

Hydration, Solvation and Hydrolysis of Multicharged Metal Ions

Natallia Torapava

Faculty of Natural Resources and Agricultural Sciences

Department of Chemistry

Uppsala

Doctoral Thesis

Swedish University of Agricultural Sciences

Uppsala 2011

Cover: Hydrated and hydrolyzed thorium(IV) complexes present in acidic aqueous solution in the pH range 0.00 to 2.35.

ISSN 1652-6880

ISBN 978-91-576-7609-2

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Print: SLU Service/Repro, Uppsala 2011

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Abstract

Structures of hydrated, solvated and hydrolyzed multicharged metal ions are determined by EXAFS and LAXS in solution, and by X-ray crystallography and EXAFS in the solid state.

During hydrolysis, the nine-coordinate hydrated thorium(IV) ion is first transformed to a dimer, $[\text{Th}_2(\mu^2\text{-OH})_2(\text{H}_2\text{O})_{12}]^{6+}$, then to a tetramer, $[\text{Th}_4(\mu^2\text{-OH})_8(\text{H}_2\text{O})_{16}]^{8+}$, and finally to a hexamer, $[\text{Th}_6(\mu^3\text{-O})_8(\text{H}_2\text{O})_n]^{8+}$ with increasing pH and thorium(IV) concentration in an aqueous solution. Coordinated water loses the protons in two steps, first with the formation of the dimer and tetramer, and finally with the formation of the hexamer.

Together thorium(IV) and iron(III) form a stable and highly soluble heteronuclear hydrolysis complex, $[\text{Th}_2\text{Fe}_2(\mu^2\text{-OH})_8(\text{H}_2\text{O})_{12}]^{6+}$, in the pH range 2.9 – 4.8 and metal concentrations 0.02 – 0.4 mol·dm⁻³. In the same solutions at pH < 2.9 two- or six-line ferrihydrite precipitates with time, while thorium(IV) remains in solution.

Palladium(II) and platinum(II) hydrolyze very slowly in acidic aqueous solution and after 25 years of storage tiny oxide-like particles are formed at pH = 0.7. The particle size has been estimated from the number of M···M distances in the formed particles and in the corresponding solid oxides from EXAFS studies. The palladium(II) and platinum(II) oxide particles grow along *a* or *b* axes and reach a size of 1 – 1.5 nm³. These results have been supported by SAXS studies.

During hydrolysis, the six-coordinate hydrated chromium(III) ion is first transformed to a dimer, then to a tetramer, $[\text{Cr}_4(\mu^2\text{-OH})_2(\mu\text{-OH})_4(\text{OH})_n(\text{H}_2\text{O})_{12-n}]^{(6-n)+}$ with increasing pH from 0 to 3.7 at chromium concentration of ca. 1 mol·dm⁻³. At pH ≥ 15, soluble $[\text{Cr}(\mu^2\text{-OH})_2(\text{OH})_2]_n^{n+}$, *n* ≈ 3, complex is formed, which at pH < 15 slowly precipitates as an amorphous solid with a structure similar to α-CrOOH.

Dimethylsulfoxide (DMSO) solvated thorium(IV) is nine-coordinate both in solution and solid state. *N,N'*-Dimethylpropyleneurea (DMPU) solvated thorium(IV) is eight-coordinate in solution. The lower coordination number is due to the space-demanding properties of the DMPU molecules upon coordination.

Keywords: hydration, hydrolysis, EXAFS, LAXS, metal ions

Author's address: Natallia Torapava, SLU, Department of Chemistry,
P.O. Box 7015, 750 07 Uppsala, Sweden
E-mail: Natallia.Torapava@slu.se

Dedication

To my parents

Begin at the beginning and go on till you come to the end; then stop.

The King, *Alice in Wonderland*

The average Ph.D. thesis is nothing but a transference of bones from one graveyard to another.

J. Frank Dobie

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List of Publications

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

- I** Torapava, N.; Persson, I.; Eriksson, L.; Lundberg, D. Hydration and hydrolysis of thorium(IV) in aqueous solution and the structures of two crystalline thorium(IV) hydrates. *Inorganic Chemistry* **2009**, *48*, 11712-11723.
- II** Torapava, N.; Radkevich, A.; Persson, I.; Davydov, D.; Eriksson, L. Formation of a heteronuclear hydrolysis complex in the Th^{IV}/Fe^{III} system. Submitted to *Dalton Transactions*.
- III** Torapava, N.; Elding, L. I.; Mändar, H.; Roosalu, K.; Persson, I. Hydrolysis of palladium(II) and platinum(II) in acidic aqueous solution. (manuscript).
- IV** Torapava, N.; Radkevich, A.; Davydov, D.; Titov, A.; Persson, I. Composition and structure of polynuclear chromium(III) hydroxo complexes. *Inorganic Chemistry* **2009**, *48*, 10383-10388.
- V** Torapava, N.; Lundberg, D.; Persson, I. A Coordination Chemistry Study of the solvated thorium(IV) ion in two oxygen donor solvents. Accepted for publication in *European Journal of Inorganic Chemistry*.
- VI** Abbasi, A.; Skripkin, M. Yu.; Eriksson, L.; Torapava, N. Ambidentate coordination of dimethyl sulfoxide in rhodium(III) complexes. *Dalton Transactions* **2011**, *40*, 1111-1118.

Papers **I**, **IV** and **VI** are reproduced with the permission of the publishers.

My contribution to the papers included in this thesis was as follows:

- I** I prepared the solutions and synthesized the crystals, prepared samples and collected EXAFS data, treated data using EXAFSPAK, and co-wrote this article.
- II** I prepared the solutions, adjusted pH during 20 months study, treated LAXS and EXAFS data, and co-wrote this article.
- III** I prepared samples and collected EXAFS data, treated data using EXAFSPAK and co-wrote this article. The SAXS studies were performed and analyzed by Dr. Mändar, Tartu University, Estonia.
- IV** I prepared the solutions, adjusted pH during two years of studies, prepared samples and collected EXAFS data, treated data using EXAFSPAK and I co-wrote this article.
- V** I prepared the solutions and synthesized the crystals, prepared samples and collected EXAFS data, treated data using EXAFSPAK and I am responsible for the writing of this article.
- VI** I prepared crystals of pentakis(dmsO-κO)mono(dmsO-κS)rhodium(III) trifluoromethanesulfonate and described the preparation in experimental part of the article.

Abbreviations

BWR	boiling water reactor
CN	coordination number
DMPU	<i>N,N'</i> -dimethylpropyleneurea
DMSO	dimethylsulfoxide
EXAFS	extended X-ray absorption fine structure
FT	Fourier transform
HA	humic acid
HLLW	high-level liquid waste
HWC	hydrogen water chemistry
LAXS	large angle X-ray scattering
<i>msap</i>	monocapped square antiprism
NWC	normal water chemistry
PGM	platina group metals
RCF	relative centrifugal force
RDF	radial distribution function
SAXS	small angle X-ray scattering
SEM	scanning electron microscopy
<i>ttp</i>	tricapped trigonal prism
WL	white line
XANES	X-ray absorption near edge structure

1 Introduction

The construction of the periodic table by Mendeleev had the same significance for chemistry as Newton's laws for physics and the Darwinian theory for biology at their time.¹ The focus of this work is the solution chemistry and structure determination of metal hydrates, hydrolysis complexes and solvates in solution and solid state. The knowledge of the structures of these complexes is essential to understand their physico-chemical properties for assessment of metal speciation and distribution in natural waters, waste waters, soil and biological systems. The structures of most hydrated metal ions are known in the solid state, but less is known about their structures in solution, including the hydrated and hydrolyzed forms.

Thorium, having a long half-life, $1.405 \cdot 10^{10}$ years, is much easier to work with than uranium, neptunium and plutonium.² The behavior of thorium(IV) in aqueous solution can serve as a model of behavior for heavier actinoids, for their migration in natural waters, and speciation in nuclear wastes. One of the main thorium applications is in experimental nuclear reactors (e.g. in Germany, USA, and India) and a possibility to use it in commercial nuclear industry is considered. Thorium can be used in the ^{232}Th - ^{233}U cycle which produces much less plutonium and minor actinoids (neptunium, americium, curium).³ The main benefits of thorium use in nuclear reactors are that thorium is three times more abundant than uranium, thorium dioxide is more chemically stable and has higher radiation resistance than uranium dioxide, and the waste produced has a low radio-toxicity.³ Although there are some challenges: the inertness of thorium(IV) oxide, ThO_2 , demands the use of hydrofluoric acid together with nitric acid for dissolution which leads to corrosion of stainless steel; much higher temperatures are necessary to produce ThO_2 -based mixed oxide fuel; irradiated thorium contains significant amounts of ^{232}U which has short half-

life, 73.6 years, and produces strong gamma products, ^{212}Bi and ^{208}Tl , therefore heavy shielding and remote operation is necessary.³

Chromium(III) is fairly toxic, whereas much less than chromium(VI), which is fortunately reduced to chromium(III) in natural waters.⁴⁻⁶ The main discharge of chromium into natural waters comes from tanning and metallurgical industries.^{7,8} The removal of chromium is made by precipitation of chromium hydroxide in the pH range 5-6, so knowledge about chromium speciation in the pH range 3-15 is very important.⁹

Metal ions belonging to different transition series have been studied in this thesis. The similarities in the hydrolysis behavior of palladium(II) and platinum(II) show their common properties. Due to the lanthanoid contraction and because in the second and third transition metal series the 4d and 5d shells are occupied, the elements of the same group show very similar chemical properties.¹⁰

The platinum group metals (platinum, palladium, rhodium, ruthenium, iridium, and osmium), or PGMs, all possess the following properties: chemical inertness, corrosion resistance, high-temperature oxidation resistance, very good ability to catalyze chemical reactions, high melting point, high strength at elevated temperatures, low coefficient of thermal expansion and stable thermo-electric properties.¹¹ Among significant areas of application of PGMs are jewelry, dental alloys, and the chemical and electronics industry.

As transition metal ions, chromium(III), rhodium(III), and iridium(III) are known for their slow kinetic properties.¹²⁻¹⁴ The hydrated, solvated and hydrolyzed species are difficult to prepare for the same reason. Rhodium(III) and iridium(III) metal ions have typical soft binding properties, as they prefer to bind to sulfur donor ligands over oxygen donor ones. Rhodium is a very important catalyst in engine exhaust systems and recovery of rhodium from spent catalysts requires dissolution of the metal in an aqueous solution, which is a difficult and energy consuming task.¹⁵ Alternatively, rhodium affinity to soft ligands could be used, and use of soft medium, e. g. DMSO, will facilitate rhodium dissolution compared to an unamended aqueous solution.

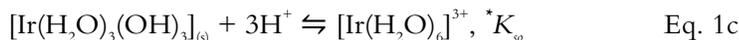
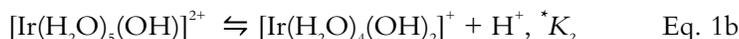
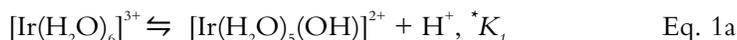
1.1 Scientific problem

A large number and variety of hydrolysis complexes, which can be formed in solution, may co-exist and it is rather difficult to identify their composition and structure, as in many systems both mono- and polynuclear hydroxo species are formed. The range of pH where soluble hydrolysis

species are present is limited due to the formation of colloids or precipitation of hydroxides and oxides.

Numerous studies of thorium hydrolysis by thermodynamic methods, such as pH- and metal ion titration, reported the formation of polynuclear hydroxo complexes of thorium of the following compositions, $[\text{Th}_6(\text{OH})_{14}]^{10+}$ and $[\text{Th}_6(\text{OH})_{15}]^{9+}$.¹⁶ A potentiometric titration gives information about metal to hydroxide-ion ratio, whereas the structure of hydrolysis complexes formed in aqueous solution is not determined. The challenges of information obtained by thermodynamic studies are discussed further in the Results and Discussion section. Numerous studies of thorium(IV) hydrolysis identify the formation of colloidal particles of various sizes.¹⁷⁻²³ However, identification of either colloidal particle or soluble hydroxo complex present in the solution is not always straightforward.

In contrast to the widely studied thorium(IV) aqueous chemistry, rhodium(III) and especially iridium(III) hydration and hydrolysis in aqueous solution are scarcely studied. Hydrolysis of rhodium(III) was studied by a variety of non-structural methods (NMR, UV-Vis spectroscopy and elution chromatography), and three different structures of trinuclear rhodium(III) hydrolysis complexes were proposed.²⁴⁻²⁶ It is proposed that trinuclear rhodium(III) hydroxo complex with three rhodium ions bound via two single hydroxo bridges to each other with four water molecules completing octahedral configuration is transformed to trinuclear rhodium(III) hydroxo complex with rhodium ions bound via one double and two single hydroxo bridges at $\text{pH} < 2$. Alternatively, to trinuclear rhodium(III) hydroxo complex with three rhodium ions bound via three single and one triple hydroxo bridges at $\text{pH} > 3$.²⁷ Iridium(III) hydrolysis was investigated by gravimetric titration and equilibrium constants *K_1 , *K_2 and $^*K_{30}$ were calculated for the following reactions at 25 °C:



These were found to be $\log ^*K_1 = -4.37 \pm 0.02$, $\log ^*K_2 = -5.20 \pm 0.15$ and $\log ^*K_{30} = 10.22 \pm 0.05$, respectively.²⁸ Despite potentiometric hydrolysis studies of rhodium(III) and iridium(III), the structures of their hydrolysis complexes present in solution have not been determined by structural methods yet.

1.2 Practical importance

The aqueous chemistry and aging processes play an important role on fuel cladding corrosion. Deposition profiles in boiling water reactors (BWR) showed that the iron content increases more or less continuously from the fuel bottom to the top. Zinc and cobalt only co-precipitate with iron, whereas nickel and chromium can deposit independently of iron.²⁹ Lin discussed the chemistry of corrosion products, formation of mixed metal oxides, the transport of corrosion products on fuel cladding surfaces, and the mechanism of deposition and release.³⁰ The solubilities of some corrosion product oxides are sensitive to pH in the aqueous phase. Normal water chemistry (NWC) or hydrogen water chemistry (HWC) conditions (a certain amount of hydrogen is injected through the feed water system to suppress the water radiolysis and minimize the production of oxidizing species in the coolant, such as hydrogen peroxide or dissolved oxygen gas) play an important role, e. g. chromium(III) oxide is insoluble under HWC, but becomes soluble under NWC due to formation of ionic HCrO_4^- or CrO_4^{2-} .³⁰ In these mixed metal ion systems an increase in the solubility is observed. This is a very important property of the system in respect to the equilibria formed in nuclear waste storage, nuclear fuel crud formation and dissolution.³⁰

An interesting aspect of platinum group metals is the recovery of the latter from spent nuclear fuel.³¹ It is shown that fission products, such as palladium, rhodium and ruthenium are distributed between two phases, which are generated by the reprocessing of spent nuclear fuel, namely, the high-level liquid waste (HLLW) and the undissolved fuel residue. Palladium and rhodium are recovered from HLLW by a hydrometallurgical process, preferably by solvent extraction and electrolytic deposition, whereas precipitation and ion exchange or extraction chromatography are less favorable. Numerous sulfur donor extractants, e.g. dialkyl sulfoxides, are more effective to extract palladium(II) in comparison with oxygen donor extractants.³¹

The waste package degradation and leachability can be a challenge.³²⁻³⁴ Cement agglomerates showed low waste permeability, hence a favorable durability, however non-homogeneity of concrete and “construction joints” represent weak points.³³ Different models, i.e. thermal, chemical environment, humid-air and aqueous corrosion, were used for assessment of the failure of waste packages.³² To study the possibility of nuclear waste leaching and contamination of groundwater, uranium migration in porous media, such as sandy soil, was evaluated.³⁵ The effect of solution pH and grain size was examined showing that pH plays an important role. In highly

acidic solution uranium is hardly stopped, whereas in a neutral solution colloids are formed and they are less mobile through pores, showing that only negligible leaching takes place.³⁵ Another study on uranium migration through the vadose zone, Figure 1, showed that uranium is immobilized by sorption to mineral surfaces. The release of uranium is limited due to very slow dissolution kinetics.³⁶ The excess of chromium makes an adverse effect on the vitrification process and chromium removal becomes a critical factor in the pretreatment of underground storage tanks containing nuclear waste.³⁷

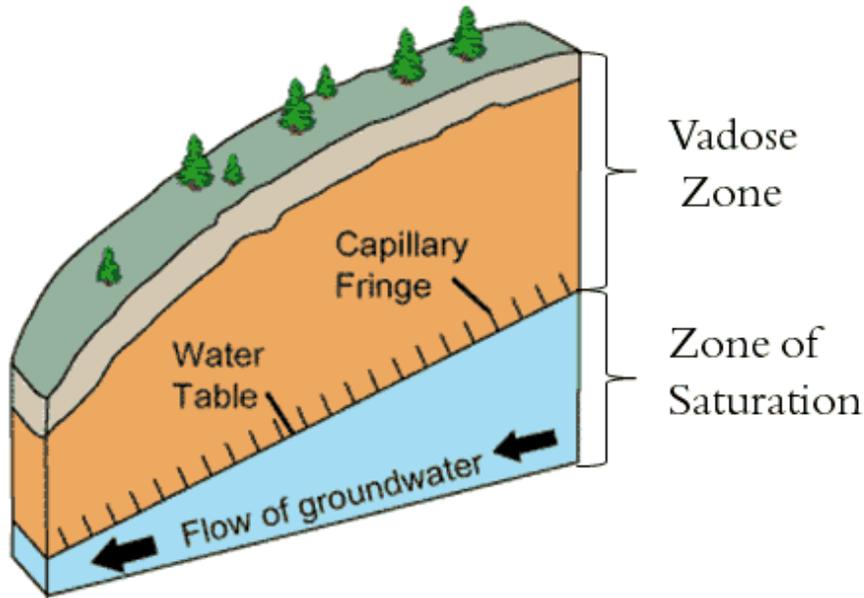


Figure 1. Cross-section of hillslope depicting water table, capillary fringe and vadose zone, picture taken from wikipedia.org.

An enhanced selective oxidative alkaline leaching process has been developed for the removal of chromium from high level waste tank sludge.³⁷ Humic acid materials, HA, such as SiO_2 -HA can be used for modeling the interaction between tetravalent actinoids and humates in groundwater.³⁸ The affinity of thorium(IV) to bind with different types of particle surfaces, e.g. smectite, biogenic, opal, manganese dioxide and calcium carbonate, varies by strength and kinetics.³⁹ To model the radionuclide mobility in repositories of radioactive waste, the solubility of ThO_2 was studied.⁴⁰ It was shown that the solubility of ThO_2 depends on the crystallinity of the solid only in acidic media, and is independent of it in a neutral or alkaline media.⁴⁰ The subsoil accumulation of secondary iron and aluminium minerals has little or no effect on the distribution of radionuclides of ^{238}U

and ^{232}Th decomposition series in soil.⁴¹ Thorium and uranium are relatively weakly bound onto sediments and their distribution does not depend on particle size, therefore thorium and uranium are associated with labile fractions in contaminated sediments.⁴²

Thorium consumption and hence production has been ceased during last decade due to high costs for disposal of thorium wastes, nevertheless thorium fuel cycle development continues involving thorium analysis.^{3,43-45} An accidental release of radionuclides into environment is dangerous and undesirable because they represent a health-risk for humans and biological systems. Therefore, knowledge about solution chemistry of actinoids is of great importance.⁴⁶

1.3 A history of the studied metals

In 1797 the French chemist Louis Nicolas Vauquelin, Figure 2, discovered the oxide of a new element in a Siberian mineral, crocoise, now known as crocoite (PbCrO_4), and in the following year isolated the metal itself by reduction using charcoal. This was subsequently named *chromium* because of the variety of colors found in its compounds, after the Greek *χρωμα* meaning color.



Figure 2. Louis Nicolas Vauquelin (1763-1829), the French analytical chemist.

William Hyde Wollaston, Figure 3, discovered *rhodium* in 1803, naming it after the Greek *ῥόδον* meaning rose because of the rose-color commonly found in the aqueous solutions of its salts. Platinum ore was dissolved in aqua regia, followed by addition of ammonium chloride to remove the platinum.⁴⁷ Zinc was added to the filtrate to remove residual platinum,

palladium, rhodium, copper and lead. Copper and lead were removed by dissolution in dilute nitric acid. The residue was dissolved in more aqua regia, followed by addition of sodium chloride. The solution was evaporated and rose-red $\text{Na}_3[\text{RhCl}_6] \cdot n\text{H}_2\text{O}$ was obtained, which was then extracted with hot alcohol and reduced with zinc to give rhodium metal.⁴⁷



Figure 3. William Hyde Wollaston (1766 – 1828), the English chemist, by John Jackson, painted before 1829.

In same year, 1803, W. H. Wollaston isolated and identified *palladium* from the mother liquor remaining after platinum had been precipitated as $(\text{NH}_4)_2\text{PtCl}_6$ from its solution in aqua regia. He named it after the newly discovered asteroid, Pallas, itself named after the Greek goddess of wisdom *παλλάδιον*.⁴⁷ Wollaston announced his discovery of a new metal in a very unusual way. Anonymous advertisements were distributed in London offering palladium for sale, formerly known as new silver.⁴⁷ Wollaston offered a reward of 20 pounds sterling for anyone who could make palladium in public before three eminent chemists. Though, only after official announcement in a paper which was read to the Royal Society on 4th July 1805, was the challenge to make palladium taken up.⁴⁷

Although Wollaston discovered and gave names to rhodium and palladium, he did not assign symbols to these elements. It was Berzelius, who originally suggested R for rhodium, which was revised to Rh and Pl, then Pa and finally Pd for palladium.⁴⁷

Impure, native platinum seems to have been used unwittingly by ancient Egyptian craftsmen in place of silver, and was certainly used to make small items of jewellery by the Incas of Ecuador before the Spanish conquest. In

1736 Antonio de Ulloa, a Spanish astronomer and naval officer, observed an unworkable metal, the Spanish *platina* meaning little silver.⁴⁸

Smithson Tennant (1761 – 1815) discovered *iridium* in 1803, and named it after the Greek goddess Iris, whose sign was the rainbow, because of the variety of colors of its compounds. Iridium was obtained from platinum ore (*platina*).⁴⁹ Two French chemists, Fourcroy and Vauquelin, who did work independently with black residue, announced their work in 1804. It is unlikely that this work was known to Tennant, and in 1814 Vauquelin attributed the discovery of iridium to Tennant.⁴⁹ Unfortunately, there is no portrait or picture left of Tennant.

Thorium was discovered by Swedish chemist Jöns Jakob Berzelius, Figure 4, in 1828 and he named it after the Scandinavian god of war, Thor. Investigating two minerals, a new earth was detected and Berzelius suggested the name “thorine”.⁵⁰ However, in 1824 he discovered that this new “thorine” is nothing but the subphosphate of yttria. Thus, not to waste a good name, Berzelius called the new element in honor of Thor, now known as thorium.⁵⁰



Figure 4. Jöns Jakob Berzelius (1779 – 1848), the Swedish chemist. Lithography portrait from 1836 made by P.H. van den Heuvell.

All thorium isotopes are radioactive, but the ^{232}Th isotope occurs naturally due to its very long half-life of $1.405 \cdot 10^{10}$ years. The only important oxidation state of thorium is +IV. The most important commercial source of thorium is monazite sand, containing up to 20% ThO_2 .

Property	Cr 24 Chromium	Rh 45 Rhodium	Pd 46 Palladium	Ir 77 Iridium	Pt 78 Platinum	Th 90 Thorium
Number of naturally occurring isotopes	4	1	6	2	6	1
Atomic weight	51.9961(6)	102.90550(2)	106.42(1)	192.217(3)	195.078(2)	232.03806(2)
Electronic configuration	[Ar]3d ⁵ 4s ¹	[Kr]4d ⁸ 5s ¹	[Kr]4d ¹⁰	[Xe]4f ⁴ 5d ⁷ 6s ²	[Xe]4f ¹⁴ 5d ⁹ 6s ¹	[Rn]6f ⁷ 7s ²
R _M (CN=12)/Å	1.28	1.34	1.37	1.355	1.385	1.79
R _L (CN = 6)/Å	0.61	0.676	0.86	0.68	0.8	0.961
MP/°C	1900	1960	1552	2443	1769	1750
BP/°C	2690	3760	2940	4550(±100)	4170	4788
ΔH _{fus} /kJ mol ⁻¹	21(±2)	21.6	17.6(±2.1)	26.4	19.7(±2.1)	16.11
ΔH _{vap} /kJ mol ⁻¹	342(±6)	494	362(±11)	612(±13)	469(±25)	513.7
Density (20°C)/g cm ⁻³	7.14	12.39	11.99	22.56	21.45	11.72
Abundance in earth crust, ppm	122	0.0001	0.015	0.001	0.01	8.1
Price in SEK for 1 gram of metal powder, Sigma-Aldrich, August 2011	17	7213	2323	2546	3084	Not available

Figure 5. Physical properties of the metals studied in the thesis.

Thorium is several times more abundant than uranium, it comprises 8.1 ppm of the earth's crust, while uranium only accounts for 2.3 ppm. This makes it an accessible source.

Thorium is used as an alloying element in magnesium imparting high strength and resistance at elevated temperatures. Thorium(IV) dioxide is used for mantles in portable gas lights, in heat-resistant ceramics like high-temperature laboratory crucibles, in glasses to create a high refractive index. Such glass is used in high-quality lenses for cameras and scientific instruments, and ThO_2 is used as catalyst as well.⁵¹ Thorium is, together with uranium, the only naturally occurring actinoid element an application as fuel for nuclear power reactors, as fertile material for producing nuclear fuel, and together with uranium is used for age-dating in geology.^{44,52}

2 Aims

This section of the thesis describes the general aim, while more detailed aims are given in the individual papers.

In general this work deals with fundamental studies of coordination chemistry of multicharged metal ions in their hydrated, hydrolyzed and solvated forms, in solid state and solution. Some structural methods, such as EXAFS, LAXS and X-ray crystallography, were used to determine the structures of these complexes. It was aimed to prepare solutions and synthesize new complexes and compounds, with subsequent determination of their structures. One of the important tasks was to make a review of existing literature and the data about hydrolysis studies and critically analyze the challenging points and complete missing information about hydrolysis of metal ions chosen for this work. Another task was to summarize known and newly obtained information of hydrolysis of multicharged metal ions into a general picture. From this literature review discussion of possible practical applications of the results obtained in this study was aimed.

3 Background

This section of the thesis discusses the highlights of the two principle topics, coordination chemistry and hydrolysis of several multicharged metal ions. The focus of this thesis is placed on hydrolysis, therefore this will be discussed first.

3.1 Hydrolysis

Hydrolysis is a chemical reaction during which molecules of water (H_2O) are split into hydrogen cations (H^+) and hydroxide anions (OH^-). For many years hydrolysis of metal ions in aqueous solution has been studied by using thermodynamic methods, such as pH-, free metal and free ligand titrations, which give information about the ratio between number of metal ions and number of hydroxo groups present in hydrolysis complexes. The use of EXAFS and LAXS brings a new angle on the view of hydrolysis. These methods give information about the structure of hydrolysis complexes in solution.

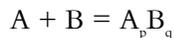
Hydrated metal ions are Lewis acids, which in accordance with the Brønsted-Lowry acid-base theory “donate” a proton, H^+ .⁵³ A hydrolysis reaction for a hydrated metal ion in aqueous solution is given by the following formula, for formation of mononuclear hydrolysis complexes shown below:⁵⁴



This equilibrium is characterized by hydrolysis constant:

$$k_{11} = ([\text{M}(\text{OH})(\text{H}_2\text{O})_{n-1}^{(m-1)+}][\text{H}_3\text{O}^+]) / [\text{M}(\text{H}_2\text{O})_n^{m+}]$$

The history of hydrolysis studies started in the beginning of the twentieth century with Bjerrum's studies of chromium(III) hydrolysis.⁵⁵ Sillén developed mathematical descriptions for formation of polynuclear complexes.^{56,57} He based his theory on two fundamental assumptions, real equilibria, and that all complexes are dissolved in the solution. As the outcome was a hypothesis about "core + links":



$A_r(A_l B)_n$, where A_r is core and $A_l B$ is link.

In their book "The hydrolysis of cations" Baes and Mesmer summarized the hydrolysis of all cations studied by that time.⁵⁸ After 1976, when the book "The hydrolysis of cations" was published, many hydrolysis studies had been reported but they had not yet been summarized in one publication. Hydrolysis of metal ions in aqueous solution is a complex process which results in the formation of mono- and polynuclear hydrolysis complexes, shown in equations 2 and 3, respectively.



Hydrolysis in aqueous solution of a metal ion leads to formation of acidic, neutral or alkaline complexes, e.g. MOH^{m+} , $M_x(OH)_y$ and $[M_x(OH)_y]_n^{n-}$, respectively.

The ability of hydrated metal ions to hydrolyze depends on the charge and size of the metal ion. Small and highly charged metal ions are very prone to hydrolysis. An increase in pH usually facilitates the hydrolysis. All hydrated metal ions in aqueous solution can be divided into several groups depending on their ability to hydrolyze, Figures 6 and 7.

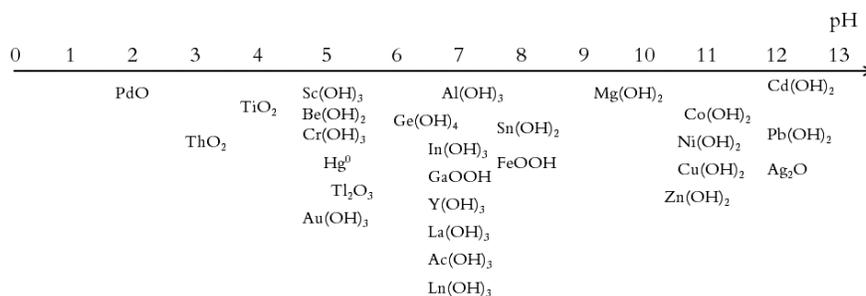


Figure 6. The pH scale for the approximate precipitation of hydroxides, oxides or other stable solids of different metal ions at $C_M = 0.1 \text{ mol} \cdot \text{dm}^{-3}$, (after Baes and Mesmer, see ref. 10).

- Metal ions which do not hydrolyze: lithium(I), sodium(I), potassium(I), rubidium(I), cesium(I), calcium(II), strontium(II), barium(II) and manganese(II).
- Metal ions which form anionic hydrolysis species: niobium, tantalum, molybdenum, tungsten, rhenium, ruthenium and osmium.
- Metal ions which form “-yl” cations: TiO^{2+} , $\text{Zr}_4(\text{OH})_8^{8+}$, $\text{Hf}_4(\text{OH})_8^{8+}$, VO^{2+} , UO_2^{2+} , NpO_2^+ and PuO_2^{2+} .
- Metal ions which hydrolyze at pH = 0-1: cerium(IV), thallium(III), palladium(II) and platinum(II).
- Metal ions which hydrolyze in pH range = 1-3: iron(III), chromium(III), mercury(II), gallium(III), indium(III), tin(II), scandium(III), aluminium(III), thorium(IV) and rhodium(III).
- Metal ions which hydrolyze at high pH = 6-8: lead(II), copper(II), nickel(II), cobalt(II), zinc(II) and cadmium(II).

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr ^{III}	Mn ^{II}	Fe ^{III}	Co ^{II}	Ni ^{II}	Cu ^{II}	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg ^{II}	Tl ^{III}	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							
			Ce ^{IV}	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			Th ^{IV}	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Figure 7. Periodic Table showing a classification of the metals according to the formation of hydrolysis complexes in aqueous solution. Yellow – do not hydrolyze, red – hydrolyze at pH = 0, green – hydrolyze at pH = 1 – 3, light grey – hydrolyze at pH = 4 – 5, purple – hydrolyze at pH = 6 – 8, orange – hydrolyze and form anionic/polymeric species, blue – hydrolyze and form “yl”-ions, dark grey – no data available.

3.2 Coordination chemistry

Coordination chemistry is the area about composition and geometry of a complex. A complex is a compound consisting of a central atom or ion and coordinated ligands (neutral or with an opposite charge).

To describe possible different structures coordination polyhedra are used. In a polyhedron each corner is occupied by an atom that forms a chemical bond to another atom in the center.⁵⁹ Metal ions are usually placed in the center of the polyhedron and the coordinated ligands are located in the corners. Structural polyhedra with equal distances from the center to the corners are called “regular”, but in reality most of the structures of the complexes are more or less distorted.

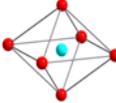
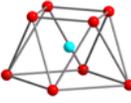
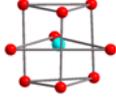
Coordination number	Polyhedra	
2	Dumb-bell	
3	Triangle	
4	Tetrahedron	
	Square	
6	Octahedron	
8	Cube	
	Square antiprism	
9	Tricapped trigonal prism	

Figure 8. Coordination polyhedra (after Giacovazzo *et al.*, see ref. 59).

“Regular” polyhedra of crystal structure representation are, Figure 8: dumb-bell, equilateral triangle, square, tetrahedron, octahedron, cube, square antiprism, and tricapped trigonal prism.

Solution chemistry comprises two aspects, thermodynamics and kinetics. Thermodynamics deals with the possibility of a chemical reaction taking place, while kinetics deals with the rate of a chemical reaction. The thermochemical properties which define whether a complex is stable or not include: the relative bond energies, stability constants, and distortions from a regular geometry.⁶⁰ These properties depend on the ground energetic state of the coordination complex.⁶⁰ For metal ions and their complexes to be able to exist in aqueous solution the hydration is important. Water being a polar solvent and having a dipole moment dissolves polar compounds well, which may dissociate into hydrated ions in water. The first hydration sphere of metal ions studied in this thesis, which consists of six to nine water molecules tightly bound to a metal ion, is possible to observe with EXAFS, while second and possible third hydration spheres are found with LAXS, Figure 9.

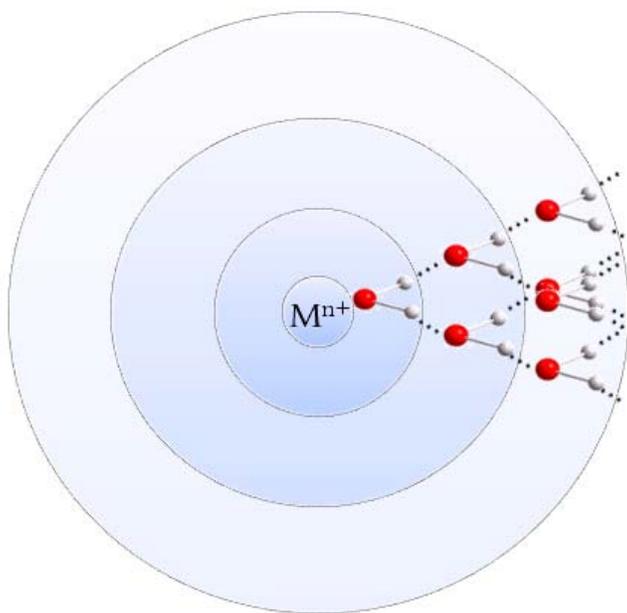


Figure 9. Representation of a metal ion with hydration spheres, blue – 1st hydration sphere, light blue – 2nd hydration sphere, very light blue – 3^d hydration sphere (only one water molecule in the 1st hydration sphere is shown for simplicity).

On the other hand dissolution is a competition between lattice energy and solvation energy, as illustrated in Figure 10.

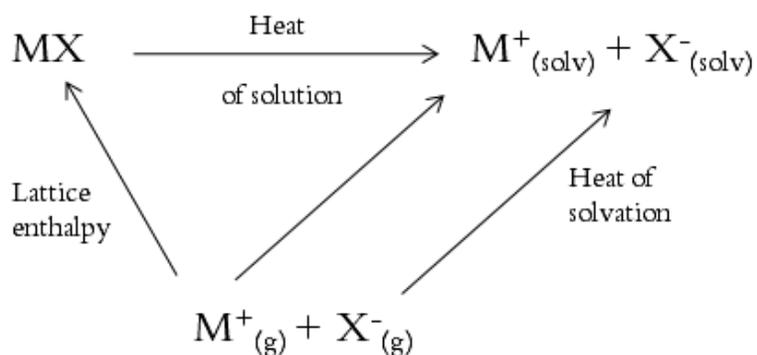


Figure 10. Scheme representing the enthalpies for dissolution of a crystal MX (after Burgess, ref. 60).

The heat of solution of a salt is the difference between the large enthalpy needed to separate the ions from each other in the crystal lattice and the enthalpy gained when these ions are introduced into the solvent.⁶⁰

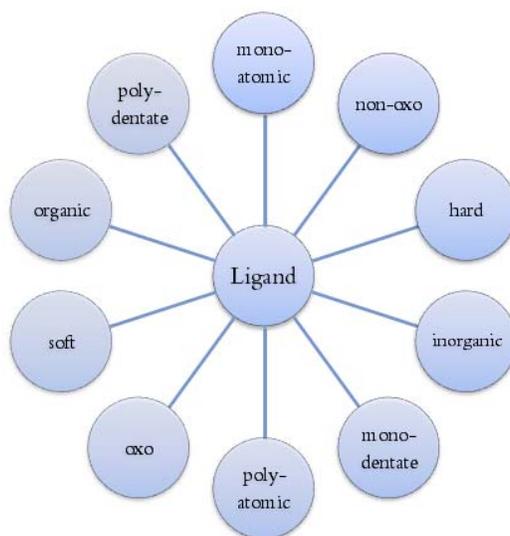


Figure 11. Classification of ligands.

The metal ion and the solvent molecules (ligands) are attracted to each other with a differing degree of strength, depending on the nature of both the metal ion and the ligands. Ligands can be classified in many ways, Figure 11.

The relative affinities of ligand atoms towards acceptor ions were summarized by Ahrlund et al.⁶¹ Two regularities were found. There are differences between coordinating elements from the same group, e. g. between nitrogen and phosphorus, oxygen and sulfur, fluorine and chlorine. There are two classes of electron-pair acceptors, normally metal ions, class “a”, those which form their most stable complexes with nitrogen, oxygen and fluorine, and class “b”, those which form their most stable complexes with the second or subsequent ligand atom from the same group. Metal ions in different oxidation states may belong to different classes, e. g. copper(I) belongs to class “b”, whereas copper(II) is on the border between the classes. The higher valences of metal ions tend to be in class “a”, while the lower valences of metal ions tend to be in class “b”. Examples of class “a” and class “b” metal ions with their affinities to the elements in groups 15-17 are given in Table 1.

Table 1. *Metal ions belonging to class “a” and class “b” and their affinity towards the elements in groups 15-17*

Acceptor ions	Ligand atoms
Class “a”	
H ⁺ , Be ²⁺ , Mg ²⁺ , Sc ³⁺ , La ³⁺ , Ce ³⁺ , Zr ⁴⁺ , Th ⁴⁺ , VO ²⁺ , Cr ³⁺ , UO ₂ ²⁺ , Pu ⁴⁺ , Fe ³⁺ , Ni ²⁺ , Cu ²⁺ , Zn ²⁺ , Ga ³⁺ , In ³⁺ , Sn ²⁺	F > Cl > Br > I O >> S > Se > Te N >> P > As > Sb > Bi
Class “b”	
Pt ²⁺ , Ag ⁺ , Cd ²⁺ , Hg ²⁺ , Tl ⁺ , Tl ³⁺ , Pb ²⁺ , Rh ³⁺ , Ir ³⁺	F < Cl < Br < I O < S ≤ Se > Te N < P > As > Sb > Bi

Later, Pearson classified these classes of metals as “hard” and “soft”, respectively, the same classification is valid for the ligands, e.g. OH⁻, NH₃, Cl⁻ are “hard” and CN⁻, CO, S₂O₃²⁻ are regarded “soft” ligands.^{62,63} The simple rule suggested by Pearson says that hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases. In general, hard acids and bases are generally small and only slightly polarizable, while the soft acids and bases tend to be larger and more polarizable. Hard-hard interactions are governed by electrostatic or ionic interactions. The smaller the ions the

stronger the attraction is between them. Soft-soft interactions are governed by covalent bonds.^{53,64}

Kinetics, as has been mentioned above, deals with the rate of different chemical processes. Whether a complex is stable or not depends on the activation energy, which is the difference between the energy of intermediate and the energy of the starting materials. The complexes of transition-metal ions vary tremendously in their kinetics. In this respect, the kinetic inertness of metal ion complexes is connected to the particular configuration of the d orbitals of the metal ion. For example, the d^3 , low-spin d^6 and d^8 configurations are very stable in the octahedral coordination and have high activation energies.⁶⁵ The high exchange rates of the d^9 copper(II) and high-spin d^4 chromium(II) are enhanced by the presence of Jahn-Teller distortions, while the d^3 chromium(III), d^6 rhodium(III), d^6 iridium(III) and d^8 platinum(II) are particularly inert, d^8 palladium(II) has an intermediate exchange rate and d^0 thorium(IV) has a high exchange rate, Figure 12.^{12-14,65-67}

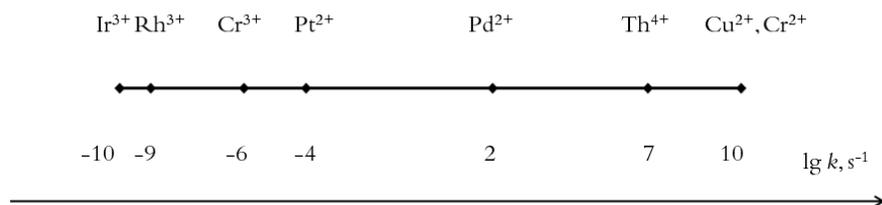


Figure 12. Comparison of rate constants for water exchange in the 1st hydration sphere for metal ions studied in the thesis (after ref. 12-14, 65-67).

4 Experimental

The experimental details of the studies in this thesis are given in the individual papers. In this section the synthesis and the preparation of solutions which are not included in the papers are described.

4.1 Preparation of solutions

4.1.1 Rhodium

Rhodium hydrolysis complexes were prepared by adaptation of a method described earlier.⁶⁸ An aqueous solution of rhodium(III) trifluoromethanesulfonate was brought to a pH of about 13 with $10 \text{ mol}\cdot\text{dm}^{-3}$ sodium hydroxide solution. After one hour the hydrolysis reaction was quenched by addition of perchloric acid to a pH of about 2.3, the total volume of rhodium(III) solution was 6.8 cm^3 . A $1\times 12 \text{ cm}$ column was filled with Sephadex SP C-25 resin to the level of 8 cm. To prepare the column, the resin was washed with 100 cm^3 of $2 \text{ mol}\cdot\text{dm}^{-3}$ sodium hydroxide, followed by 100 cm^3 of distilled water, 100 cm^3 of $2 \text{ mol}\cdot\text{dm}^{-3}$ hydrochloric acid and finally with 100 cm^3 of distilled water.⁶⁹ For elution $0.5 \text{ mol}\cdot\text{dm}^{-3}$ sodium perchlorate (2 cm^3), $1 \text{ mol}\cdot\text{dm}^{-3}$ sodium perchlorate (3 cm^3), $2 \text{ mol}\cdot\text{dm}^{-3}$ sodium perchlorate (3 cm^3), $4 \text{ mol}\cdot\text{dm}^{-3}$ sodium perchlorate (20 cm^3), $6 \text{ mol}\cdot\text{dm}^{-3}$ sodium perchlorate (10 cm^3) were used. Hydrolysis products of rhodium(III) were absorbed on the resin and the sodium perchlorate solutions in $0.02 \text{ mol}\cdot\text{dm}^{-3}$ perchloric acid, were used to elute the hydrolysis fractions.

4.1.2 Iridium

Iridium(III) solutions were prepared via a methodology described elsewhere.^{70,71} One gram of $\text{Na}_3\text{IrCl}_6\cdot x\text{H}_2\text{O}$ was dissolved in 230 cm^3 freshly prepared $0.4 \text{ mol}\cdot\text{dm}^{-3}$ sodium hydroxide. The obtained solution was stirred

on a magnetic stirrer for about five hours at 40 °C. Ascorbic acid was added after one hour to the iridium solution to prevent atmospheric oxidation. After five hours the solution was cooled to about 5 °C in the ice bath. 2 mol·dm⁻³ perchloric acid was added until pH ≈ 6 was reached and a yellow-cream precipitation was produced. The obtained iridium(III) hydroxide precipitate was separated by centrifugation and washed with distilled water. After dissolution in 70 % concentrated perchloric acid yellow solution was produced. The solution was transferred to a round-bottomed flask and refluxed for about a week under nitrogen in an oil bath, after which the solution became dark blue! The heating led to at least partial oxidation of iridium(III) to iridium(IV)! Purple iridium(III) trifluoromethanesulfonate solution was prepared in the same way.

4.1.3 Cerium

Cerium(IV) perchlorate was obtained by dissolving cerium(IV) hydroxide in 70 % concentrated perchloric acid. While heating the solution changed color from yellow to bright orange, then to a dark red-orange, finally, after about 2.5 hours of heating to just below the boiling point, the solution became yellow again. But irradiation applied in EXAFS and LAXS methods led to the reduction of yellow cerium(IV) to colorless cerium(III). It was not possible to collect data on cerium(IV)!

4.2 Methods

A brief description of the methods used in the thesis is given.

4.2.1 EXAFS

The absorption of electromagnetic radiation in the X-ray region (0.3 to 2 Å) in connection with the absorption edge is used to obtain structural information. The oscillating electric field of the electro-magnetic radiation interacts with the electrons bound in an atom.⁷² The X-rays kick out an inner-core electron and produce an inner-shell vacancy “core-hole”, Figure 13. The energy which is necessary to release the photoelectron is called the threshold energy, E_0 . The energy of the irradiating beam is called the excitation energy, E . The difference between the excitation energy, E , and the threshold energy, E_0 is the energy of the photoelectron wave. The outgoing and the backscattered photoelectron waves will interfere. The EXAFS region is characterized by weak oscillations arising from backscattering of the photoelectron’s wave, mostly in the single back-scattering processes.⁷² The interference, destructive (minimum in the

absorption) and constructive (maximum in the absorption), produces oscillations in the absorption observed after the absorption edge, which can be related to the structure of the material. EXAFS can be used for samples in any aggregation state and environment, solutions, amorphous material, crystalline solids, and gases. EXAFS is sensitive to near-neighbors of the absorber, whereas crystallography is sensitive to long-range order.⁷³

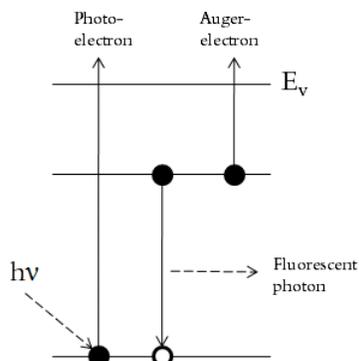


Figure 13. The effect of radiation on the electrons (after Jalilehvand, see ref. 72).

Therefore, EXAFS focuses on the local environment of specific X-ray absorbing atoms and provides accurate bond distances.⁷⁴ The drawback of EXAFS spectroscopy is that it does not provide full stereo-chemical details. Two commonly used detection methods in EXAFS are transmission and fluorescence. The data treatment includes the following steps: 1) pre-edge background removal, 2) normalization, 3) energy calibration and conversion to k-space, 4) spline fitting and isolation of fine-structure oscillations, and 5) conversion by Fourier transform to real space. The program packages EXAFSPAK and GNXAS were used for data treatment.⁷⁵

4.2.2 LAXS

Large angle X-ray scattering is a method which uses X-ray diffraction to get structural information about complexes in solution. The following requirements should be fulfilled: there should preferably be at least one element heavier than iron present in the dominating complex for sufficient scattering, and rather high, $0.5 \text{ mol}\cdot\text{dm}^{-3}$ or higher, concentrations of dominating complex are necessary, because in LAXS the distances between all atoms present in solution contribute to the scattering.⁷⁶ One complex should dominate in the solution. LAXS determines the interference between pairs of atoms. Hence, we get distances between pairs of atoms. All atoms contribute to the scattered structure-dependent intensity. Therefore,

to obtain the structure of a specific complex in a solution, its contributions to the total scattering should be separated from those of other complexes.⁷⁷ LAXS provides contributions from outer coordination shells, i.e. it gives unique information about the second hydration sphere, for example. First, information from X-ray diffraction is obtained as an intensity function, by Fourier transformation it is converted into a radial distribution function, RDF, which gives the distribution of interatomic distances in the solution. Data is collected using a theta-theta diffractometer, usually with MoK α radiation ($\lambda = 0.7107 \text{ \AA}$), though AgK α ($\lambda = 0.5608 \text{ \AA}$) radiation can be used as well, e.g. for molybdenum, zirconium or uranium, because MoK α radiation produces fluorescence with an energy similar to the absorption edge of these elements. CuK α ($\lambda = 1.54 \text{ \AA}$) radiation is not used in LAXS because s -range, $s = \frac{4\pi\sin\theta}{\lambda}$, will be too short to detect short interactions with proper resolution, because part of the outer intensity function, corresponding to short distances, cannot be determined.

4.2.3 Single crystal X-ray diffraction

The scattering of X-rays by electrons is called Thomson scattering. It occurs when an electron oscillates in the electric field of the incoming X-ray beam, thereby radiating an electromagnetic beam. Therefore, X-rays are scattered from the electron at the same frequency as the primary beam. However, most electrons radiate π radians (180°) out of phase with the incoming beam. X-rays scattered from each atom in the unit cell contribute to the overall scattering pattern. Since each atom acts as a source of scattered X-rays, the waves will add constructively or destructively in varying degrees, depending upon the direction of the diffracted beam and the atomic positions.⁷⁸ For data collection MoK α ($\lambda=0.71073\text{\AA}$) or CuK α ($\lambda = 1.54 \text{ \AA}$) radiation can be used in laboratory conditions. CuK α X-ray tubes produce a higher flux of incident photons than MoK α (for the same power settings) and these are diffracted more efficiently than MoK α radiation. Copper radiation is useful for small or otherwise weakly diffracting crystals. For crystals with long unit cell dimensions, reflections are further apart when the longer wavelength copper radiation is used and this can minimize reflection overlap. If crystals contain only elements lighter than silicon, copper radiation is usually chosen. On the other hand, absorption effects are generally less serious with molybdenum radiation and this can be crucial if heavy elements are present.⁷⁹ Crystal structure determination from diffraction data includes three steps: 1) determination of lattice parameters and assignment of crystal symmetry and space group, 2) structure solution, and 3) structure refinement.^{80,81}

4.2.4 SEM

A beam of electrons is used to scan the surface of a sample to build a three-dimensional image of the specimen. A finely focused electron beam scanned across the surface of the sample generates secondary electrons, backscattered electrons, and characteristic X-rays. These signals are collected by detectors to form images of the sample which are then displayed on a screen. The features seen in the SEM image may then be immediately analyzed for elemental composition. A Hitachi TM-100 μ Dex scanning electron microscope with an EDAX detector for elemental analysis was used. The samples were attached to a carbon film and placed into the SEM. The instrument used detects only elements heavier than sodium; hence, such elements as oxygen and hydrogen were not detected.⁸²

4.2.5 Powder diffraction

Powder diffraction is a method using X-ray, neutron, or electron diffraction on a powder or microcrystalline sample to obtain structural information about unknown materials, mixtures of phases or materials in polycrystalline form.^{83,84} This is done by comparison of experimental data with standard data in crystallographic databases. A crystalline pattern consists of a series of sharp peaks, whereas amorphous materials produce a broad background signal. Each peak represents a certain Miller plane or set of Miller planes and can therefore be characterized by Miller indices.⁸⁵ As an X-ray source for powder diffraction both laboratory X-ray diffractometers and synchrotron radiation can be used.

4.2.6 Dialysis

The two-cell dialysis method was used to determine metal ion distributions between its mononuclear and polynuclear hydroxo forms in an aqueous solution. Cellophane with a pore diameter of 2-4 nm was used as the semipermeable membrane. The results of dialysis are expressed as dialysis coefficients (K_{dial}) and retention percent (α) by the following equations:

$$K_{dial} = \frac{C_{outer}}{C_{inner}} \quad \alpha_r = \frac{1 - K_{dial}}{1 + K_{dial}} \cdot 100\%$$

where C_{inner} is the concentration of metal ion or complexing anion in the "inner" solution of dialyzer (dialyzate) and C_{outer} is the concentration in the "outer" solution (diffusate).

4.2.7 Ultrafiltration and ultracentrifugation

The ultrafiltration experiments were carried out using an ultrafiltration unit with cellophane semipermeable membranes (pore size 2-5 nm). Before the experiment the membranes were kept for 24 hours in Millipore filtered deionized water. The working pressure in the unit during the ultrafiltration was 3.5 bar.

Beckman XL70 with rotor SW-41TI, at 10,000 rpm (RCF = $0,68 \cdot 10^5$ g) and Beckman J2-HS with JA-18 rotor, at 18000 rpm (RCF = 47900 g) ultracentrifuges were used.

4.2.8 Spectrophotometry

The spectrophotometer quantitatively compares the fraction of light that passes through a reference solution and a test solution. Discrete frequencies are transmitted through the test sample. Then the intensity of the transmitted light is measured with a photodiode or other light-sensor, and the transmittance value for this wavelength is then compared with the transmission through a reference sample.

4.2.9 Atomic absorption spectrophotometry

This technique is used to determine the concentration of a specific metal element in a sample. The electrons of the atoms in the atomizer can be promoted to a higher orbital for a short amount of time by absorbing a set quantity of energy (i.e. light of a given wavelength). This amount of energy (or wavelength) is specific to a particular electron transition in a particular element, and in general, each wavelength corresponds to only one element. This makes the technique elemental selective.

5 Results and discussion

In this section published and unpublished results about metal ions studied in the thesis are briefly presented. A more thorough description is given in the individual papers I – VI.

5.1 Thorium

Thorium coordination was studied in an acidic aqueous solution and the oxygen-donor organic solvents DMSO and DMPU.

5.1.1 Thorium in aqueous solution

Thorium(IV) hydrolysis has been studied in acidic aqueous solutions by EXAFS and LAXS in the pH range $-0.7 - 2.35$ and the thorium(IV) concentration range $0.53 - 1.06 \text{ mol}\cdot\text{dm}^{-3}$. Very low pH (-0.7) is crucial for maintaining thorium(IV) as a hydrated ion. However, such low pH was achieved by addition of $10 \text{ mol}\cdot\text{dm}^{-3}$ perchloric acid. This resulted in too few water molecules being present to allow the completion of a second hydration sphere around thorium as found by LAXS, *ca.* 13 instead of 18 water molecules. It was shown that the hydrated thorium(IV) ion is nine-coordinate in a highly acidic aqueous solution with a mean Th-O bond distance of $2.45(1) \text{ \AA}$, and with *ca.* 18 water molecules completing the second hydration sphere (paper I, Figures 2 and 4). The CN was deduced from the strong correlation between ionic radii and coordination numbers as shown by Shannon.⁸⁶ The fairly large number (135) of reported crystal structures of actinoid(IV) ions with organic and inorganic monodentate oxygen donor ligands was summarized (paper I, Table 4 and Figure 8). The revised ionic radii for the actinoid(IV) ions were calculated by subtracting the oxygen atom radius of 1.34 \AA , a value suggested by Beattie et al,⁸⁷ (paper I, Table 5).

Two crystal structures, octaqua(κ^2 O-perchlorato)thorium(IV)perchlorate hydrate, $[\text{Th}(\text{H}_2\text{O})_8(\text{ClO}_4)](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ and aquaoxoniumhexaaquatris(κ O-trifluoromethanesulfonato)thorium(IV)trisaquahehexakis(κ O-trifluoromethanesulfonato)thorium(IV), $\text{H}_5\text{O}_2[\text{Th}(\text{H}_2\text{O})_6(\text{OSO}_2\text{CF}_3)_3][\text{Th}(\text{H}_2\text{O})_3-(\text{OSO}_2\text{CF}_3)_6]$ were crystallized from aqueous solutions of perchloric and trifluoromethanesulfonic acids, respectively. Thorium(IV) is nine-coordinate in both structures in *ttp* and *msap* configurations, (paper I, Figures 1 and 3), however in $[\text{Th}(\text{H}_2\text{O})_8(\text{ClO}_4)](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ the tenth oxygen atom belonging to a perchlorate ion is bound to thorium at a much longer Th-O bond distance, 2.757(8) Å, resulting in severe distortion of nine-coordinate *ttp*. Coordinated oxygen from perchlorate ion was forced to take that place due to the tetrahedral structure of the perchlorate ion, which is bound to thorium(IV) at a “normal” Th-O bond distance of 2.516(6) Å. Crystallographic support is important for deduction of CN of thorium(IV) in solution, because EXAFS gives accurate bond distance but does not give direct information about CN, if no significant scattering within the first coordination shell is present, as in e.g. octahedral complexes.

It was found that at high thorium(IV) concentrations, *ca.* 1 mol·dm⁻³, at pH = 1.23 a dimer and a tetramer were the dominating hydrolysis species. RDF of the LAXS data of thorium(IV) solution at pH = 1.23 indicated a large contribution at 4.0 Å and smaller contributions at 4.7 and 6.6 Å, (paper I, Figure 6). The Th··Th distance at 4 Å corresponds to Th··Th distance via double hydroxo bridges found in thorium dimers, $[\text{Th}_2(\mu^2\text{-OH})_2(\text{H}_2\text{O})_{12}]^{6+}$, described crystallographically.⁸⁸⁻⁹¹ However, the number of such Th··Th distances was higher than if it was just a contribution of the dimer alone. Furthermore, Th··Th distances at 4.7 and 6.6 Å correspond to Th··Th distances in a diamond shaped thorium tetramer, $[\text{Th}_4(\mu^2\text{-OH})_8(\text{H}_2\text{O})_{16}]^{8+}$, Figure 16. Therefore, the solution at pH = 1.23 contains both a dimer and a tetramer in *ca.* 50:50 ratio. The ratio of Th··Th distances of 4.0 Å per thorium atom in a dimer and in a tetramer is 0.5 and 1, respectively. Refinement of LAXS data showed that the number of Th··Th distances of 4.0 Å is about 0.75 per thorium atom, which gives a composition of *ca.* 50% dimers and 50% tetramers present in the solution at pH = 1.23. The double bridged thorium dimer is obviously a building block in the thorium tetramer.

Further hydrolysis was studied by increasing the pH to 2.35. A further increase of pH led to precipitation of hydrated thorium(IV) oxide/hydroxide. The RDF of the LAXS data indicated three Th··Th distances at 4.0, 4.7 and 6.5 Å, respectively. The number of Th··Th distances was refined to 1.33, 0.83 and 0.33 per thorium respectively. This

set of distances corresponds to Th···Th distances in a hexamer which consists of two perpendicular diamond shaped tetramers, with triple μ^3 O-oxo bridges forming a rhomboctahedral configuration, Figure 15. A hexanuclear $[\text{Th}_6(\mu^3\text{O})_4(\mu^3\text{-OH})_4(\text{HCOO})_{12}(\text{L}_\text{T})_6]$, where $\text{L}_\text{T} = \text{H}_2\text{O}$ or CH_3OH) complex was synthesized and studied crystallographically.⁹² For uranium a hexanuclear $[\text{U}_6(\mu^3\text{O})_4(\mu^3\text{-OH})_4(\text{HCOO})_{12}(\text{L}_\text{T})_6]$, where $\text{L}_\text{T} = \text{H}_2\text{O}$ or CH_3OH) and $[\text{U}_6(\mu^3\text{O})_8(\mu^2\text{OTf})_{12}(\text{H}_2\text{O})_3] \cdot 23\text{H}_2\text{O}$, where two uranium(IV) and four uranium(V) are present, were synthesized in a crystalline state.^{92,93}

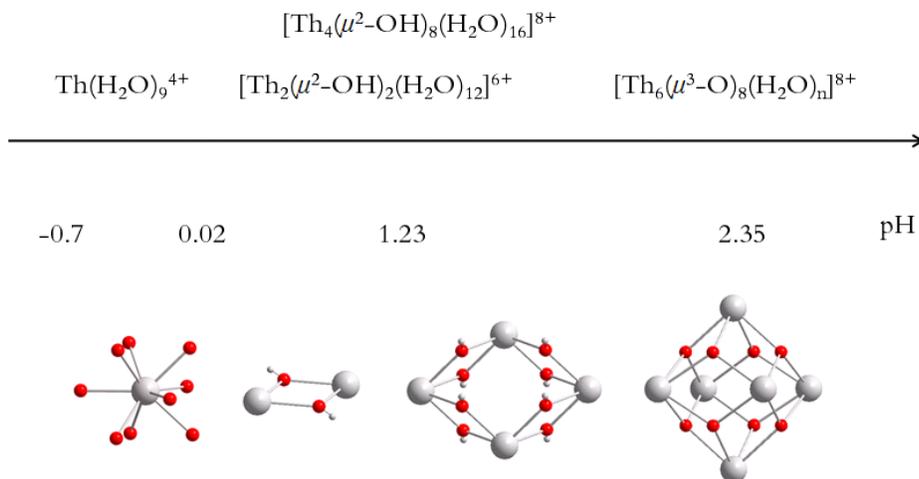


Figure 15. Thorium(IV) complexes present in acidic aqueous solution depending on pH.

As has been mentioned in the Introduction, thermodynamic studies of thorium hydrolysis reported polynuclear hydroxo complexes of thorium of composition $[\text{Th}_6(\text{OH})_{14}]^{10+}$ and $[\text{Th}_6(\text{OH})_{15}]^{9+}$.¹⁶ However, the given composition for thorium hexamers is erroneous and cannot exist due to the sterical crowdedness created by 16 hydroxo groups, Figure 16.

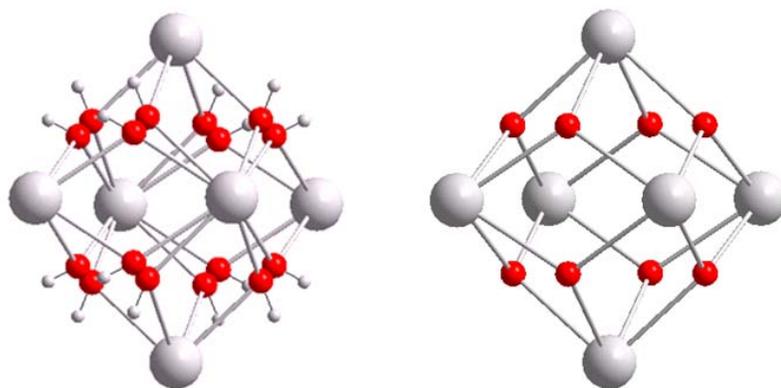


Figure 16. The model of an erroneous $[\text{Th}_6(\text{OH})_{16}]^{8+}$ and a correct hexamer $\text{Th}_6\text{O}_8^{6+}$.

Instead, 16 hydroxo groups are replaced by eight oxo groups which give the hydrolyzed thorium hexamer the composition $\text{Th}_6\text{O}_8^{6+}$. On the other hand, the potentiometric response from either 16 hydroxo or eight oxo groups is the same, therefore to determine the correct composition based only on pH titration was not possible.

Thorium(IV) hydrolysis therefore represents a rather peculiar case, as with an increase of pH the oxygen ligand changes from H_2O at $\text{pH} = 0$, to OH^- at $\text{pH} = 1.23$ and finally O^{2-} at $\text{pH} = 2.35$. A similar hydrolysis pattern is observed for uranium(IV)/(V) in an aqueous solution.⁹³

5.1.2 Thorium in oxygen donor organic solvents

The solvation of thorium(IV) in two oxygen donor organic solvents, DMSO and DMPU, was studied by EXAFS in solution. It was found that thorium(IV) is nine-coordinate in DMSO solution with a mean Th-O bond distance of 2.45 Å, Figure 17.

The crystal structure of oxoniumbis(nonakis(κO -dimethylsulfoxide)-thorium(IV)trifluoromethanesulfonatedihydrate, $(\text{H}_3\text{O})[\text{Th}((\text{CH}_3)_2\text{SO})_9]_2(\text{CF}_3\text{SO}_3)_6 \cdot 2\text{H}_2\text{O}$, **C**, consists of two independent structural units with nine-coordinate thorium in *ttp* configuration in both.

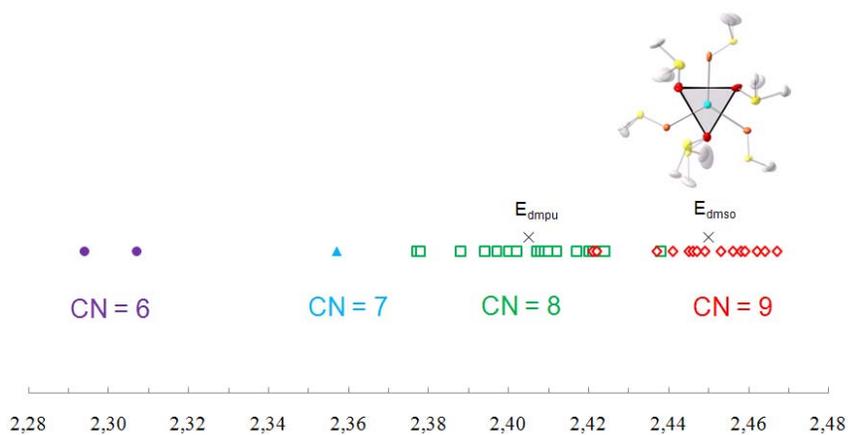


Figure 16. Overview of the previously reported $\text{Th}^{\text{IV}}\text{-O}$ bond distances and their corresponding CN with oxygen donor ligands, see paper **I**. E_{dmpu} and E_{dmsol} are the Th-O bond distances obtained by EXAFS for solvated thorium(IV) in DMPU solution and DMSO solution and solid respectively.

The mean Th-O bond distance is 2.47 Å for Th1, however, the mean Th-O bond distance for Th2 is 2.43 Å, after riding motion correction is applied. The much shorter Th-O bond distance in Th2 is a result of highly irregular thermal ellipsoids, which brought large uncertainty in distances. The mean Th-O bond distance based on Th1 and Th2, after geometrical correction was applied, was 2.45 Å, which was the expected value for nine-coordinate thorium(IV), Figure 16. The EXAFS study of **C** gave Th-O and Th...S distances of 2.449 and 3.665 Å, respectively. Therefore, the results from EXAFS support the crystallographic investigation. Hence, both hydrated and DMSO solvated thorium(IV) are nine-coordinate in solution and solid solvates.

The DMPU solvated thorium(IV) is eight-coordinate with a mean Th-O bond distance of 2.40 Å, Figure 16. The lower CN observed in the DMPU solvate in comparison to the thorium hydrate and DMSO solvate, is most probably due to the space-demanding properties upon coordination of the DMPU molecule as discussed elsewhere.⁹⁴⁻⁹⁷

5.2 Thorium and iron

Three series of iron(III)/thorium(IV) solutions were prepared and stored for 24 months (paper **II**, Table 1). It was noticed that all solutions with pH \geq 2.9 stayed transparent without any visible precipitate for at least 24 months, whereas in solutions with pH $<$ 2.9 precipitates were formed with time

(paper **II**, Table 1). The precipitates formed at pH values 2.0 and 2.3 were identified as six- and two-line ferrihydrites, respectively (paper **II**, Figure 1).

EXAFS and LAXS data indicated Th···Th and Fe···Fe distances of 3.94 and 3.04 Å in thorium(IV) and iron(III) hydrolysis dimers, respectively.ⁱⁱ Both Th L_3 and Fe K edge EXAFS, and LAXS data, indicated Th···Fe and Fe···Th distances at 3.40 and 3.42 Å, respectively.ⁱⁱ It is important to underline that neither diagonal Th···Th nor Fe···Fe distances in square-planar configuration, both expected at 4.8 Å, were observed. It should be stressed that the heteronuclear hydrolysis complex formed was prepared by mixing acidic iron(III) and thorium(IV) solutions with a subsequent increasing of pH values with sodium hydroxide. Solubility of thorium(IV) hydrolysis complexes and colloids has been widely studied.^{18-23,98} In all these studies thorium dioxide or thorium(IV) hydroxide was dissolved in acidic solution of either sodium or magnesium chloride or perchlorate at several different pH values. The observed high solubility of thorium(IV) is due to the dissolution of hydrated oxyhydroxides $\text{ThO}_n(\text{OH})_{4-2n}(\text{am})$, or in the case of crystalline thorium dioxide by formation of colloids of ultra-small size and the presence of polynuclear species. It is shown that ultra-small colloids are not removed by ultracentrifugation at $\text{RCF} = 1.5 \cdot 10^5 \text{ g}$ and 2 nm ultrafiltration. To prove that the formed heteronuclear hydrolysis complex of iron(III)/thorium(IV) is a true soluble complex the following has been taken into account:

- Solutions A-2.9, A-4.2, A-4.5 and A-4.8 (paper **II**, Table 1) were centrifuged at $\text{RCF} = 0,68 \cdot 10^5 \text{ g}$ for five hours. It is shown that different centrifugation times isolate different sizes of colloidal particles.⁹⁹ A small amount of precipitation was only formed in solution A-4.8.
- The WL in the Th XANES region is shown to be stronger for soluble species in comparison to colloidal particles in solution.²⁰ The WL for solution A-2.9 is markedly stronger than the WL for the solid $[\text{Th}(\text{H}_2\text{O})_8(\text{ClO}_4)](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$, or the hydrated and hydrolyzed thorium(IV) ions in aqueous solution (paper **II**, Figure 2).
- The estimated size of a complex is 16 Å in square and ca 7 Å thick, with the second hydration sphere taken into account.
- The LAXS technique is very sensitive to long interactions⁷⁷ and the Th···Th distances in crystalline thorium(IV) dioxide at 5.6, 6.9 and 7.9 Å^{100,101} would be seen in RDF of LAXS data. However, there were no contributions observed in the RDF of a heteronuclear complex beyond 5 Å, which is a strong indication that the complex of the proposed composition, $[\text{Fe}_2\text{Th}_2(\mu^2\text{-OH})_8(\text{H}_2\text{O})_{12}]^{6+}$ exists as an individual unit in aqueous solution.

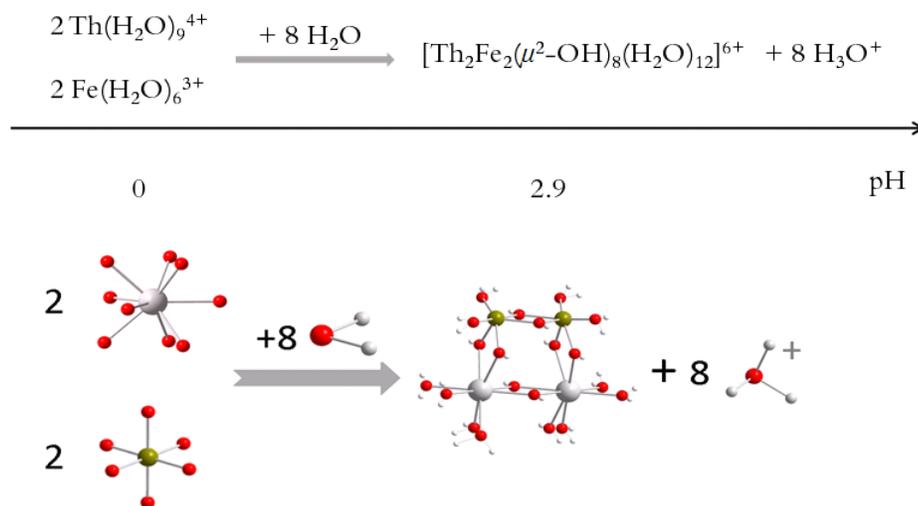


Figure 18. The scheme of chemical reaction of formation of a heteronuclear iron(III)/thorium(IV) hydrolysis complex.

All the above gives strong indications of a true soluble heteronuclear complex, $[\text{Fe}_2\text{Th}_2(\mu^2\text{-OH})_8(\text{H}_2\text{O})_{12}]^{6+}$, formed in an aqueous solution at $2.9 \leq \text{pH} \leq 4.8$. The heteronuclear complex consists of hydrolyzed iron(III) and thorium(IV) connected via double hydroxo bridges, where each iron(III) and thorium(IV) bind additional two and four water molecules to complete six- and eight-coordination respectively, Figure 18. EXAFS data on Th L_3 and Fe K edges and their respective FT can be found in paper **II** (Figures 3 and 4 and RDF of LAX data in Figure 6).

5.3 Palladium and platinum

The hydrolysis products of palladium(II) and platinum(II) have been studied in an acidic aqueous solution after 25 years of storage in a refrigerator. Palladium(II) solution was transparent and without any visible precipitate, while platinum(II) solution contained visible light brown fine-dispersed precipitate on the bottom of the test-tube. Centrifugation at $\text{RCF} = 4.7 \cdot 10^4$ g of both palladium and platinum solutions did not lead to visible precipitate.

EXAFS data of hydrolyzed palladium(II) solution showed Pd...Pd distances identical to those of crystalline palladium(II) oxide (paper **III**, Table 1), however the intensity of FT peaks corresponding to Pd...Pd distances is much lower.¹⁰²⁻¹⁰⁴ EXAFS data collected for crystalline

palladium(II) oxide were used to find the number of Pd···Pd distances in hydrolysis products. Since the number of distances and Debye-Waller coefficients cannot be refined simultaneously, Debye-Waller coefficients found for crystalline palladium(II) oxide were used as fixed parameters to get the number of Pd···Pd distances in hydrolyzed palladium(II) solution. It was found that the number of Pd···Pd distances is reduced in hydrolyzed palladium(II) solution in comparison to crystalline palladium(II) oxide.

Obtained results correspond to very small particles of size *ca.* two unit cells, $11 \times 11 \times 9 \text{ \AA}$ (*ca.* 1.0 nm^3) growing along the *a* or *b* axis, present in hydrolyzed palladium(II) solution, Figure 19. The growth in direction *c* would produce different ratio of Pd···Pd distances, and was therefore ruled out. SAXS results confirm that palladium(II) oxide particles formed in the acidic aqueous solution are extremely small.

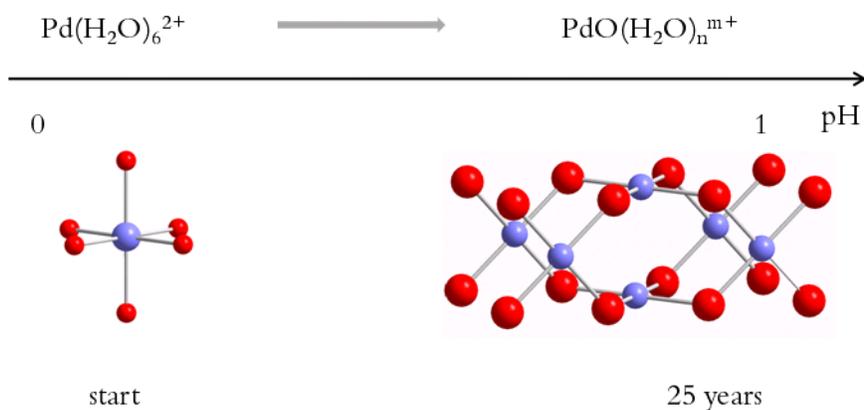


Figure 19. Palladium aging with time in acidic aqueous solution with the formation of palladium(II) oxide type structure (growing in *b* axis), palladium (purple) and oxygen (red).

The Pt···Pt distances obtained by EXAFS for platinum(II) hydrolysis complexes in an acidic aqueous solution (paper **III**, Table 3) are identical with those found for amorphous platinum(II) oxide filtered from the solution, but different from those reported in crystalline platinum(II) oxide.¹⁰³ The Debye-Waller coefficients of the Pt···Pt distances are larger in platinum(II) in comparison to Pd···Pd distances in palladium(II) oxide, which supports the amorphous state of the studied platinum(II) oxide.

Powder diffraction data of filtered platinum(II) oxide identified an amorphous sample with one diffraction peak coinciding with crystalline platinum(II) oxide (paper **III**, Figure 1). EXAFS data showed that the size of platinum(II) oxide particles is somewhat larger than the size of palladium(II) oxide particles and constitutes *ca.* 3 unit cells, growing in the *a* or *b* axis, giving particles of a size 1.0-1.5 Å in diameter, 1.0 nm³.

Thus, both palladium(II) and platinum(II) hydrolysis products formed in acidic aqueous solutions, are metal(II) oxides with the size of couple of unit cells. Terminal metals bind water molecules to maintain a formed complex in a soluble state, Figure 19.

5.4 Chromium

Chromium(III) hydrolysis has been studied in aged solutions by dialysis, ultrafiltration, centrifugation, EXAFS and LAXS in the pH range 2-15 and a chromium(III) concentration range $2 \cdot 10^{-4}$ to $1.5 \cdot 10^{-1}$ mol·dm⁻³. pH was checked and adjusted in chromium(III) solutions over two years. Time plays an important role for the establishment of equilibrium in hydrolyzed chromium(III) solutions. The spectrophotometry, retention and centrifugation data showed that chromium(III) hydrolyzes in solution with increasing pH with the formation of soluble hydrolysis species, (paper **IV**, Figures 1 and S1). The transition from hydrated chromium(III) to the hydrolyzed species took place within a narrow pH range, less than one pH unit, (paper **IV**, Figure S2). By potentiometric titration the OH⁻/Cr^{III} ratio at pH = 3.7 was found to be *ca.* 2.3, which is in assumption that a tetramer was formed. This gave the composition of the chromium(III) hydrolysis complex as [Cr₄(OH)₉]³⁺.

EXAFS and LAXS studies of chromium(III) hydrolysis at pH = 3.7 and chromium(III) concentration 0.98 mol·dm⁻³ indicated the formation of a tetramer with the composition [Cr₄(μ²-OH)₂(μ-OH)₄(OH)_n(H₂O)_{12-n}]⁽⁶⁻ⁿ⁾⁺, n ≈ 3. Cr···Cr distances of 2.98(1) and 3.59(1) Å were found by EXAFS and LAXS, and a long Cr···Cr distance at 6.85 Å by LAXS, Figure 20. This may indicate the formation of a tetramer with a very similar structure to that found in the crystal state.¹⁰⁵⁻¹⁰⁸ Stunzi and Marty proposed the formation of a dimer, a trimer and a tetramer with pK_{a1} values 3.68, 4.35 and 2.55, respectively.¹⁰⁹ This indicates that the tetramer should be formed at the expense of the monomer and trimer at pH = 3.7. It was shown that equilibrium establishment in the tetramer solution took a longer time than in the monomer, dimer or trimer solutions.¹⁰⁹ In the trimer three chromium

(dimethylsulfoxide)rhodium(III) complexes were characterized.^{115,116} The Rh-O bond distance *trans* to κ -S DMSO is longer than the Rh-O bond distance to the four κ -O DMSOs in the perpendicular plane, 2.143 and 2.019 Å, respectively. The κ -S DMSO ligand coordinated *via* one κ -S is probably due to a steric factor, κ -O-coordinate DMSO is less space-demanding in comparison to κ -S-coordinate DMSO. Chlorotris(DMSO- κ O)bis(DMSO- κ S)rhodium(III) trifluoromethanesulfonate, **2**, consists of three κ O-coordinate DMSO *trans* to one chloride ion and two κ -S-coordinate DMSO, (Paper VI, Figure 2). Rh-O bond distance in **1** is shorter than Rh-O bond distance in **2**, 2.019 and 2.077 Å respectively. The longer Rh-O bond distance in **2** is explained by *trans* influence of the coordinated chloride ion and κ -S DMSO.

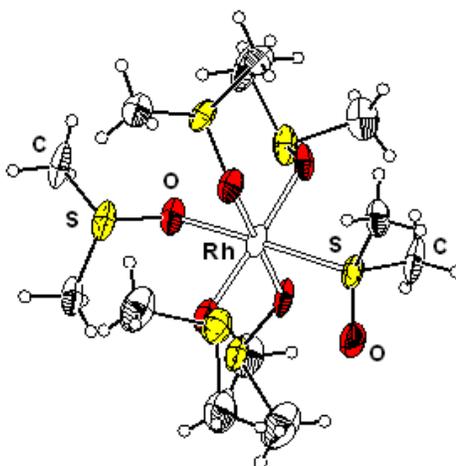


Figure 21. The pentakis(dmsO- κ O)mono(dmsO- κ S)rhodium(III) complex at 100 K with 50% probability ellipsoids.

Rhodium(I) being a typical class “b” metal ion binds three κ -S DMSO ligands in a neutral $\text{RhCl}(\text{DMSO})_3$ complex, whereas less soft cationic complex $[\text{Rh}(\text{DMSO-}\kappa\text{O})_2(\text{DMSO-}\kappa\text{S})_2]\text{PF}_6$ has both sulfur- and oxygen-bound DMSO ligands.¹¹⁷ A less “soft” metal center in the cationic complex allows both κ -S and κ -O DMSO ligands in rhodium(I) complex.¹¹⁸ The Rh-S bond distance *trans* to chloride ligand is shorter than Rh-S bond distance *cis* to chloride ligand, 2.21 and 2.27–2.29 Å, respectively. DMSO solvate structures with two κ -O and two κ -S DMSO ligands bound to “soft” metal ions were found for iridium(I), platinum(II) and palladium(II).¹¹⁸⁻¹²⁰ Hexakis-(dimethylsulfoxide)ruthenium(II) cation coordinates three κ -O and three κ -S dmsO ligands.¹²¹ In all four DMSO

solvates κ -O DMSO is *trans* to κ -S DMSO, with a “hard” atom on one side and a “soft” atom on the other side.

6 Additional studies

Hydrolysis of rhodium(III) and hydrolysis and hydration of iridium(III) and iridium(IV) in acidic aqueous solution have been studied by EXAFS. The rhodium(III) hydrolysis complexes were prepared by the adaptation of a methodology described elsewhere.^{24,68} Preliminary EXAFS data analysis showed that Rh-O bond and Rh...Rh distances at 2.02 and 3.04 Å respectively, are similar to those found in rhodium(III) dimers in a crystalline state.^{24,122,123}

Iridium(III) perchlorate and trifluoromethanesulfonate were prepared by the adaptation of a methodology described elsewhere.^{70,124} EXAFS data was collected on three iridium(III)/(IV) solution, two iridium(III)/(IV) solids, perchlorate and trifluoromethanesulfonate. It was found that iridium(III) is six-coordinate in an octahedral configuration in three of the solutions studied (yellow and blue perchlorate, and purple trifluoromethanesulfonate), with a mean Ir-O bond distance of 2.03 Å, similar to hexaaquairidium(III) in a crystalline state.¹²⁵ One perchlorate iridium solution appeared to contain a hydrolyzed iridium(IV) complex. Interestingly, two solutions, perchlorate and trifluoromethanesulfonate, have a dark blue-purple color, while one perchlorate solution has a light yellow color, all three containing hydrated iridium(III) ions. Such intense and strong color could be explained by the presence of mixed-valance iridium(III)/(IV) complexes in an acidic aqueous solution.

Cerium(IV) hydrolysis solution was prepared, but EXAFS and LAXS data collection led to reduction of cerium(IV) to cerium(III) caused by the radiation applied. Quick EXAFS may be used to study cerium(IV) hydrolysis complexes in the future.

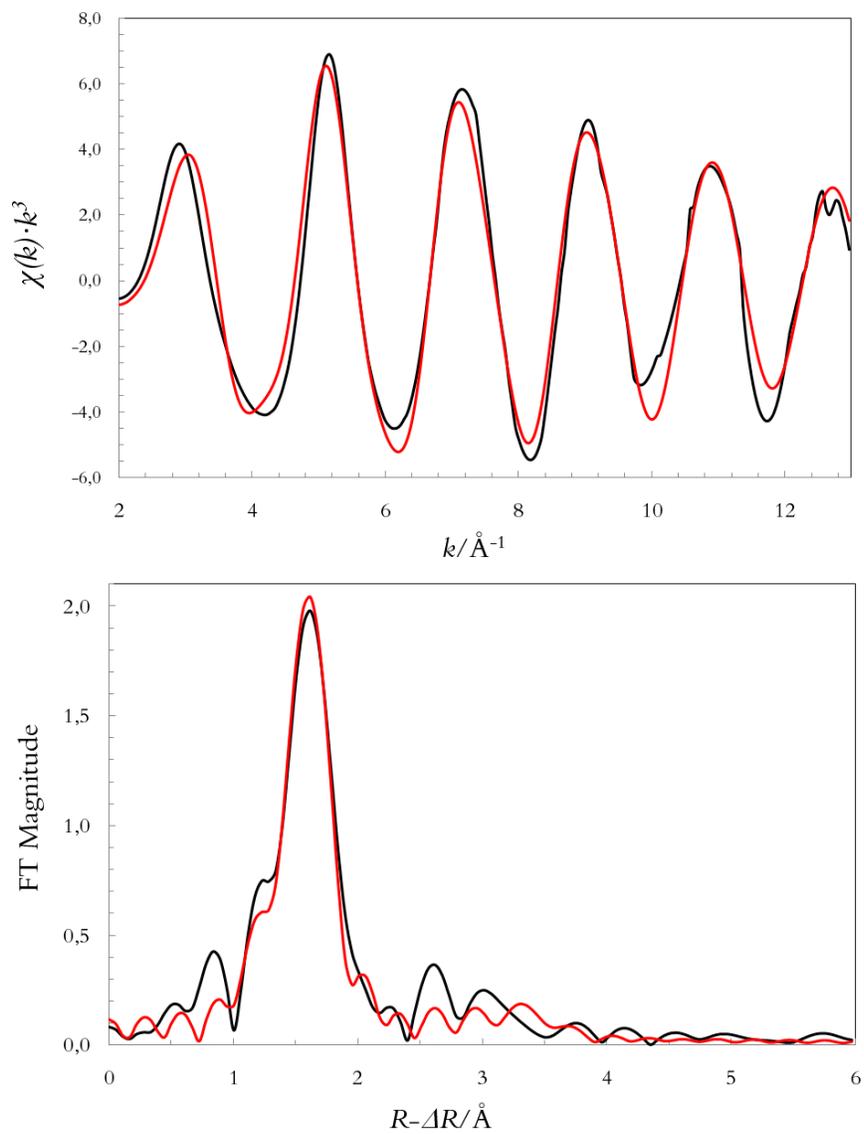


Figure 22. Fit of EXAFS data and its respective Fourier transform for hydrated iridium(III) ion in an acidic aqueous solution (red line – model, black line – experimental data).

7 Conclusions

Hydrolysis of some multicharged metal ions has been studied by structural methods and summarized to form a general picture. Three different hydrolysis patterns have been found for the metal ions studied, Figure 23. One group of metals hydrolyzes with the formation of polynuclear hydroxo bridged hydrolysis complexes, e.g. chromium(III). Another group of metals hydrolyzes with the formation of polynuclear hydrolysis complexes with hydroxo- and oxo- bridges at higher pH, e.g. thorium(IV). Finally, a third group of metals hydrolyzes with the formation of small oxide particles over a very long period of time in an acidic solution without addition of alkali, e.g. palladium(II) and platinum(II).

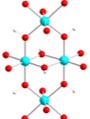
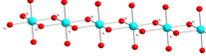
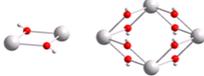
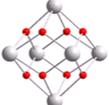
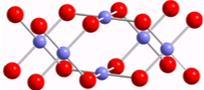
Metal	pH = 0	pH = 1 – 2	pH = 2 – 4	pH ≥ 15
Cr				
Th				ThO ₂ (s)
Pd			PdO(s)	PdO(s)

Figure 23. A summarized hydrolysis pattern for multicharged metals studied in the thesis.

Heteronuclear hydrolysis complex of thorium(IV) and iron(III) has been prepared and characterized. The formation of such a complex might be a reason for higher solubility of iron(III) and thorium(III) hydrolysis complexes when present together.

Crystal structures of new compounds have been synthesized and characterized, two thorium(IV) hydrates and DMSO solvates of thorium(IV) and rhodium(III). Rhodium(III) is a “soft” metal ion and coordinates DMSO via either oxygen or sulfur. It was shown that thorium(IV) DMPU solvate revealed lower CN due to the space-demanding properties of the DMPU molecule upon coordination.

Improved ionic radii of the actinoid(IV) ions have been proposed based on an analysis of the crystallographic data available for 135 compounds.

Possible application of fundamental studies conducted in this thesis have also been discussed.

8 Perspectives

In this section of the thesis several areas of future study are highlighted.

- Further thermodynamic studies of palladium(II) and platinum(II) hydrolysis products.
- Preparation and structural characterization of iridium(III) and iridium(IV) hydrolysis complexes.
- Hydrolysis studies of other multi-metal systems.
- Deeper studies of increased solubility of thorium(IV)/iron(III) hydrolysis complex and possible impact on the storage of nuclear waste.

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Acknowledgements

Ещё одно последнее сказанье,
И летопись окончена моя.
А. С. Пушкин¹

I know that this is one of the few chapters in the thesis that many of you will look at, and I'll try to make it an exciting read.

First of all I'd like to thank my supervisor **Ingmar Persson** for being a great mentor! To paraphrase Stephen King, good teachers are truly priceless! I am truly grateful to **Ingmar** for giving me an opportunity to become a Ph.D. student in Sweden, which drastically changed my life. One of the properties of being such a good teacher is a patience to explain something over and over again, until comprehensive understanding is reached. Being a Ph.D. student in Sweden is not only about science and research, it comprises priceless experience of teaching, when you start to understand that it is hard work demanding a lot of responsibility and sensitivity of human chemistry. Being a Ph.D. student opens a whole new world, could I even in my wildest dreams to imagine of traveling to Australia or the US?! Thank a lot to **Ingmar** for giving me an opportunity to participate in international conferences held all over the world. My time as a Ph.D. student was like climbing a mountain, a journey which is hard, dangerous yet very exciting. There is a saying "the more you sweat in training, the less you will bleed in battle", let's hope it will be so!

Thank to my assistant supervisor, **Lars Eriksson**, also known as Lasse ☺, for help with solving crystal structures and interesting, fruitful lectures,

¹ Yet one last tale,
And my chronicle is done.
A. S. Pushkin

which were given with a great sense of humor, during “X-ray crystallography” course.

I am grateful to **Yuri Petrovich Davydov** for accepting me as a Ph.D. student at **Radiochemical Laboratory 06** in Sosny, Minsk and to **Dmitri Davydov** for introducing me to **Ingmar Persson**, negotiation about possible exchange visits to Sweden and discussion of possible research area.

I would like to thank all ex-colleges at **Radiochemical Laboratory 06** in Sosny, Minsk for a nice, peaceful and warm atmosphere where I made my first steps as a scientist.

Lena Johansson and her successor **Sonja Jansson** took care about all paper-work and organizational questions. Tack så mycket!

I would like to thank former and present Ph.D. students, **Joris, Johan B., Gunnar, Lena O., Olesya, Kai, Charles, Gustav** for a nice company during long teaching hours and **Johan M., Pierre, David, Eric, Lars, Lena L.,** and **Christina** for a nice company during fika and parties at the chemistry department.

During all those five years I could at least for a short moment feel at home, thanks to intelligent conversations in Russian with **Vadim Kessler** and **Gulaim Seisenbaeva** about science, chemistry, history, and many other exciting topics. Special thank to **Gulaim** for the help with SEM measurements.

Funny and talkative, smart and wit, annoying yet intriguing, tough and thorny, always knowing everything about anything; can you guess who I’m talking about? Of course it is **Daniel Lundberg**, who I would like to thank for reading my thesis, for correcting and improving my English and Swedish, for being my roommate and answering a good half of a million questions.

I just could not possibly forget to mention **Bernt Andersson** and his trusty sidekick “satellite” **Linus** for help with solving all possible problems during teaching process.

Other colleges at the department left a print of their individuality in my heart, joking **Lennart Kenne**, attentive and bearing a warm smile **Corine Sandström**, trying to say something in Polish to me **Suresh Gohil**, always absorbed with teaching **Anders Sandström**, happy **Rolf Andersson**, always ready with wit comments **Jan Eriksson**, and self-composed **Anders Broberg**.

Surely, I am happy to have such friends as **Elsa Coucheney, Ania Placzek, Satomi Shibutani, Anke Herrmann, Cecile Monard, Irene Palacios Romero** (oj-~~oj-~~oj-~~oj-~~oj~~~~~~~~) ☺) and **Julia Paraskova**. We sure did

have a great time here! ☺ **Julia** thank you for helping me to make correct decisions!

My once upon a time roommates, co-travelers and night-shift pals at MAX Lab **Samson Sajido** and **Önder Topel** deserve a special mention for all the funny times we shared.

The apologetic free electron traveling between England and Sweden, always saying “sorry”, is of course **Sam Grice**. Thank you for help with your ridiculously posh English, sorry! ☺

Now it's the turn of my Russian-speaking company of friends: **Olesya Nikonova** who was dragging me to all disco-clubs in Uppsala, as well as helping me with couple of powder diffractograms, **Lena Ossipova** who was answering my numerous questions about everything during my first visit to Sweden and being good fika company, **Lyudmila Babak** who my outlook on life, **Paruir** for readiness to help, **Natalie** and **Katya** who shared with me their alternative views on this world, **Nastya** who helped me to look better and have a nice haircut. What a time we had together!

There are two people who were always ready and did help during those years, **Stefan** and **Theo**.

My far-away best friend **Volha (Lola ☺)**, who I have known for 24 years, had always strong faith in me and was supportive throughout.

During my time in Sweden I felt support from my parents' friends; the **Petropavlovsky, Bogatyryov, Golev, Smirnov, Silanova, Gusev** and **Chupaeva** families, thank you!

I would like to thank my relatives for support and “brain-wash” when it was needed: aunt **Luda** and uncle **Vitya, Vovik, Mishka**; aunt **Galya, Vova, Vika**, granny **Nina** and grannies **Galya** and **Masha**. ☺

The last come the dearest, my **mother** and my **brother**, who were overcoming difficulties with me, thank you so much!

And, finally, my **father**, who unfortunately passed away, but still lives in my heart, who would be proud of me and who, being a chemist, always wanted me to become a chemist too, just like everyone in our family ☺.

Special thank goes to those of you who had a patience to read this thesis from the first to the last page.

If you didn't find your name here, it is just because of my forgetful goldfish-like memory, you know, but I say thanks to you too!