny's group synthesized a reverse Keggin ion comprising 12 PhSb units in the addenda positions and a central MO₄ (M = Mn, Zn) group.⁹

To our knowledge, only one organoantimony-containing polyoxotungstate $\text{Cs}_9[\{\text{PhSb}(\text{OH})\}_3(\text{A-}\alpha\text{-PW}_9\text{O}_{34})_2]\cdot 24\text{H}_2\text{O}$ (Fig. 6.1) has been reported to date, which was synthesized by Körtz's group in 2007 with the hydrothermal reaction of Ph_2SbCl_3 and $\text{Na}_9[\text{A-}\alpha\text{-PW}_9\text{O}_{34}]\cdot 13\text{H}_2\text{O}$ in an aqueous acidic medium.¹⁰

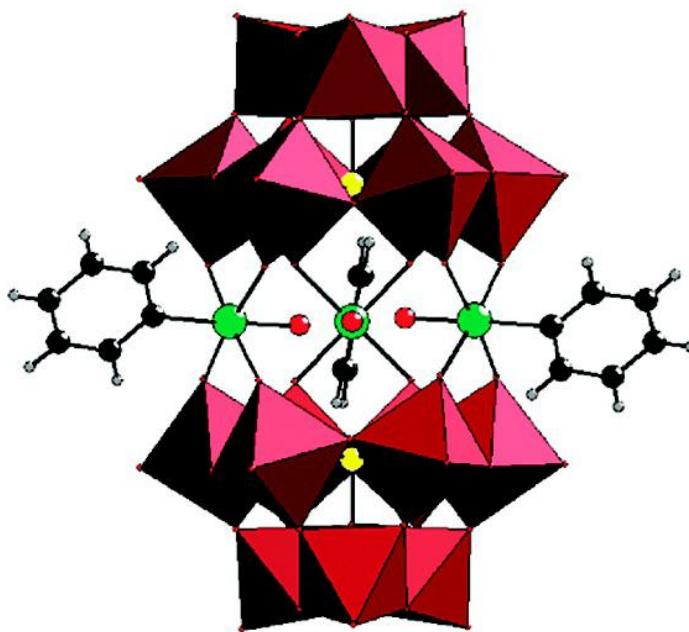


Figure 6.1 Combined polyhedral/ball-and-stick representation of $[\{\text{PhSb}(\text{OH})\}_3(\text{A-}\alpha\text{-PW}_9\text{O}_{34})_2]^{9-}$. Colour code: WO_6 octahedra, dark red; antimony, green; oxygen, red; phosphorus, yellow; carbon, black; hydrogen, grey.

As the result of the further work on systematic synthesis of polyoxotungstates functionalized by organoantimony units we obtained three novel compounds, $(\text{NH}_4)_{12}[\{\text{PhSb}\}_4(\text{A-}\alpha\text{-GeW}_9\text{O}_{34})_2]\cdot 20\text{H}_2\text{O}$ (**NH₄-8**), $\text{Rb}_9\text{Na}[\{\text{PhSb}\}_4(\text{A-}\alpha\text{-PW}_9\text{O}_{34})_2]\cdot 20\text{H}_2\text{O}$ (**RbNa-9**), $\text{Rb}_3[\{2\text{-(Me}_2\text{NCH}_2\text{C}_6\text{H}_4)\text{Sb}^{\text{III}}\}_3(\text{B-}\alpha\text{-AsW}_9\text{O}_{33})]\cdot 7\text{H}_2\text{O}$ (**Rb-10**). The obtained POMs were characterized in the solid state by single-crystal XRD, TGA, elemental analysis and FT-IR spectroscopy and in solution by multinuclear NMR spectroscopy.

6.1 Synthetic Procedures

(NH₄)₁₂[{PhSb}₄(A- α -GeW₉O₃₄)₂] $\cdot$ 20H₂O (NH₄-8): Na₁₀[A- α -GeW₉O₃₄] $\cdot$ 21H₂O (0.417 g, 0.145 mmol) was dissolved in 20 ml distilled water, whereas 0.078 g (0.290 mmol) of PhSbCl₂ was dissolved in a separate beaker in a minimum amount of ethanol. The solution of the organoantimony-containing compound was added drop-wise to the precursor solution under vigorous stirring. The resulting solution was stirred for 30 min, and then it was filtered, layered with a few drops of 1 M NH₄Cl and cooled to 4 – 5 °C. After 1 day yellow crystals suitable for XRD measurements were obtained. Yield: 0.315 g, (73 % based on {W}). Elemental analysis (%) calcd: N 2.84, H 1.84, C 4.87, Sb 8.23, Ge 2.46, W 56.0; found: N 2.91, H 1.92, C 4.77, Sb 8.12, Ge 2.48, W 55.9. IR (2% KBr pellet, ν/cm^{-1}): 3142(s), 1625(m), 1401(s), 1184(w), 1065(w), 926(s), 879(s), 780(s), 721(s), 618(sh), 533(m), 479(m).

Rb₉Na[{PhSb}₄(A- α -PW₉O₃₄)₂] $\cdot$ 20H₂O (RbNa-9): Na₉[A- α -PW₉O₃₄] $\cdot$ 13H₂O (0.417 g, 0.145 mmol) was dissolved in 20 ml distilled water, whereas 0.078 g (0.290 mmol) of PhSbCl₂ was dissolved in a separate beaker in a minimum amount of ethanol. The solution of the organoantimony-containing compound was added drop-wise to the precursor solution under vigorous stirring. The resulting solution was stirred for 30 min, filtered, layered with a few drops of 0.5 M RbCl and cooled to 4 – 5 °C. After 1 day yellow crystals were obtained. Yield: 0.345 g, (68 % based on {W}). Elemental analysis (%) calcd: Rb 12.01, Na 0.36, H 0.94, C 4.50, Sb 7.60, P 0.97, W 51.65; found: Rb 11.53, Na 0.30, H 1.05, C 4.73, Sb 9.34, P 1.10, W 51.25. IR (2% KBr pellet, ν/cm^{-1}): 1619 (m), 1478 (w), 1428 (w), 1185 (w), 1066 (s), 1013 (m), 942 (s), 913 (s), 892 (sh), 822(sh), 741 (s), 592 (w), 516 (m), 459 (m).

Rb₃[{2-(Me₂NCH₂C₆H₄)Sb^{III}]₃(B- α -AsW₉O₃₃)] $\cdot$ 7H₂O (Rb-10): Powdered Na₉[B- α -AsW₉O₃₃] $\cdot$ 12H₂O (0.134 g, 0.05 mmol) was dissolved in 10 ml of water. Powdered [2-(Me₂NCH₂C₆H₄)]Sb^{III}Cl₂ (0.047 mg, 0.15 mmol) was dissolved in ethanol and heated to

40 °C. The solution of the organoantimony-containing compound was added drop-wise to the precursor solution under vigorous stirring. The mixture was stirred for 30 minutes at room temperature and filtered off. 1 ml of 0.5 M RbCl was added to the resulting solution. Yellow crystals were obtained after several days, filtered off and air dried. Yield: 0.080g (46% based on {W}). IR (2% KBr pellet, ν/cm^{-1}): 1618 (m), 1437 (m), 1360 (w), 1287 (w), 1208 (w), 1113 (w), 1031 (w), 997 (s), 955 (s), 854 (s), 790 (s), 749(s), 692(s), 655(s), 481(m), 447 (m).

6.2 Single Crystal XRD

The single-crystal X-ray analysis shows that the polyoxotungstates **NH₄-8** and **RbNa-9** crystallize in the triclinic crystal system, space group *P*-1 and they are isomorphous. The anion $[\{\text{PhSb}\}_4(\text{A}-\alpha\text{-XW}_9\text{O}_{34})_2]^{n-}$ ($\text{X}=\text{Ge}^{4+}$, P^{5+}) in **NH₄-8** and **RbNa-9** has a dimeric, sandwich-type structure with two $\{\text{A}-\alpha\text{-XW}_9\text{O}_{34}\}$ units capping four $\{\text{PhSb}\}$ fragments (Fig. 6.2). The antimony centers exhibit a highly distorted tetrahedral geometry. Selected bond distances for the polyanions are shown in Table 6.1.

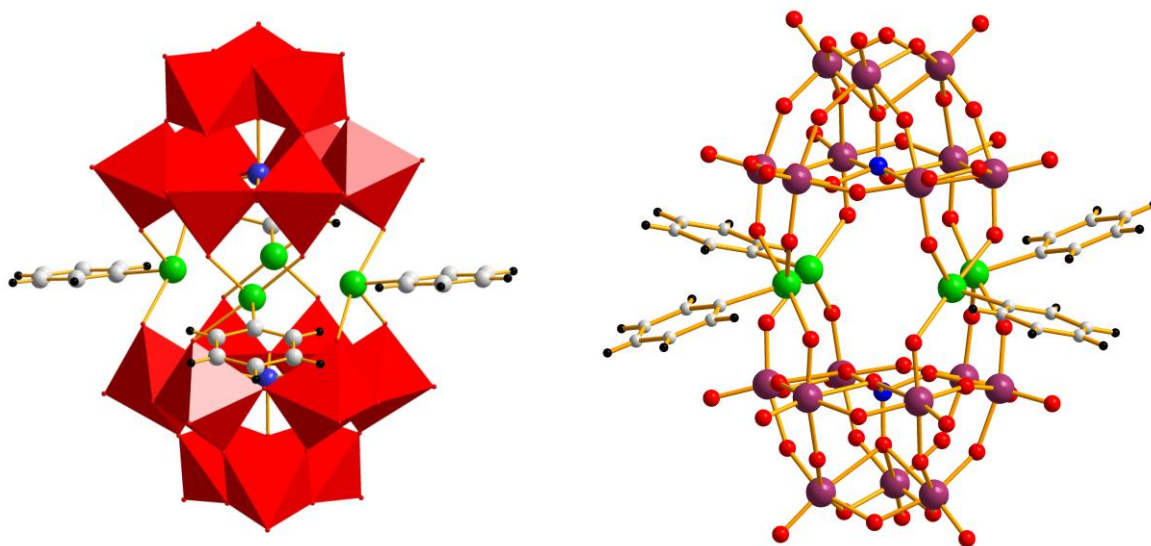


Figure 6.2 Combined polyhedral/ball-and-stick (left) and ball-and-stick (right) representations of $[\{\text{PhSb}\}_4(\text{A}-\alpha\text{-XW}_9\text{O}_{34})_2]^{n-}$ ($\text{X}=\text{Ge}^{4+}$, P^{5+}). Color code: WO_6 red octahedral and the balls represent W (plum), O (red), Sb (green), X (blue), C (grey), H (black).

Table 6.1 Ranges of selected bond lengths [Å] for the anion
$$[\{\text{PhSb}\}_4(\text{A}-\alpha-\text{XW}_9\text{O}_{34})_2]^{n-} \text{ (X=Ge}^{4+}, \text{P}^{5+}) \text{ in } \mathbf{NH_4-8} \text{ and } \mathbf{RbNa-9}.$$

	NH₄-8	RbNa-9
W–O _t	1.708(18) – 1.754(18)	1.719(12) – 1.746(12)
W–O(X)	2.192(16) – 2.305(16)	2.365(11) – 2.427(10)
W–O(W)	1.817(18) – 2.089(17)	1.816(12) – 2.061(12)
W–O(Sb)	1.790(19) – 1.898(17)	1.793(11) – 1.883(12)
Sb–O	1.991(16) – 2.386(19)	2.000(12) – 2.335(11)
Sb–C	2.133(13) – 2.156(13)	2.152(8) – 2.174(8)
X–O	1.731(16) – 1.793(17)	1.527(11) – 1.576(11)

The anion $[\{2-(\text{Me}_2\text{NCH}_2\text{C}_6\text{H}_4)\text{Sb}^{\text{III}}\}_3(\text{B}-\alpha-\text{AsW}_9\text{O}_{33})]^{3-}$ in **Rb-10** is composed of a $[\text{B}-\alpha-\text{AsW}_9\text{O}_{33}]^{9-}$ subunit and three $[2-(\text{Me}_2\text{NCH}_2\text{C}_6\text{H}_4)\text{Sb}^{\text{III}}]^{2+}$ moieties resulting in a polyanion with C_3 symmetry (Fig. 6.3).

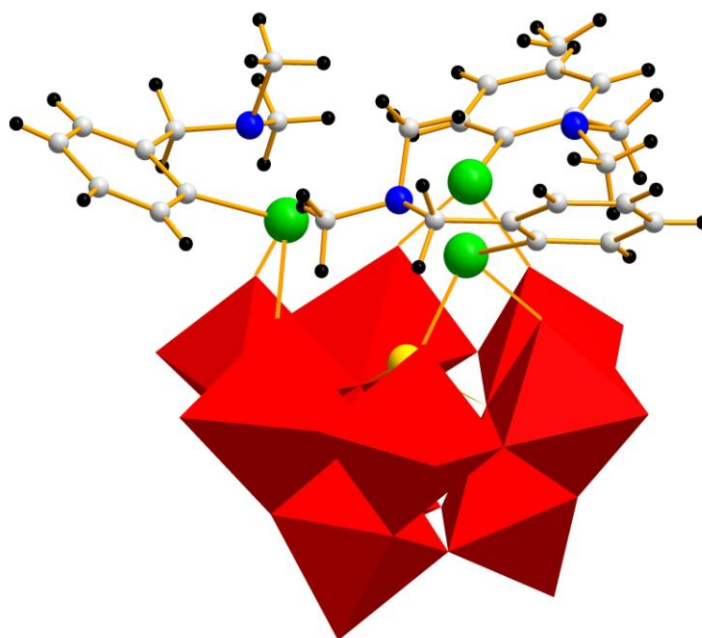


Figure 6.3 Combined polyhedral/ball-and-stick representation of $[\{2-(\text{Me}_2\text{NCH}_2\text{C}_6\text{H}_4)\text{Sb}^{\text{III}}\}_3(\text{B}-\alpha-\text{AsW}_9\text{O}_{33})]^{3-}$. Color code: WO_6 red octahedral, Sb green, As yellow, N blue, C grey, H black.

The $[B-\alpha\text{-AsW}_9\text{O}_{33}]^{9-}$ fragment consists of a central lone pair containing $\{\text{AsO}_3\}$ hetero group and three corner-shared $\{\text{W}_3\text{O}_{13}\}$ triads (composed of three edge-shared WO_6 octahedra). In the polyanion the vacant positions of the $[B-\alpha\text{-AsW}_9\text{O}_{33}]^{9-}$ subunits are filled by three $[2\text{-(Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{)Sb}^{\text{III}}]^{2+}$ groups. Selected bond distances for the polyanion are shown in Table 6.2.

Table 6.2 Ranges of selected bond lengths [Å] for the polyanion

$[\{2\text{-(Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{)Sb}^{\text{III}}\}_3(B-\alpha\text{-AsW}_9\text{O}_{33})]^{3-}$ in **Rb-10**.

W–O _t	1.690(14) – 1.735(13)
W–O(As)	2.298(12) – 2.380(12)
W–O(W)	1.901(12) – 1.926(12)
Sb–O(W)	1.950(13) – 2.144(12)
Sb–C	2.100(19) – 2.144(12)
As–O	1.770(12) – 1.789(12)

Crystallographic data for the compounds **NH₄-8**, **RbNa-9** and **Rb-10** are summarized in Table 6.3.

Table 6.3 Crystal data and structure refinement for **NH₄-8**, **RbNa-9** and **Rb-10**.

	NH₄-8	RbNa-9	Rb-10
empirical formula	C ₂₄ H ₁₀₈ Ge ₂ N ₁₂ O ₈₈ Sb ₄ W ₁₈	C ₂₄ H ₆₀ NaO ₈₈ P ₂ Rb ₉ Sb ₄ W ₁₈	C ₂₇ H ₅₂ AsN ₃ O ₄₀ Rb ₃ Sb ₃ W ₉
molecular weight [g mol ⁻¹]	5914.70	6407.18	3409.95
crystal system	Triclinic	Triclinic	Monoclinic
space group	P-1	P-1	P2(1)/c
<i>a</i> [Å]	13.8872(10)	12.7882(16)	15.5607(4)
<i>b</i> [Å]	17.9325(14)	13.9014(16)	17.8585(5)
<i>c</i> [Å]	20.7047(14)	16.236(2)	22.9320(7)
<i>α</i> [°]	74.469(3)	73.118(7)	90.00
<i>β</i> [°]	77.786(3)	77.083(8)	100.200(1)
<i>γ</i> [°]	88.189(3)	65.203(7)	90.00
<i>V</i> [Å ³]	4853.7(6)	2490.0(6)	6271.9(3)
<i>Z</i>	2	1	4
<i>T</i> [K]	173(2)	173(2)	173(2)
<i>ρ</i> _{calcd} [Mg m ⁻³]	4.047	4.273	3.611
<i>μ</i> [mm ⁻¹]	23.054	26.277	20.631
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]			
<i>R</i> ₁ ^[a]	0.0580	0.0430	0.0450
<i>wR</i> ₂ ^[b]	0.1393	0.1272	0.1039
<i>R</i> indices (all data)			
<i>R</i> ₁ ^[a]	0.1146	0.0621	0.0620
<i>wR</i> ₂ ^[b]	0.1793	0.1607	0.1117

$$^{[a]} R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^{[b]} wR_2 = [\sum w (F_o^2 - F_c^2)^2 / \sum w (F_o^2)^2]^{1/2}$$

6.3 FT-IR Spectroscopy

FT-IR spectra recorded on the sample of **NH₄-8** is shown on Figure 6.4. The stretching and bending vibrations of the C–H and C–C bonds of the phenyl rings appear at 1184, 1065, 721 and 618 cm⁻¹.¹¹ The band at 780 cm⁻¹ corresponds to Ge–O vibrations. The other peaks below 1000 cm⁻¹ are assigned to terminal W=O as well as bridging W–O–W stretching modes.¹² The bands at 3142 and 1401 cm⁻¹ corresponds to NH₄⁺ ions. The broad band at 1625 cm⁻¹ belongs to asymmetric vibrations of the crystal waters.¹³

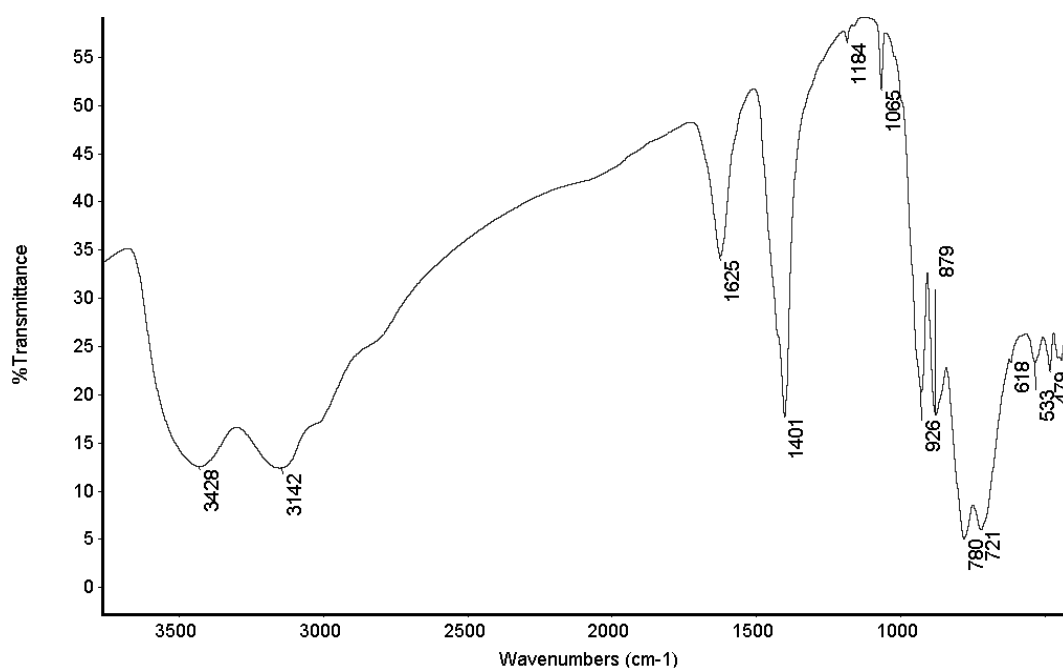


Figure 6.4 IR spectrum of **NH₄-8**.

FT-IR spectra recorded on the sample of **RbNa-9** is shown on Figure 6.5. The stretching and bending vibrations of the C–H and C–C bonds of the phenyl rings appear in the region between 1478 and 1066 cm⁻¹, 721 and 618 cm⁻¹.¹¹ The band at 1013 cm⁻¹ corresponds to P–O antisymmetric stretching modes. The other peaks below 1000 cm⁻¹ are assigned to terminal W=O as well as bridging W–O–W stretching modes.¹² The broad band at 1619 cm⁻¹ belongs to asymmetric vibrations of the crystal waters.¹³

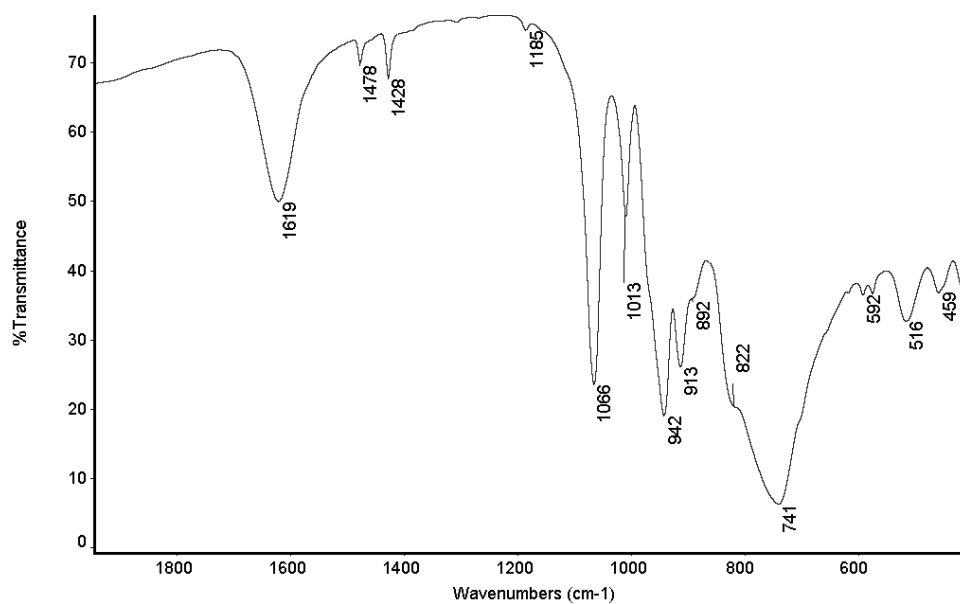


Figure 6.5 IR spectrum of **RbNa-9**.

FT-IR spectra recorded on the sample of **Rb-10** is shown on Figure 6.6. The stretching and bending vibrations of the C–H and C–C bonds of the organic groups appear in the region between 1437 and 1031 cm^{-1} and at 749 and 692 cm^{-1} .¹¹ The band at 854 cm^{-1} corresponds to As–O antisymmetric stretching modes. The other peaks below 1000 cm^{-1} are assigned to terminal W=O as well as bridging W–O–W stretching modes.¹² The broad band at 1618 cm^{-1} belongs to asymmetric vibrations of the crystal waters.¹³

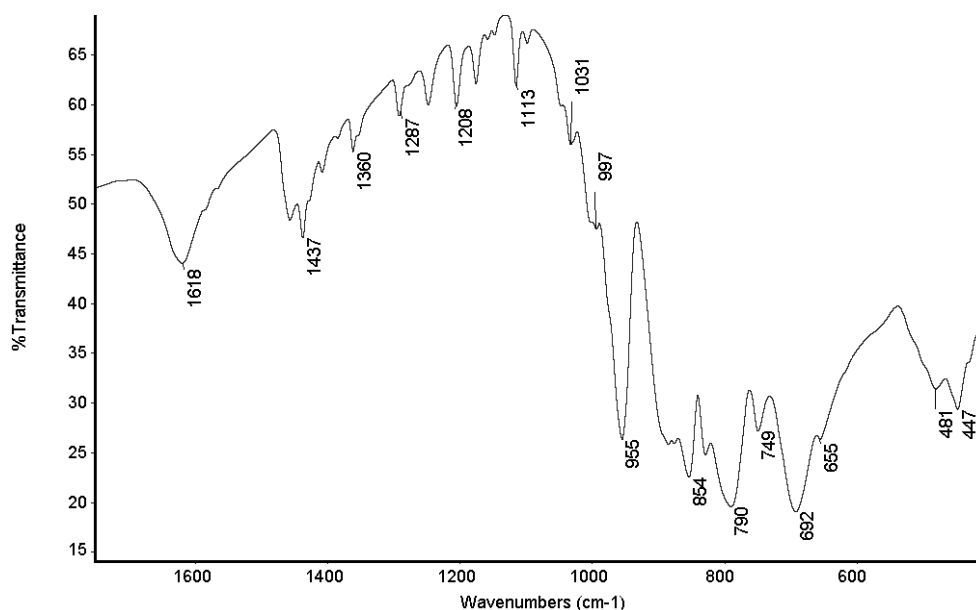


Figure 6.6 IR spectrum of **Rb-10**.

6.4 Thermogravimetric Analysis

The thermogravimetric process of **NH₄-8** revealed several weight-loss steps (see Fig. 6.7). The first step occurs between 25 and 172 °C and corresponds to the loss of 20 water molecules per formula unit. The several consecutive weight loss steps covering the temperature range 172 – 499 °C are attributed to the release of phenyl groups and ammonia ions per formula unit. The total observed weight loss for **NH₄-8** at 1000°C is 17.8%.

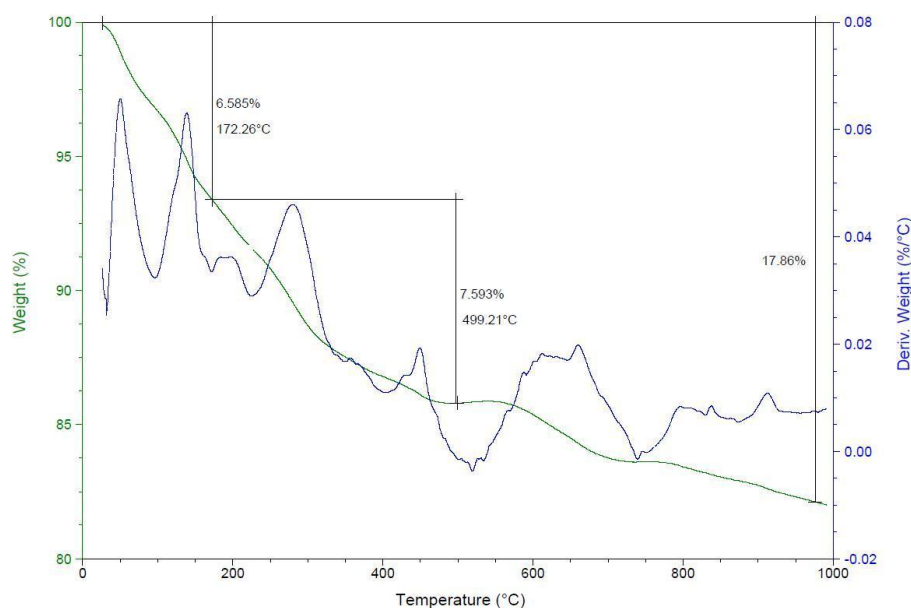


Figure 6.7 Thermogram of **NH₄-8**.

The thermogram of **RbNa-9** also showed several weight-loss steps (see Fig. 6.8). The first step occurs between 25 and 192 °C and corresponds to the loss of 16 water molecules per formula unit. The number of water molecules determined by TGA is slightly lower than that obtained by crystallography (20 molecules). This fact can be easily explained by partial loss of crystal waters during sample drying. Single crystals for XRD measurements were taken directly from the mother liquid, put in oil and frozen under nitrogen flow on the diffractometer, whereas the samples for TGA were air-dried for at least one day. The

combustion of four phenyl groups per formula unit proceeds in the temperature range of 377 – 601 °C. The total observed weight loss for **RbNa-9** at 1000 °C is 10.7 %.

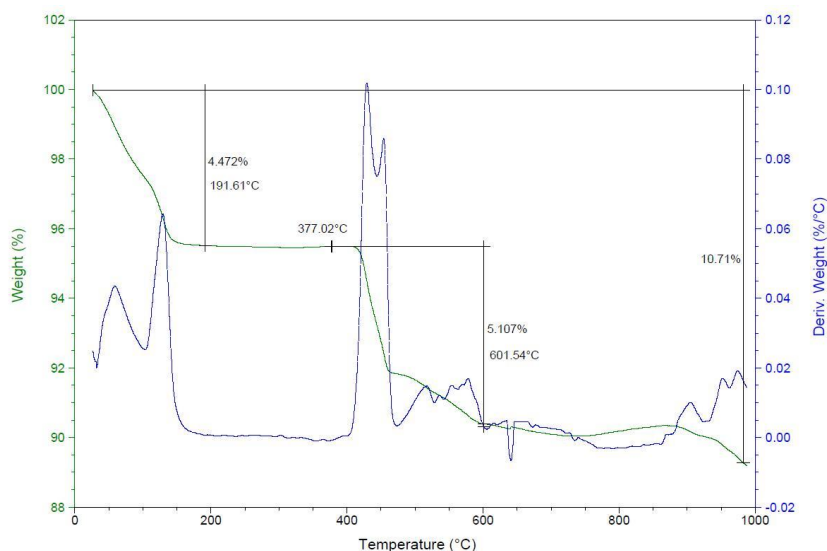


Figure 6.8 Thermogram of **RbNa-9**.

In case of **Rb-10** the first step on the thermogram occurs between 25 and 226 °C and corresponds to the loss of 9 water molecules per formula unit of **Rb-10**. Dehydration is followed by the release of the organic moieties confirmed by the series of steps between 226 and 590 °C. The total observed weight loss for **Rb-10** at 800 °C is 28.4 % (Fig. 6.9).

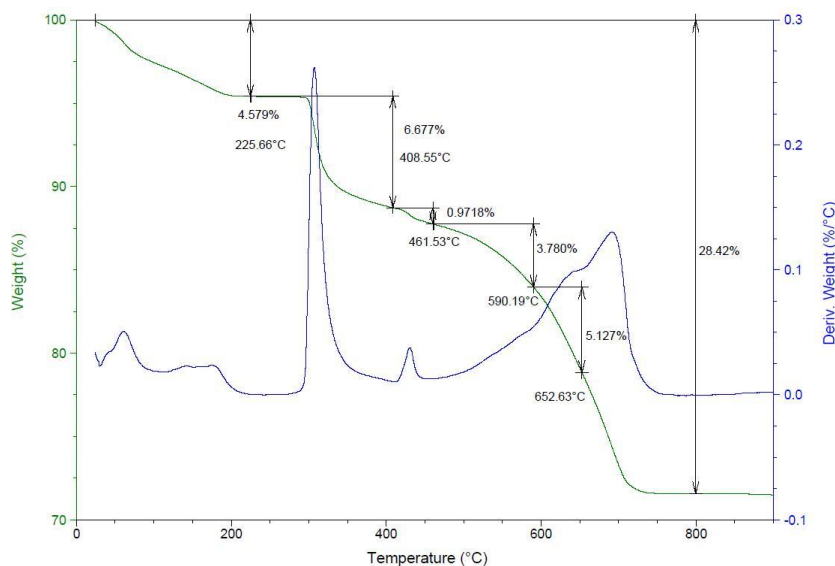


Figure 6.9 Thermogram of **Rb-10**.

6.5 NMR Spectroscopy

The solution properties of **NH₄-8**, **RbNa-9** and **Rb-10** were investigated by multinuclear NMR spectroscopy. The experiments were carried out on the solutions of the compounds in H₂O/D₂O. The ¹⁸³W NMR spectra of isomorphous **NH₄-8** and **RbNa-9** showed the supposed five peaks (at -78, -93, -102, -148, -195 ppm for **NH₄-8** and at -105, -112, -115, -168, -178 ppm for **RbNa-9**) with an intensity ratio of 2:1:2:2:2 fully consistent with the crystal structure and thus with the solution stability of the polyanions. (Fig. 6.10). The ¹³C NMR spectra of **NH₄-8** and **RbNa-9** are as expected for phenyl groups (Fig. 6.11). The ¹H NMR spectra of **NH₄-8** and **RbNa-9** also prove the presence of phenyl groups as well as NH₄⁺ ions in case of **NH₄-8** (Fig. 6.12). The ³¹P NMR spectra of **RbNa-9** revealed the expected one signal at -11.1 ppm (Fig. 6.13).

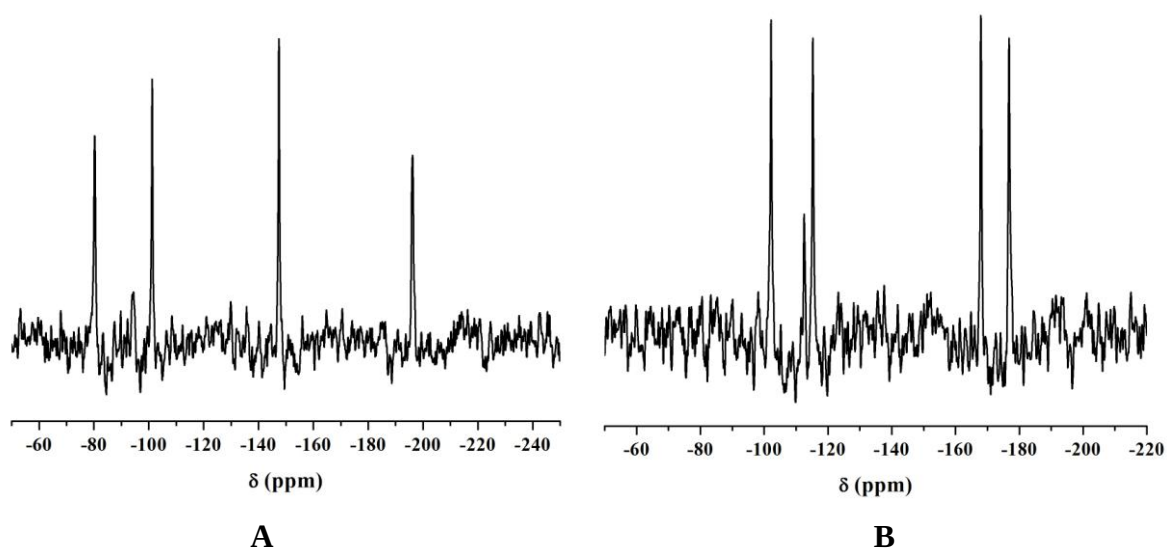


Figure 6.10 ¹⁸³W NMR spectrum of **NH₄-8** (A) and **RbNa-9** (B).

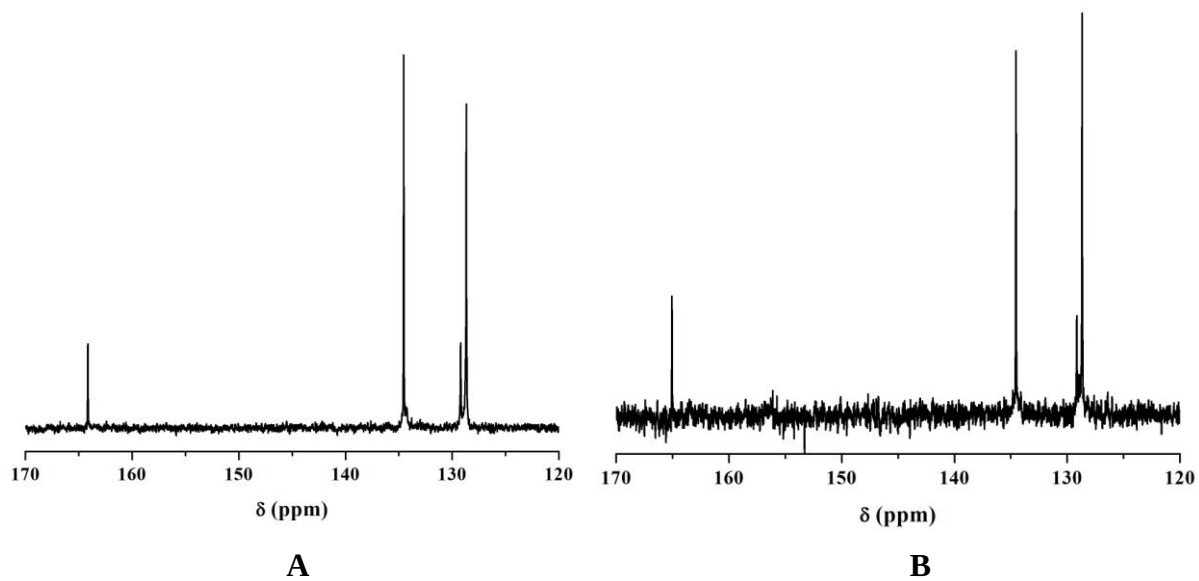


Figure 6.11 ^{13}C NMR spectra of $\text{NH}_4\text{-8}$ (A) and RbNa-9 (B).

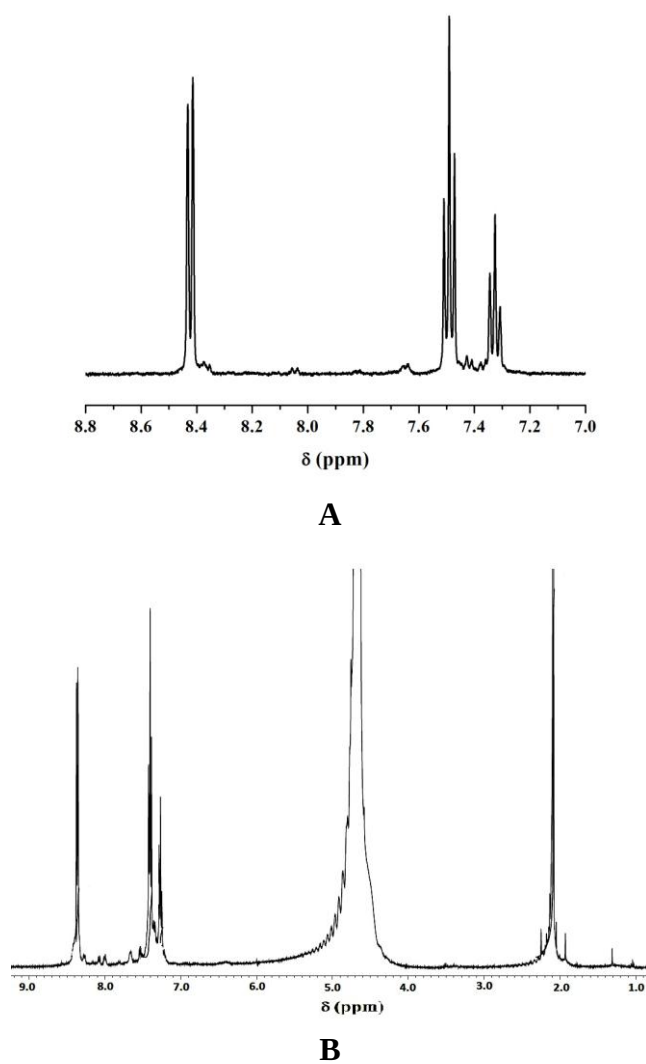


Figure 6.12 ^1H NMR spectra of $\text{NH}_4\text{-8}$ (A) and RbNa-9 (B).

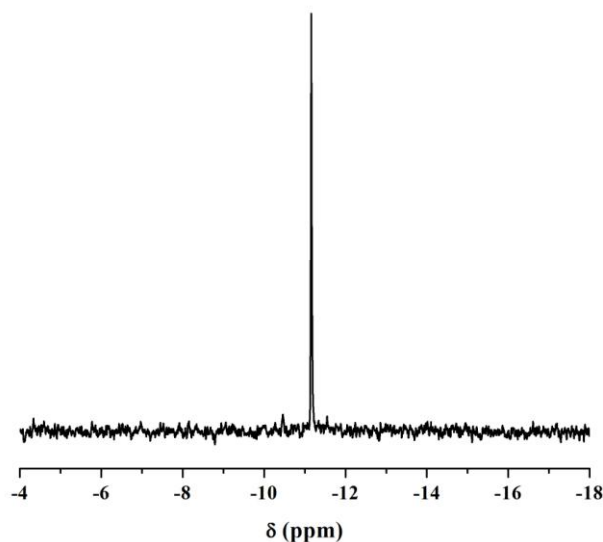


Figure 6.13 ^{31}P NMR spectrum of **RbNa-9**.

Due to the low solubility of **Rb-10** we were not able to carry out solution ^{183}W NMR study on the compound. The ^1H NMR spectrum of **Rb-10** proves the presence of $[\text{Me}_2\text{NCH}_2\text{C}_6\text{H}_4]^-$ groups (Fig. 6.14).

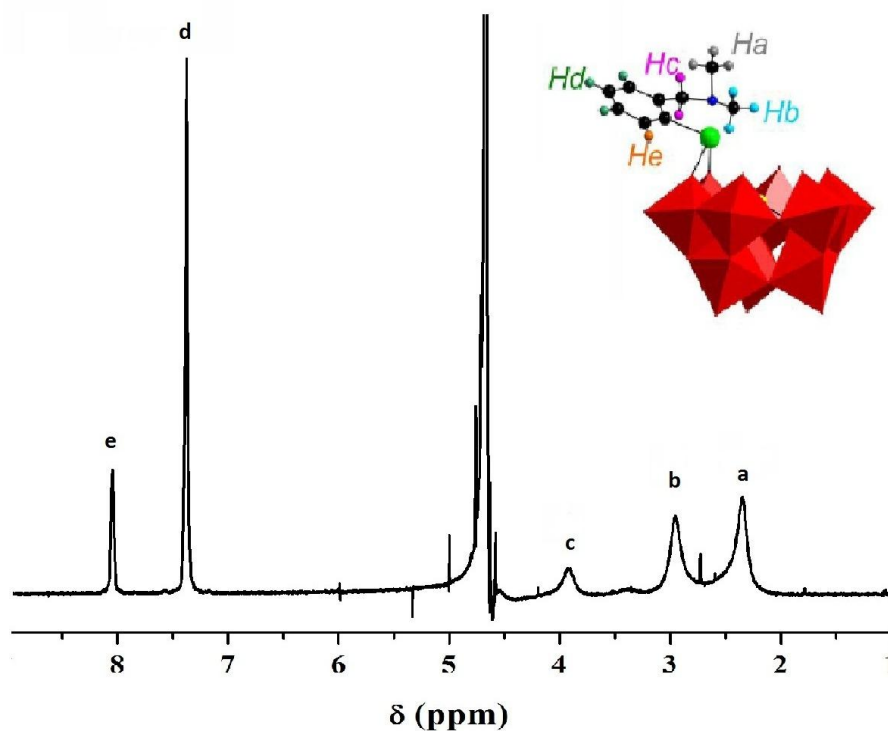


Figure 6.14 ^1H NMR spectrum of **Rb-10**. Two $[2-(\text{Me}_2\text{NCH}_2\text{C}_6\text{H}_4)\text{Sb}^{\text{III}}]^{2+}$ groups in the polyanion of **Rb-10** were omitted for clarity.

6.6 Conclusions

In summary, we have synthesized three novel polyoxotungstates functionalized by organoantimony units, $(\text{NH}_4)_{12}[\{\text{PhSb}\}_4(\text{A}-\alpha\text{-GeW}_9\text{O}_{34})_2]\cdot 20\text{H}_2\text{O}$ (**NH₄-8**), $\text{Rb}_9\text{Na}[\{\text{PhSb}\}_4(\text{A}-\alpha\text{-PW}_9\text{O}_{34})_2]\cdot 20\text{H}_2\text{O}$ (**RbNa-9**), $\text{Rb}_3[\{2\text{-(Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{)Sb}^{\text{III}}\}_3(\text{B}-\alpha\text{-AsW}_9\text{O}_{33})]\cdot 7\text{H}_2\text{O}$ (**Rb-10**). The obtained POMs were characterized in the solid state by single-crystal XRD, TGA and FT-IR spectroscopy. The multinuclear NMR study of the resulting compounds redissolved in $\text{H}_2\text{O}/\text{D}_2\text{O}$ reveals their solution stability.

6.7 References

1. a) Proust, A.; Thouvenot, R.; Gouzerh, P. *Chem. Commun.* **2008**, 1837–1852; b) Dolbecq, A.; Dumas, E.; Mayer, C. R.; Mialane, P. *Chem. Rev.* **2010**, *110*, 6009-6048.
2. Coronado, E.; Curreli, S.; Giménez-Saiz, C.; Gómez-García, C. J.; Roth, J. *Synth. Met.* **2005**, *154*, 241-244.
3. a) Coronado, E.; Gómez-García, C.J. *Chem. Rev.* **1998**, *98*, 273-296; b) Coronado, E.; Galán-Mascarós, J.R. *J. Mater. Chem.* **2005**, *15*, 66-74; c) Coronado, E.; Giménez-Saiz, C.; Gómez-García, C.J. *Coord. Chem. Rev.* **2005**, *249*, 1776-1796; d) Coronado, E.; Day, P. *Chem. Rev.* **2004**, *104*, 5419-5448.
4. Carraro, M.; Sandei, L.; Sartorel, A.; Scorrano, G.; Bonchio, M. *Org. Lett.* **2006**, *8*, 3671-3674.
5. a) Knoth, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 759-760; b) Knoth, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 2211-2213; c) Zonnevjlle, F.; Pope, M. T. *J. Am. Chem. Soc.* **1979**, *101*, 2731-2732; d) Knoth, W. H.; Domaille, P. J.; Roe, D. C. *Inorg. Chem.* **1983**, *22*, 818-822; e) Xin, F.; Pope, M. T. *Organometallics* **1994**, *13*, 4881-4886; f) Xin, F.; Pope, M.T.; Long, G. J.; Russo, U. *Inorg. Chem.* **1996**, *35*, 1207-1213; g) Xin, F.; Pope, M.T. *Inorg. Chem.* **1996**, *35*, 5693-5695; h) Yang, Q. H.; Dai, H. C.; Liu, J. F. *Transition Met. Chem.* **1998**,

- 23, 93-95; i) Wang, X. H.; Dai, H. C.; Liu, J. F. *Polyhedron* **1999**, *18*, 2293-2300; g) Wang, X.H.; Dai, H. C.; Liu, J. F. *Transition Met. Chem.* **1999**, *24*, 600-604; k) Wang, X.H.; Liu, J. F. *J. Coord. Chem.* **2000**, *51*, 73-82; l) Sazani, G.; Dickman, M. H.; Pope, M. T. *Inorg. Chem.* **2000**, *39*, 939-943; m) Wang, X. H.; Liu, J. T.; Zhang, R. C.; Li, B.; Liu, J. F. *Main Group Met. Chem.* **2002**, *25*, 535-539; n) Bareyt, S.; Piligkos, S.; Hasenknopf, B.; Gouzerh, P.; Lacote, E.; Thorimbert, S.; Malacria, M. *Angew. Chem. Int. Ed.* **2003**, *42*, 3404-3406; o) Sazani, G.; Pope, M. T. *Dalton Trans.* **2004**, 1989-1994; p) Bareyt, S.; Piligkos, S.; Gouzerh, P.; Lacote, E.; Thorimbert, S.; Malacria, M.; Hasenknopf, B. *J. Am. Chem. Soc.* **2005**, *127*, 6788-6794; q) Belai, N.; Pope, M. T. *Polyhedron* **2006**, *25*, 2015-2020; r) Micoine, K.; Thorimbert, S.; Lacote, E.; Malacria, M.; Hasenknopf, B. *Organic Letters* **2007**, *9*, 3981-1984; s) Boglio, C.; Micoine, K.; Derat, E.; Thouvenot, R.; Hasenknopf, B.; Thorimbert, S.; Lacôte, E.; Malacria, M. *J. Am. Chem. Soc.* **2008**, *130*, 4553–4561; t) Micoine, K.; Hasenknopf, B.; Thorimbert, S.; Lacôte, E.; Malacria, M. *Angew. Chem. Int. Ed.* **2009**, *48*, 3466–3468.
6. a) Hussain, F.; Reicke, M.; Kortz, U. *Eur. J. Inorg. Chem.* **2004**, *43*, 2733-2738; b) Hussain, F.; Kortz, U.; Clark, R.J. *Inorg. Chem.* **2004**, *43*, 3237-3241; c) Hussain, F.; Kortz, U. *Chem. Commun.* **2005**, 1191-1193; d) Kortz, U.; Hussain, F.; Reicke, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 3773-3777; e) Hussain, F.; Kortz, U.; Keita, B.; Nadjo, L.; Pope, M.T. *Inorg. Chem.* **2006**, *45*, 761-766; f) Reinoso, S.; Dickman, M.H.; Reicke, M.; Kortz, U. *Inorg. Chem.* **2006**, *45*, 10422-10424; g) Hussain, F.; Dickman, M.H.; Kortz, U.; Keita, B.; Nadjo, L.; Khitrov, A.; Marshall, A.G. *J. Clust. Sci.* **2007**, *18*, 173-191; h) Reinoso, S.; Dickman, M.H.; Matei, M.F.; Kortz, U. *Inorg. Chem.* **2007**, *46*, 421,4383–4385; i) Reinoso, S.; Dickman, M.H.; Praetorius, A.; Piedra-Garza, L.F.; Kortz, U. *Inorg. Chem.* **2008**, *47*, 8798–8806; j) Reinoso, S.; Piedra-Garza, L.F.; Dickman, M.H.; Praetorius, A.; Biesemans, M.; Willem, R.; Kortz, U. *Dalton Trans.* **2010**, 248–255; k) Reinoso, S.; Dickman, M.H.;

- Kortz, U. *Eur. J. Inorg. Chem.* **2009**, 947–953; l) Piedra-Garza, L.F.; Reinoso, S.; Dickman, M.H.; Sanguineti, M.M.; Kortz, U. *Dalton Trans.* **2009**, 6231–6231; m) Reinoso, S.; Bassil, B.S.; Barsukova, M.; Kortz, U. *Eur. J. Inorg. Chem.* **2010**, 2537-2542.
7. Liu, B.-y.; Ku, Y.-t.; Wang, M.; Wang, B.-y.; Zheng, P.-j. *J. Chem. Soc., Chem. Commun.* **1989**, 651-652.
8. *Polyoxometalates: From Platonic Solids to Antiretroviral Activity*; Pope, M.T., Müller, A., Eds.; Kluwer: Dordrecht, 1994.
9. Baskar, V.; Shanmugam, M.; Helliwell, M.; Teat, J.S.; Winpenny, R.E.P. *J. Am. Chem. Soc.* **2007**, 129, 3042-3043.
10. Piedra-Garza, L. F.; Dickman, M. H.; Moldovan, O.; Breunig, H. J.; Kortz, U. *Inorg. Chem.* **2009**, 48, 411-413.
- 11 Pretsch, E.; Buehlmann, P.; Affolter, C. *Structure Determination of Organic Compounds: Tables of Spectral Data*; Springer Verlag: Berlin, 2000.
12. Rocchiccioli-Deltcheff, C.; Fournier, M.; Franck, R.; Thouvenot, R. *Inorg. Chem.* **1983**, 22, 207-216.
13. Nakamoto K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds-Part A: Theory and Applications in Inorganic Chemistry, 5th ed.*, Wiley and Sons, New York, 1997.

Conclusions and Outlook

In summary, we have systematically studied the ability of the $\{\text{Pd}^{\text{II}}_{12}\text{O}_8\text{L}_8\}$ palladium-oxo shell to incorporate transition metal or lanthanide ions. As a result, the following compounds were obtained: 1) $\text{L} = \text{PhAsO}_3^{2-}$, $\text{M} = \text{Y}^{\text{III}}$, $\text{Pr}^{\text{III}} - \text{Lu}^{\text{III}}$, Sc^{III} , Mn^{II} , Fe^{III} , Co^{II} , Ni^{II} , Cu^{II} , Zn^{II} ; 2) $\text{L} = \text{SeO}_3^{2-}$, $\text{M} = \text{Mn}^{\text{II}}$, Fe^{III} , Co^{II} , Cu^{II} , Zn^{II} , Lu^{III} ; 3) $\text{L} = \text{PhPO}_3^{2-}$, $\text{M} = \text{Cu}^{\text{II}}$, Zn^{II} ; 4) $\text{L} = \text{PO}_4^{3-}$, $\text{M} = \text{Mn}^{\text{II}}$, Fe^{III} , Co^{II} , Cu^{II} , Zn^{II} . All these polyoxopalladate nanocubes were prepared in simple one-pot reactions in aqueous medium of $\text{Pd}_3(\text{CH}_3\text{COO})_6$, precursor of capping group L , and the respective salt of $\text{M}^{\text{n}+}$. Moreover, a double-cuboid-shaped, copper(II)-containing polyoxo-22-palladate(II), $[\text{Cu}_2\text{Pd}^{\text{II}}_{22}\text{P}_{12}\text{O}_{60}(\text{OH})_8]^{20-}$, containing more palladium ions than any other polyoxopalladate known to date, was obtained. The formation of such compound shows that certain combinations of central metal ion and capping group can lead to a transformation of the $\{\text{Pd}^{\text{II}}_{12}\text{O}_8\text{L}_8\}$ assembly, resulting in novel polyoxopalladates with different shapes, sizes, and properties.

In future work it could be interesting (i) to try and incorporate different capping groups L in the $\{\text{Pd}^{\text{II}}_{12}\text{O}_8\text{L}_8\}$ shell, which can perhaps lead to polyoxopalladates with various composition, charge, properties (stability, solubility, catalytic activity, etc.), as well as (ii) to prepare polyoxopalladates with two, or even more, types of capping groups:

- $\text{L} = \text{XO}_4$ groups ($\text{X} = \text{Sb}^{\text{V}}$, Bi^{V} , Si^{IV} , Ge^{IV} , B^{III} , Al^{III} , Ga^{III} , S^{VI} , Te^{VI});
- Lone pair-containing $\text{L} = \text{XO}_3$ groups ($\text{X} = \text{As}^{\text{III}}$, Sb^{III} , Bi^{III} , Te^{IV});
- $\text{L} = \text{RXO}_3$ groups with organic functionalities ($\text{X} = \text{Si}^{\text{IV}}$, Ge^{IV} , Sb^{V} ; $\text{R} = \text{alkyl, aryl}$).

We also believe that by using an appropriate template we might be able to prepare even larger polyoxopalladate shells. Large metal ions such as early transition metals (e.g. Zr^{4+} , Hf^{4+}) could be interesting in this context. Furthermore, small cationic oxoclusters of transition metals (e.g. $[\text{M}^{\text{IV}}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$, $\text{M} = \text{Zr, Hf}$) or even small POMs (e.g. $[\text{XMo}_6\text{O}_{24}]^{\text{n}-}$ or

[Mo₆O₁₉]²⁻) could be used for this purpose. Also, one could potentially expand this family to other d⁸ transition metals such as Pt^{II} or Au^{III}.

We have also synthesized and structurally characterized the yttrium-containing isopolytungstate [YW₁₀O₃₆]⁹⁻. In the future one could perhaps try and prepare other derivatives of the [MW₁₀O₃₆]ⁿ⁻ type, where M = Pt⁴⁺, Zr⁴⁺, Hf⁴⁺.

Moreover, three heteropolytungstates functionalized by organoantimony linkers were obtained, [{PhSb}₄(A- α -XW₉O₃₄)₂]ⁿ⁻ (X = P^V, Ge^{IV}) and [{2-(Me₂NCH₂C₆H₄)Sb^{III}}]₃(B- α -As^{III}W₉O₃₃)]³⁻. These discrete polyanions could be investigated in solution for their antifouling, antibacterial, antiviral, antitumor and anticarcinogenic activities, as well as for their potential towards vesicle formation (“blackberries”). We propose to extend the family of organic-inorganic hybrid POMs by the synthesis of new compounds in which di- and tri- organoantimony units bridge two or more lacunary or plenary polyoxotungstate fragments. This approach could result in large to very large discrete POMs with cavities, as well as porous 1D, 2D and 3D materials with unprecedented architectures and properties (“POM-based analogues of MOFs”).

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The Qualification of the Engineer, Specialization “Standardization and Certification”, honours degree

09/2000 to 06/2004 **Tomsk Polytechnic University, Tomsk, Russia**

Bachelor of Engineering and Technology, Specialization “Metrology, Standardization and Certification”, honours degree

Research Experience

05/2008 to date **Jacobs University, Bremen, Germany**

Project: Synthesis of novel polyoxometalates (POMs). Solution characterization of the compounds by multinuclear NMR, UV–Vis spectroscopy, electrochemistry (cyclic voltammetry), dynamic laser light scattering, and solid state characterization of the compounds by FT-IR, single crystal XRD, thermogravimetric analysis.

10/2007 to 03/2008 **Jacobs University, Bremen, Germany**

Project: Synthesis and characterization of novel POMs. Investigation of the possibility to apply solution electrochemical treatment for the synthesis of novel POMs.

- 07/2005 to 10/2007** **Tomsk Polytechnic University, Tomsk, Russia**
Project: Study of physical-chemical processes taking place in a solution at electrochemical treatment. Search of solution properties that could show changed state of solutions after the electrochemical treatment. Development of electrochemical method for production of washing liquids for cleaning solid surfaces from organic and mineral contaminations.
- 10/2003 to 06/2005** **Tomsk Polytechnic University, Tomsk, Russia**
Project: Investigation of change regularities of composition and physical and chemical properties of solutions of electrolytes after electrochemical treatment depending on the process conditions. Study of nature of causal effects of changed physical and chemical properties of solutions of electrolytes with intensification of second physical and chemical processes taking place in previously electrochemically treated aqueous medium. For the research electrochemical and spectroscopic analytical techniques were used.

Skills and Achievements

Instrumentation Skills: hands-on experience with various analytical instruments such as:

- Single-crystal X-ray diffractometer (Bruker Kappa Apex II)
- NMR spectrometers (Jeol ECX 400 MHz with 5 and 10mm probes)
- FT-IR spectrometer (Nicolet-Avatar 370)
- UV-vis spectrophotometer (Varian Cary 100 Bio)
- AA spectrometer (Varian SpectrAA220)
- Electrochemistry equipment (Princeton Applied Research)
- TGA-DSC (Thermal Analysis Q 600)
- GC (Varian 3900)
- Dynamic laser light scattering (Malvern HPPS)

Languages **Russian:** Mother tongue
 English: Fluent
 German: Intermediate

Conferences

- 09/2011** GDCh-Wissenschaftsforum Chemie 2011, Bremen, Germany (poster presentation).
09/2010 13. Norddeutsches Doktorandenkolloquium, Greifswald, Germany (oral presentation).
08/2010 3rd EuCheMS Chemistry Congress, Nuernberg, Germany (poster presentation).
07/2010 The Euroscience Open Forum (ESOF) 2010, Torino, Italy.
06/2010 The Lindau Nobel Laureate Meeting 2010, Lindau, Germany.
10/2009 12. Norddeutsches Doktorandenkolloquium, Oldenburg, Germany (poster presentation).
07/2009 International Polyoxometalate Symposium, Bremen, Bremen, Germany (poster presentation).
05/2007 VIII All-Russian student scientific practical conference “Chemistry and Chemical Technology in XXI century”, Tomsk, Russian Federation (oral presentation).
09/2005 Electrochem 2005, Newcastle-upon-Tyne, United Kingdom (oral presentation).
05/2005 VI All-Russian student scientific practical conference “Chemistry and Chemical Technology in XXI century”, Tomsk, Russian Federation (oral presentation).
05/2004 V All-Russian student scientific practical conference “Chemistry and Chemical Technology in XXI century”, Tomsk, Russian Federation (oral presentation).

Awards and Fellowships

- 2010** The ESOF-Fellowship of the Robert Bosch Stiftung for participation in The Euroscience Open Forum (ESOF) 2010, Torino, Italy.
- 2010** The DAAD-Fellowship for visiting The Lindau Nobel Laureate Meeting 2010, Lindau, Germany.
- 2009** DAAD scholarship (Ref. 325 № A/08/80942).
- 2007** 1) Special state scholarship from The Government of Russian Federation.
2) DAAD scholarship (Ref. 325 № A/06/91416).
3) Grant for development of the project “Design of Pilot Electrochemical Cell for Production of Environmentally Appropriate Cleaning Solutions”.
- 2005** 1) Grant of Russian Foundation for Basic Research for participation with oral presentation in 12-th Int. Conference “Electrochem 2005”, Newcastle-upon-Tyne, Great Britain, 4-7 September, 2005.
2) The medal “For services to Tomsk Polytechnic University”.
3) Diploma of First Degree for plenary report in VI All-Russian student scientific practical conference “Chemistry and Chemical Technology in XXI century”.

Publications

1. M. Barsukova-Stuckart, N. V. Izarova, G. B. Jameson, V. Ramachandran, Z. Wang, J. van Tol, N. S. Dalal, R. N. Biboum, B. Keita, L. Nadjo, U. Kortz, Synthesis and Characterization of the Dicopper(II)-Containing 22-Palladate(II) $[\text{Cu}^{\text{II}}_2\text{Pd}^{\text{II}}_{22}\text{P}^{\text{V}}_{12}\text{O}_{60}(\text{OH})_8]^{20-}$, *Angew. Chem.* **2011**, 123, 2688-2692; *Angew. Chem. Int. Ed. Engl.* **2011**, 50, 2639-2642.
2. M. Barsukova, N. V. Izarova, R. N. Biboum, B. Keita, L. Nadjo, V. Ramachandran, N. S. Dalal, N. S. Antonova, J. J. Carbó, J. M. Poblet, U. Kortz, Polyoxopalladates Encapsulating Yttrium and Lanthanide Ions, $[\text{X}^{\text{III}}\text{Pd}^{\text{II}}_{12}(\text{AsPh})_8\text{O}_{32}]^{5-}$ (X = Y, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), *Chem. Eur. J.*, **2010**, 16, 9076-9085.
3. S. Reinoso, B. S. Bassil, M. Barsukova, U. Kortz, pH-Controlled Assemblies of Dimethyltin-Functionalized 9-Tungstophosphates with Guanidinium as Structure-Directing Cation, *Eur. J. Inorg. Chem.*, **2010**, 17, 2537-2542.
4. E.E. Visser, M.S. Barsukova, E.B. Chernov, Patent RU 2326746 C1, “Method of Cleaning of Solid Surfaces from Mineral and Organic Contaminations”, Federal service for intellectual property, patents and trademarks, Bulletin N17.
5. M. Barsukova, M. H. Dickman, E. Visser, U. Kortz, Synthesis and structural characterization of the yttrium containing isopolytungstate $[\text{YW}_{10}\text{O}_{36}]^{9-}$, *Z. Anorg. Allg. Chem.*, **2008**, 634, 2423-2427.
6. M. S. Barsukova, E.E. Visser, E.B. Chernov, Methods of Experimental Design for Investigation of Cleaning Ability of Solutions after Electrochemical Treatment, *Zav. Lab. Diag. Mat.*, **2008**, 74, 71-75.

B. Published Articles

1. M. Barsukova-Stuckart, N. V. Izarova, G. B. Jameson, V. Ramachandran, Z. Wang, J. van Tol, N. S. Dalal, R. N. Biboum, B. Keita, L. Nadjo, U. Kortz, Synthesis and Characterization of the Dicopper(II)-Containing 22-Palladate(II) $[\text{Cu}^{\text{II}}_2\text{Pd}^{\text{II}}_{22}\text{P}^{\text{V}}_{12}\text{O}_{60}(\text{OH})_8]^{20-}$, *Angew. Chem.* **2011**, 123, 2688-2692; *Angew. Chem. Int. Ed. Engl.* **2011**, 50, 2639-2642.
2. M. Barsukova, N. V. Izarova, R. N. Biboum, B. Keita, L. Nadjo, V. Ramachandran, N. S. Dalal, N. S. Antonova, J. J. Carbó, J. M. Poblet, U. Kortz, Polyoxopalladates Encapsulating Yttrium and Lanthanide Ions, $[\text{X}^{\text{III}}\text{Pd}^{\text{II}}_{12}(\text{AsPh})_8\text{O}_{32}]^{5-}$ (X = Y, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), *Chem. Eur. J.*, **2010**, 16, 9076-9085.
3. S. Reinoso, B. S. Bassil, M. Barsukova, U. Kortz, pH-Controlled Assemblies of Dimethyltin-Functionalized 9-Tungstophosphates with Guanidinium as Structure-Directing Cation, *Eur. J. Inorg. Chem.*, **2010**, 17, 2537-2542.
4. M. Barsukova, M. H. Dickman, E. Visser, U. Kortz, Synthesis and structural characterization of the yttrium containing isopolytungstate $[\text{YW}_{10}\text{O}_{36}]^{9-}$, *Z. Anorg. Allg. Chem.*, **2008**, 634, 2423-2427.