The Coordination Chemistry of Solvated Metal Ions in DMPU

A Study of a Space-Demanding Solvent

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Abstract

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This thesis summarizes and discusses the results of several individual studies on the solvation of metal ions in the solvent *N,N'*-dimethylpropyleneurea, DMPU, including the iron(II), iron(III), zinc(II), cadmium(II), and lanthanoid(III) ions. These studies have shown that the solvation process in DMPU is sometimes very different to those in corresponding aqueous systems. This is due to the the space-demanding properties the DMPU molecule has when coordinating to metal ions, with its two methyl groups close to the coordinating oxygen atom. The methyl groups effectively hinder/hamper the metal ion from reaching the coordination numbers present in hydrate and solvate complexes with solvent molecules with much lower spatial demands.

The investigations were performed with different X-ray techniques, including extended X-ray absorption fine structure (EXAFS), large angle X-ray scattering (LAXS), and single crystal X-ray diffraction (XRD) and included both studies in solution (EXAFS and LAXS) and solid state (EXAFS and XRD).

A coordination number reduction, compared to the corresponding hydrates, was found in all of the studied systems, except cadmium(II). Furthermore, the coordination number in solution was in several cases not the same as in the respective solid state. In solvents where five-coordinated metal ion solvates are dominating, there is an increase in the ability to form complexes, *e.g.* fairly strong iron(III) bromide complexes are formed in DMPU. All DMPU solvated lanthanoid(III) ions, except lutetium(III), are seven-coordinated in solution, whereas they are six-coordinated in the solid state, as well as the DMPU solvated lutetium(III) ion in solution. The DMPU solvated zinc(II) and cadmium(II) ions are four- and six-coordinated in the solid state, but both show indications of having a relatively large fraction of transient five-coordinated complexes in solution. This indicates associative and dissociative ligand exchange processes, respectively. The first four-coordinated cadmium(II) iodide with atomic parameters, bis[1,3-dimethyl-3,4,5,6-tetrahydropyrimidin-2(1*H*)-one-*κ*O]diiodocadmium(II), has been structurally determined.

Keywords: N,N'-dimethylpropyleneurea (DMPU), cadmium(II), iron(II), iron(III), lanthanoid(III), zinc(II), five-coordination, EXAFS, LAXS, solvation.

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Abstract

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Diese Dissertation ist eine Zusammenfassung und Diskussion mehrerer separater Studien über die Solvatisierung von Metallionen im Lösemittel *N,N'*-Dimethylpropylenharnstoff (DMPU), darunter Eisen(II)-, Eisen(III)-, Zink(II)-, Kadmium(II)- und Lanthanoid(III)-Ionen. Frühere Studien haben gezeigt, dass sich der Solvatisierungsprozess in DMPU teilweise stark von denen in wässrigen Systemen unterscheidet. Dies liegt am Platzbedarf des DMPU-Moleküls bei der Koordination mit den Metallionen, wo die beiden Methylgruppen nahe am koordinierenden Sauerstoffdonator-Atom liegen. Die Methylgruppen hindern das Metallion effektiv daran, die hohen Koordinationszahlen zu erreichen, die man bei hydratisierten Komplexen und anderen Lösemitteln ohne diesen Platzbedarf beobachtet.

Die Untersuchungen wurden mit unterschiedlichen Arten von Röntgentechniken durchgeführt, darunter die Extended X-ray Absorption Fine Structure (EXAFS), Large Angle X-ray Scattering (LAXS) und Einzelkristall-Röntgenstrahlenbeugung. Die Studie umfasst sowohl Untersuchungen in gelöstem (EXAFS und LAXS) als auch in festem Zustand (EXAFS und Einzelkristall-Röntgenstrahlenbeugung).

Die Studie ergab in vielen der untersuchten Systeme eine Reduktion der Koordinationszahl und fand klare Beispiele, bei denen die Koordinationszahl in der Lösung von der im festen Zustand verschieden ist. Ein beobachteter Effekt davon ist der Anstieg der Bromidkomplex-Formationsfähigkeit von Eisen(III), das einen im wesentlichen trigonalen planaren Komplex in der DMPU-Lösung bildet.

Überdies sind, mit Ausnahme von Lutetium(III), alle in DMPU-Lösung solvatisierten Lanthanoid(III)-Ionen sieben-koordiniert, wogegen sie im festen Zustand sechs-koordiniert sind (wie auch DMPU-solvatisiertes Lutetium(III) in der Lösung). Die DMPU-solvatisierten Zink(II)- und Kadmium(II)-Ionen sind im festen Zustand vier- und sechs-koordiniert. Bei beiden gibt es Anzeichen dafür, dass sie während des (assoziativen und dissoziativen) Liganden-Austauschs vorübergehend einen beträchtlichen Anteil an fünf-koordinierten Komplexen in der Lösung besitzen.

Das erste vier-koordinierten Kadmium(II)-Iodid mit vollständigen Strukturparametern, bis[1,3-Dimethyl-3,4,5,6-Tetrahydropyrimidin-2(1*H*)-one-*κ*O]Diiodokadmium(II), wurde bestimmt. Iodid-Ionen sind dafür bekannt, dass sie die Koordinationszahlen in anderen Lösemitteln verringern.

Schlagwörter: *N,N'*-Dimethylpropylenharnstoff (DMPU), Kadmium(II), Eisen(II), Eisen(III), Lanthanoid(III), Zink(II), Fünf-Koordination, EXAFS, LAXS, Solvatisierung.

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Абстракт

Лундберг, Д., 2006, *Координационная химия сольватированных ионов металлов в ДМПМ - исследование роли обьемистых молекул растворителя.* Диссертация на соискание ученой степени кандидата химических наук.
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Работа посвящена обобщению и обсуждению результатов ряда исследований сольватации ионов различных металлов в растворителе *N,N'*-диметилпропиленмочевина, ДМПМ, в частности, железа(II), железа(III), цинка(II), кадмия(II), и лантаноид(III) ионов. Предшествующие исследования показали, что сольватация в ДМПМ иногда весьма отлична от сольватации в водных растворах. Причиной тому являются стерические требования молекулы ДМПМ, содержащей две метильные группы в непосредственной близости к донорному атому кислорода. Метильные группы эффективно препятствуют достижению атомом металла высоких координационных чисел обычных для водных растворов и комплексов с другими, стерически менее требовательными лигандами.

Исследования проводились с использованием различных рентгеновских методов, включая спектроскопию тонкой структуры рентгеновской полосы поглощения (EXAFS), широкоугловое рентгеновское рассеяние (LAXS), и рентгеноструктурный анализ монокристаллов. Исследования проводились как в растворе (EXAFS и LAXS) так и в твердой фазе (EXAFS и рентгеноструктурный анализ).

Исследования показали, что уменьшение координационного числа характерно для большинства изученных систем, причем в некоторых случаях координационное число в растворе отлично от наблюдаемого в твердом состоянии. Наиболее заметен этот эффект в случае бромидного комплекса железа(III), где комплекс в растворе ДМПМ имеет плоскотреугольную конфигурацию.

Более того, за исключением лютеция(III), все ДМПМ-сольваты лантаноидов имеют координационное число семь в растворе и шесть - в твердом состоянии, ДМПМ-сольват лютеция(III) шестикоординирован и в растворе. ДМПМ сольваты цинка и кадмия имеют в твердом состоянии координационные числа четыре и шесть. В случае обоих этих комплексов имеются указания на образование в растворе промежуточного пятикоординационного состояния в ходе (ассоциативного и диссоциативного) процессов обмена лигандов.

В работе определена структура первого четырехкоординационного иодидного комплекса кадмия с атомными координатами, бис[1,3-диметил-3,4,5,6-тетрагидропиримидин-2(1*H*)-он-*κ*O]дииодокадмий(II). Способность иодид-ионов к снижению координационного числа была отмечена и в случае других растворителей.

Ключевые слова: *N,N'*-диметилпропиленмочевина (ДМПМ), кадмий(II), железо(II), железо(III), лантаноид(III), цинк(II), пятикоординационный, EXAFS, LAXS, сольватация.

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Om man skulle tänka sig att man har en
stor låda, en, eh, två gånger en meter …
Och fyllde den med molekyler, ända upp
till kanten, så den var alldeles proppfull,
så skulle det ändå få plats en molekyl till!

atomubåtsman Malte Lindeman ur *Gula Hund* (1964)

Well we artistic types are so misunderstood.
While everyone’s a critic,
they don’t know when something’s good.
Just let us have our space and freedom to create,
and when the work is finished,
we’ll tell you if it’s great.

Stephen’s Exhibition (1996), Stuart Davis

Contents

Appendix

Papers I-V

This thesis is based on the following scientific articles, which will be referred to by their Roman numerals:

I. Lundberg, D. and Eriksson, L., Bis[1,3-dimethyl-3,4,5,6-tetrahydropyrimidin-2(1*H*)-one-κ*O*]diiodocadmium(II), Acta Crystallographica, E**62**, 2006, m400-m401.

II. Lundberg, D., Eriksson, L, D'Angelo, P. and Persson, I., A structural study of the *N,N'*-dimethylpropyleneurea solvated zinc(II) and cadmium(II) ions in solution and crystalline state.
Accepted for publication *Journal of Molecular Liquids*

III. Lundberg, D., Ullström, A.-S., D'Angelo, P., Warminska, D. and Persson, I., On the structure and complex formation of iron(III) bromide in solution and crystalline state in the space-demanding solvent *N,N'*-dimethylpropyleneurea.
Submitted to *Dalton Transactions*

IV. Lundberg, D., Ullström, A.-S., D'Angelo, P., and Persson, I., A structural study of the hydrated and the dimethylsulfoxide, *N,N'*-dimethylpropyleneurea, and *N,N*-dimethylthioformamide solvated iron(II) and iron(III) ions in solution and solid state.
Submitted to *Inorganica Chimica Acta*

V. Lundberg, D., D'Angelo, P., De Panfilis, S. and Persson, I., An EXAFS study of N,'N-dimethylpropyleneurea solvated lanthanoid(III) ions in solution and solid state
In manuscript

The reprint of Paper I is granted on behalf of the International Union of Crystallography, publishers of Crystallography Journals Online.

My contributions to the papers were:

I. I synthesized the crystals and structurally solved the crystal structure with my co-author, Dr. Eriksson, with whom I also planned and wrote the article.

II. I worked up samples for EXAFS measurement, measured on them and solved the structure with EXAFS data treatment software. I co-wrote the article with Dr. Eriksson and Dr. Persson.

III. I synthesized the crystals myself and solved the structure with Mrs. Ullström. The article was written by me and Dr. Persson, with assistance by Dr. D'Angelo

IV. I worked up samples for EXAFS measurement, measured on them and solved the structure with EXAFS data treatment software. I co-wrote the article with Dr. D'Angelo and Dr. Persson..

V. Same contributions as for Paper IV.

1 Introduction

This thesis is written as part of the requirement for obtaining a Ph.D. degree in chemistry at the Swedish University of Agricultural Sciences, Uppsala, Sweden. It is meant to give an overview of the ever-growing field of coordination chemistry with a focus on solvate complexes in solution and solid state, and also a historical summary of the discovery of lanthanoids, a vital part of the Swedish contribution to the periodic table of elements.

It is thus the wish of the author that the introductory chapters are easily understood by readers with only basic knowledge of the principles in chemistry. Furthermore, with an equally great ambition, the author hopes that the full extent of this work is acknowledged by researchers in other chemical fields. It may be used as a good description of coordination chemistry of metal ions in solution (with special emphasis on solvents with space-demanding properties) and as a helpful historical narrative of inorganic chemistry as a subject.

1.1 Scope of this coordination study

The work in this thesis is part of a larger project where the changes to a chemical system brought on by a space-demanding ligand, compared to the non-sterically hindered systems, are studied. The familiarity with the latter, where water is a fundamental part, is very well documented and sometimes even leads to a slightly biased view. When the solvent ligand is *space-demanding at coordination*, and thereby reducing the ability of the metal ion to opt its coordination number, the importance of other solvating properties is enhanced. The increase in the complex formation properties of nickel(II) in DMPU is one noted effect of such a change.[1] To better understand of these effects, the scientific knowledge from other similar systems is needed.

Before the start of this thesis project, systems involving the following metal ions and the solvent DMPU had been evaluated: bismuth(III), hafnium(IV), lanthanum(III), lithium(I), molybdenum(IV), nickel(II), samarium(II), samarium(III), scandium(III), thallium(I), thallium(III), ytterbium(III), and yttrium(III) (listed in Paper II). Half of these are part of the same larger project as this thesis, which with its appended papers continues the quest of DMPU solvation with a few of the most common metal ions, including iron(II), iron(III), cadmium(II), and zinc(II). However, it is equally important to perform a *systematic* study where the trends in the results can be interpreted more easily. Such an investigation would include comparisons over a broad spectrum of similar ions, preferably with the same charge. Furthermore, the ions should cover a fairly wide range of radii, have similar chemistry, be readily available, and non-hazardous. A quick look at the first row transition elements reveals that they are not suitable in spite of the fact that they fulfil many of these criteria. Their ionic radii vary in a rather disorderly fashion, regardless of which ionic charge we choose (Fig. 1). Instead, if we go down to the lanthanoid series, we find exactly what we are looking for. The series has a unique electron build-up, which together with the other two rare earth metals yields no less than seventeen nearly identical elements (Fig. 2).

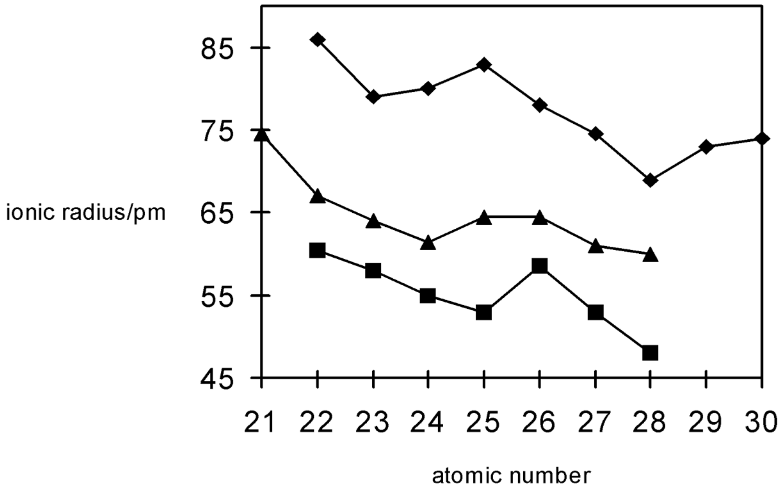


Fig. 1. Ionic radii of the bi- (♦), tri- (▲), and tetravalent (■) ions of the first row transition metals. The ionic radii values are taken from Shannon (ref. 2).

The explanation for this similarity is explained in Chapter 2.6, but for non-chemists is perhaps best described in the way the lanthanoids were discovered. The history of the these elements is also interesting from a Swedish point-of-view, as the origin of the minerals in which the metals were discovered and their explorers were Swedish or at least somehow connected to Sweden, a leading nation in chemistry at the time. A review of this history is given in Chapter 1.3.2.

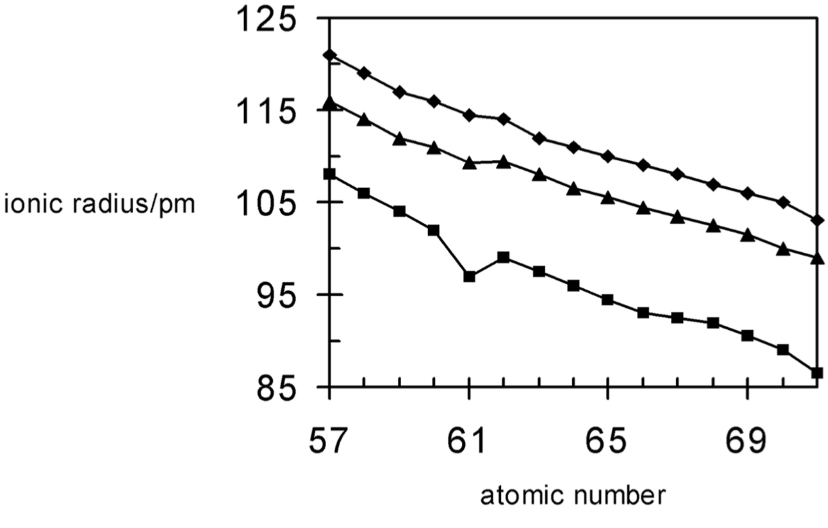


Fig. 2. The ionic radii of the nine- (♦), eight- (▲), and six -coordinated (■) lanthanoid(III) ions. The values are taken from Shannon (ref. 2). The irregularity seen for the value of six-coordinated promethium (element 61) is clearly erroneous.

1.2 Coordination chemistry

Coordination chemistry is the branch of chemistry, which lets us know how metal complexes are built. A complex is a cluster of ions and/or molecules, which can exist independently, but prefers to join together in a structurally well-defined manner. A metal complex consists of a metal ion, often referred to as the *central atom* (or ion), which binds a number of ions and/or molecules, called *ligands*. Usually coordination chemistry is regarded as a branch of inorganic chemistry, but this may be misleading to a certain degree. A quick glance at the coordination compounds included in this thesis, and one immediately recognizes that they are both traditionally inorganic (metal ions) and organic (solvents). Regardless of the classification, coordination chemistry is the chemistry of organized structures. The story of coordination chemistry is young, in a way as young as the *science* chemistry itself.

1.2.1 History of coordination chemistry

At the end of the 18th century, when chemistry was still trying to be fully accepted, John Dalton (1766-1844) successfully managed to merge three separate concepts: the strictly theoretic atomic idea of the Greek philosophers Democritus and Leucippus,[2] the law of definite proportions introduced by French chemist Louis-Joseph Proust,[3] and Antoine-Laurent Lavoisier's attention to quantitative measurement.[4, 5] Dalton added an idea of his own, that all atoms within an element are exactly the same, which resulted in the notion that all compounds are simple combinations of separate elements and reactions are really only rearrangements of atoms. Around this conglomerate of ideas he and a few others started building the foundation of the chemistry we know today.[6]

The main blemish in Dalton's atomic theory was a presupposed fact that water consists of one hydrogen atom and one oxygen atom, whereas the true ratio is two to one. Nevertheless, he managed to extract approximate relative atomic masses for twenty elements (Fig. 3), as his groundbreaking atomic theory was not totally dependent on this faulty assumption. At the time, there was still no real need for coordination chemistry as we know it today, but Dalton's contribution was a giant leap in a discipline that started to make sense.

1.2.1.1 Early coordination chemistry

Another great mind in chemistry, Jöns Jacob Berzelius (1779-1848), lived at the same time side-by-side with Dalton in the northern outskirts of Europe, in Sweden. Berzelius was an extraordinary analyst, which is reflected in the fact that he alone is credited with the discovery of the three elements (silicon, selenium and thorium) and the fact that he determined or refined the atomic weights of forty-five of at the time forty-nine accepted elements.[7] If one adds the discoveries of those ascribed to his students and those shared as simultaneous findings with other chemists (including tantalum, lithium, cerium, lanthanum, didymium, erbium, and terbium), the translation of chemical nomenclature to the Germanic languages, and his logical system of chemical abbreviations which essentially is the one we still use today, his contribution is simply stunning.[8-10]

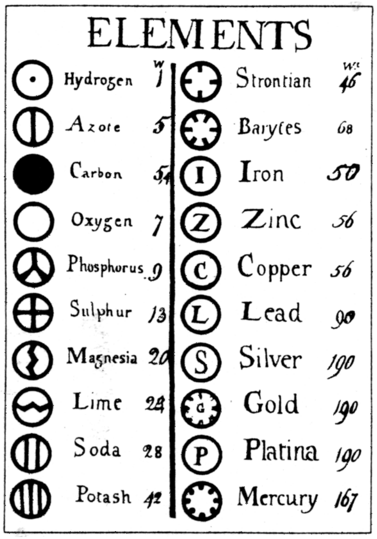
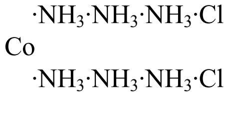


Fig. 3. Dalton's list of known elements.

Berzelius vigorously tried to sort all chemical compounds in a pair-wise system, the *two-component theory*, in where most inorganic compounds conformed.[11] When it came to the organic ones, he ended up in trouble, even though he altered the concept slightly to make it work better. It was, at least to some extent, a correct theory. As more and more elements were added to the complex world of chemistry order was needed, something offered by the vast achievement of Dmitri Mendeleyev (1834-1907), in the construction of the periodic table of elements.[12, 13] Mendeleyev was by no means the first or last chemist to suggest ordered patterns among the elements, but he was the first one to suggest a governing structure that would successfully predict not yet discovered elements primarily through meticulous analysis of many different properties.[14, 15] This made some of the attention to start to shift away from single elements and more towards compounds. The configuration and constitution of compounds were written in accordance with an organic view, essentially following the pairing system Berzelius had introduced.[16] When two Swedish chemists, Christian Wilhelm Blomstrand and Per Teodor Cleve, in detail described metal ammonias (today called metal ammines), they used a slightly different chemical orthography. For instance, hexaamminecobalt(II) chloride, today written out $[Co(NH_3)_6]Cl_2$ in shorthand notation, was represented by a slightly unusual formula (Fig. 4). In Blomstrand's view, the ammonias were linked to one another in chains. It was known, however, that different units of the formula had slightly distinct functions.



$$\begin{array}{l} \quad \cdot NH_3 \cdot NH_3 \cdot NH_3 \cdot Cl \\ Co \\ \quad \cdot NH_3 \cdot NH_3 \cdot NH_3 \cdot Cl \end{array}$$

Fig. 4. Representation of a coordination compound, hexaamminecobalt(II) chloride before Werner's contribution (after Werner, ref. 16).

Some of the acid residues (the chlorides in Fig. 4) were more tightly bound and others a bit weaker. Blomstrand modified his structure by assuming that a stronger bond could exist between the metal and a residue, and a looser bond was found at the terminal position of the ammonia chain.[16] This was the prevailing view before Alfred Werner resolved the situation.

1.2.1.2 Alfred Werner (1866-1919)

Alfred Werner was born in Mülhausen in Alsace, in today's France, December 12, 1866. He went to school in his hometown and early showed an interest in chemistry. At the age of 18 he completed his first independent study in chemistry, an investigation on caffeine and theobromine written in French.[17] Shortly after that, during his military service in Karlsruhe, Werner attended lectures held by Carl Engler at the Technische Hochschule, a leading combustion chemist at the time.[18] He received his first degree (in Technical Chemistry) in 1889 from Eidgenössisches Polytechnikum in Zürich, where he was trained mainly as an organic chemist by Georg Lunge and William Dupré Treadwell, much influenced by co-worker professor Arthur Hantzsch.[19, 20] The impact is seen in the scientific articles produced by Werner between 1890 and 1896: twenty dealt with organic chemistry and ten were in the inorganic field.[18] It was also with Hantzsch which he cooperated writing an article that unfolded the stereochemistry of nitrogen, a paper that was part of Werner's doctoral thesis. In that paper they stated that in *"certain compounds, the three valances of the nitrogen atom are directed toward the corners of a (in any case irregular) tetrahedron whose fourth corner is occupied by the nitrogen atom itself"*.[18, 21]

Perhaps it was his background as an organic chemist that made Werner the one person that could interpret the coordination chemistry found in inorganic compounds. He first presented his coordination theory at a lecture in 1892, at the age of 26, where Werner suggested that single atoms (or ions) act as central positions, where a certain number of other compounds, atoms, ions or other molecules are ordered in simple geometric patterns.[18, 20] The idea is said to have come to Werner at 2 a.m. one morning, after he had pondered a long time, and by 5 p.m. the theory was essentially completed.[20] Every pattern expresses the number of atoms thus grouped round a central nucleus called *second valence*, which Werner changed to *coordination number*, a term separate from the *first valence* (ionic charge).[16] This theory could successfully explain why certain compounds existed in only two forms, instead of three (see Chapter 2.4.4.1). Werner's theory could also explain the behaviour of different amminecobalt(III) chlorides when reacting with silver ions, forming certain equivalent ratios of solid silver chloride, and why they did not react at all with acid (Table 1).

Table 1. A comparison between the old way of writing coordination compounds. Only Werner's way offers an easy overview of the correct structure.

Old formula	Colour	Eqv. AgCl formed	Werner's formula
$CoCl_3 \cdot 6\ NH_3$	orange	3	$[Co(NH_3)_6]Cl_3$
$CoCl_3 \cdot 5\ NH_3$	purple	2	$[Co(NH_3)_5Cl]Cl_2$
$CoCl_3 \cdot 4\ NH_3$	green	1	$[Co(NH_3)_4Cl_2]Cl$
$CoCl_3 \cdot 3\ NH_3$	green	0	$[Co(NH_3)_3Cl_3]$

The difference between these compounds was in the way the chloride was bound to the metal ion, either as a tightly bound, directly coordinating *chloro* ligand or as a one-step removed more loosely bound *chloride* counter ion. He also made clear why two different ammineplatinum(II) chlorides, with seemingly different structure in Blomstrand's view, showed the same level of conductivity (zero).(Table 2)

Werner was offered a professorship in 1893 from Universität Zürich in Switzerland, a position he held for the rest of his life. In 1913, Alfred Werner was awarded the Nobel Prize in Chemistry *"in recognition of his work on the linkage of atoms in molecules by which he has thrown new light on earlier investigations and opened up new fields of research especially in inorganic chemistry."*[22] Werner's contributions to coordination chemistry is used almost in unchanged condition today and a wider study of the philosophical implications of the history of stereochemistry has been presented by Ramberg.[23] It was Werner that developed the long form of the periodic table of elements, a version first used by Victor von Lang.[24] He also continued to produce articles after he received his Nobel Prize, mainly in the field of organic chemistry.[25, 26] Alfred Werner died in 1919.

Table 2. A comparison between Blomstrand's and Werner's notation. Werner's way of writing describes the proper configuration seen in Chapter 2.4.2.

Blomstrand notation	Free Cl^-	Werner notation	Free Cl^-
$Pt(NH_3\text{-}NH_3\text{-}Cl)Cl$	1	*trans*-$[Pt(NH_3)_2Cl_2]$	0
$Pt(NH_3\text{-}Cl)_2$	2	*cis*-$[Pt(NH_3)_2Cl_2]$	0

1.2.2 Modern coordination chemistry

The way of writing complexes today is the modern style of the one originally proposed by Werner. It describes how a coordination complex of any kind, ML_n, where n peripheral atoms, ions or molecules L (ligands or ligand atoms) are bound to the central atom M. By determining the internal geometrical shape formed when linking the locations of the L atoms to one another we can group different complexes (Fig. 5).[27] A detailed description of the most common configurations and geometries is given in Chapter 2.4.

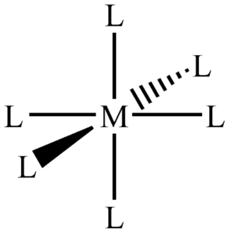


Fig. 5. A graphical representation of a typical octahedral complex. The short notation is ML_6.

Coordination chemistry is of course not limited to the fairly simple ammine complexes Werner studied, but has grown into a large sub-division of both inorganic and organic chemistry. Coordination chemistry often revolvs around the elements found in the centre portion of the periodic table of elements, including but not limited to the transition elements, Group 12, and the lanthanoids.

The ligands are often divided into how many possible donor atoms they contain, normally one to six. The L atoms can all belong to separate molecules or be part of a larger ligand. Werner's example ammonia has one donor atom (the nitrogen), and is referred to as a *monodentate* ligand. Other ligands have two or more donor atoms, and are named *bi-, tri-, tetra-, penta-*, *hexa- etc.* using the prefixes accordingly. The collective term *chelate* is applied to polydentate ligands that form ringlike structures.[28] One common chelating compound is ethylenediaminetetraacetic acid (EDTA), which has a total of six donor atoms (four oxygen and two nitrogen ones) and thus is *hexadentate*.[29] This fairly general definition of a coordination compound is the one that will be used for the remainder of this thesis.

1.3 Lanthanoids – a troublesome group

Today, there are quite a few different names used to describe the group of elements that include the row starting with lanthanum and ending with lutetium. The International Union of Pure and Applied Chemistry (IUPAC) has since 1965 recommended that the name *lanthanoid* should be used when referring to these elements *alone*, a ruling followed in this thesis.[29, 30] The main reason for the decision, moving away from the old term *lanthanide*, is that the ending *-ide* only should be used describing monoatomic anions (or polyatomic homonuclear ions) such as chloride (Cl^-) and sulfide (S^{2-}). In spite of this, a few exceptions (hydroxide, cyanide, *etc.*) are allowed to exist due to their historical and widespread use. Table 3 lists a few of the group of names that should be used to describe the lanthanoids and related elements, indicating which other elements that are included in that name. It should be stressed, however, that in older documents and other scientific papers not following the IUPAC recommendation, the terms and definitions used are unfortunately at the discretion of the author. Some of the reluctance to use the word lanthanoid for lanthanum is warranted, as the meaning is "lanthanum-like". On the other hand, what other element could be more alike than the element itself? Some recommended and outdated names of the individual lanthanoid elements are treated in Chapter 1.3.1.4

Table 3. The collective names approved by IUPAC that include the lanthanoids.

Collective name	Sc	Y	La-Lu	Ac-Lr
lanthanoids, Ln			×	
Group 3 metals	×	×	×	×
Rare earth metals, RE	×	×	×	
f-block elements			×	×

1.3.1 Lanthanoids in the periodic table of elements

At the time when Dmitri Mendeleyev published his periodic table of elements, in 1869, he had no good place for the lanthanoids (Fig. 6).[13] This was in line with the knowledge of the period, considering the fact that most lanthanoids were not yet discovered (see Chapter 1.3.2.3) and those that had been described still were swamped with anomalies and thus lower credibility, even if Mendeleyev did not know this. His building effort has been compared to completing a jigsaw puzzle where one third of the pieces are missing and others bent.[15] Hence, the lanthanoids were somewhat unmanageable from the start, but not really needed to finalize the periodic studies – later dubbed *Mendeleyev's periodic law* – which he performed on the main series elements. The importance of finding all lanthanoids was, at least in Mendeleyev's view, low. In fact, the Russian was so determined that he was correct and instead put the blame on others suggesting that some atomic weights were calculated erroneously and essentially saying that "*science was wrong and he was right!*"[7] Also, he was daring enough to simply leave positions empty, where he expected an element to be, giving specific properties (with overwhelming accuracy) of the elements to be discovered. Later, this strategy turned out to be a sensible one, as the empty spaces were filled with elements that fit Mendeleyev's predictions very well (see Chapter 1.3.2.3), and this is the reason why he is considered the true father of the periodic table.[7, 14]

Over 30 years later, when all but one of the lanthanoids were discovered, Mendeleyev's system was questioned once again. Scandium, one of the rare earths, had supported the scheme, but there was no obvious place for the remaining rare earth elements. The final solution, presented principally by Carl Benedicks in 1904, was based on the molar volumes of the lanthanoids, in spite of the fact that not all were firmly established.[31]

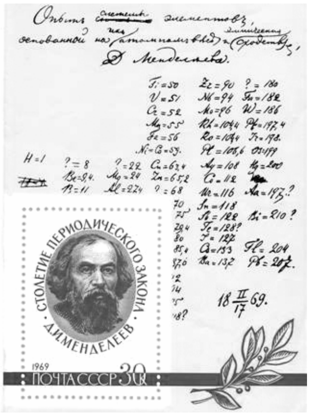


Fig. 6. A commemorative stamp issued on the 100th anniversary of Mendeleyev's original publication of the periodic table. The notes shown are reprints of Mendeleyev's own, dated February 17, 1869 (March 1, 1869 in the Gregorian Calender).

The molar volumes were estimated from the oxides, chlorides, and sulfates, and he deducted that the linearity seen between cerium and tungsten should reduce all of the lanthanoids to one single spot in the periodic table. This reasoning was accepted, and once and for all saved the layout that Mendeleyev originally had proposed thirty-five years earlier. The periodic table of elements has undergone some changes over the since then, and new elements are still added.[32, 33] A decisive suggestion to the placement of the start and end of the lanthanoid series in the periodic table was proposed in 1982 by Jensen.[34]

1.3.2 History, discovery and etymology

If there is one place on Earth that is more tightly linked to the periodic table of elements than all others, the honour is likely to fall on the quartz and feldspar quarry Ytterby on the island Resarö in the Stockholm archipelago in Sweden.[4, 35] Its name has been the root for no less than four elements (yttrium, terbium, erbium, and ytterbium), and should probably receive at least partial credit for the name of an additional three (scandium, holmium, and thulium), and was also the origin of the discovery of yet another element (tantalum). In 1989, the importance of the Ytterby mine was designated historical landmark in the history of metals by the American Society of Metals.[36] This fascination for one single locale is explained by the combined historical facts of Swedish porcelain manufacturing, geological novelty, and some of the greatest experimental chemists in history.

1.3.2.1 Swedish porcelain and the Ytterby quarry

The production of porcelain in Sweden started a few years after two Germans, Johann Friedrich Böttger and Ehrenfried Walther von Tschirnhaus, 1708 had discovered the secret of feldspar-based ceramics.[37] Up until then China was the producer of finer pottery, still reflected in the words *china* and *chinaware*. Possibly the most famous Swedish factory, Rörstrand, was founded in 1726 in Stockholm, to be followed by Marieberg in 1758 and later Gustavsberg in 1825. This created a large demand for both quartz and feldspar and this was just what the Ytterby quarry could supply. The excavation had started in the 17th century, but increased significantly during the latter half of the 18th century. The extracted igneous rock, pegmatite, consists mainly of typical minerals quartz, red and white feldspar, and dark mica.[38, 39] Pegmatites are known for their large crystals, formed late in the cooling process from aqueous solutions.[40] This often leads to high concentrations of unusual minerals, as in the pegmatite deposit found at the Ytterby mine.

The first recognition of the unusual properties of the Ytterby rocks was made by Carl Axel Arrhenius who found a black mineral which he named *ytterbite*, later described as the mineral with the greatest importance for the development of inorganic chemistry.[41] The first scientific description of the mineral was performed by Bengt Reinhold Geijer whom Arrhenius sent a sample. He describes it as a rock with a *"considerable [specific] gravity, found in a red, mixed with silver-coloured mica, feldspar, in considerable amounts."*[42] The first chemical analysis, however, was performed by a chemist from Finland (which at the time was part of Sweden) by the name of Johan Gadolin, who reported that 38% of the mineral consisted of an unknown earth.[43] The discovery of this oxide of the unknown element was shortly thereafter confirmed by other chemists in Sweden, France and Germany, and a proposal of changing the name of the mineral to *gadolinite* was later accepted.

Two other important minerals found at Ytterby were *fergusonite* and *yttrotantalite* in which tantalum eventually would be discovered. Their composition are listed in Table 4 together with gadolinite, but it was through gadolinite that Ytterby received most of its fame. The quarry at Ytterby was in use until 1933 when stone production stopped completely. Today, the former mine is little more than a overgrown hole in the ground, though the names Rörstrand and Gustavsberg still attract attention.

Table 4. The composition of some of the minerals found at the Ytterby and Bastnäs locales. The minerals are sometimes divided into subcategories, indicating which part of the lanthanoid series that is overrepresented. (RE = rare earth element)

Mineral	General formula
gadolinite	$(RE)_2FeBe_2Si_2O_{10}$
fergusonite	$(RE)(Nb,Ta)O_4$
yttrotantalite	$(Fe,RE,U)(Nb,Ta)O_4$
cerite	$(Ca,Mg)_2(RE)_8(SiO_4)_7 \cdot 3H_2O$
bastnäsite	$(RE)FCO_3$

1.3.2.2 Bastnäs, another geological curiosity

In a rock originally found on the other side of Lake Mälaren, at the iron and copper mine at Riddarhyttan, more precisely the Bastnäs field,[44] a similar discovery was done prior to the ytterbite/gadolinite observation at Ytterby. The unknown iron mineral had been discovered and analyzed in 1751 by Axel Fredrik Cronstedt, and he classified it as “tungsten from Bastnäs”.[45, 46] Thirty years later Swedish pharmacist and chemist Carl Wilhelm Scheele and Spanish chemists Juan Jose and Fausto de Elhuyar separately re-examined the mineral, but they neither found indications of the tungsten oxide Scheele had found in 1781 nor the tungsten metal the Spanish brothers successfully had described in 1783. Moreover, they did not find any new elements either to explain the composition.[47] It was not until 1803 when Jöns Jacob Berzelius and Wilhelm Hisinger revealed the true nature of the mineral, an unknown one, which they named *cerite* after the newly discovered asteroid Ceres.[48] Another mineral found 1838 at the same location, named *bastnäsite* 1841 by French mineralogist Jean Jaqcues Nicolas Huot, signals the connection between the mine and the lanthanoids. It was nevertheless cerite, together with gadolinite, that would be the starting materials in which all the naturally occurring lanthanoids ultimately would be obtained.

1.3.2.3 Sorting the mixtures

In these early days of chemistry, the discovery of a new element did not necessarily mean that the actual element was isolated. The identification of a new *earth*, an obsolete word of alchemic origin meaning *oxide*, was enough evidence for a new element. Based on this premise, the two minerals gadolinite and cerite can be said to be the origin of two different family lines, the yttrium earth (*yttria*) line and the cerium earth (*ceria*) line (see Chapter 1.3.2.4). The 38 per cent "unknown earth" that Gadolin unveiled in the first report was believed to be one single oxide and was aptly named after the point of origin. Gadolin's original suggestion was ytterbium, but it was changed by Anders Gustaf Ekeberg to the shorter *yttrium*.[35] The name ytterbium would, however, reappear later.

The joint effort of Hisinger and Berzelius took a analogous twist, but they could not find the earth described by Gadolin and realized that they had new element on their hands, which they called *cerium*.[48, 49] The story did not end there, in fact, it had just started. Carl Gustaf Mosander, a student whom Berzelius had put to work on various cerium compounds, noted that part of the cerium did not conform to the duality in oxidation state the true metal showed, but did not inform Berzelius about this discovery, possibly out of respect. In late 1838 Berzelius eventually learned about the discrepancy, and after being fully convinced he announced Mosander's accomplishment to the scientific community. Berzelius even gave a suggestion for the name of the new element, *lanthanum*, after the Greek word for "to escape notice" *lanthanein* – after all it had been hiding from him for a third of a century.[4] Mosander continued the work on lanthanum, and discovered in 1840 (though published first in 1842) yet another element in the mist, which he called *didymium*, after *didymos* the Greek word for "twin".

The hidden elements in the cerium earth, also made Mosander work on the yttrium earth, as other elements possibly also were hiding there. In the fall of 1842, he did in fact come to realize that the yttrium oxide found by Gadolin was a mixture of another oxide. At first he intended to call the new metal odinium after the Norse god Odin, but continuing investigations showed that there was a total of three oxides, and followed a different scheme. The one with the highest basicity kept the name *yttrium*, the next in one in order (a rose coloured salt) was called terbium, and the least basic one a deep yellow peroxide was named erbium. Repeated investigations performed by Swedish chemist Nils Johan Berlin only found yttrium and the rose coloured salt, which he re-named *erbium*. Since Mosander's terbium could not be found again, Berlin's name was accepted. Later, when Marc Delafontaine recovered the yellow peroxide again, Mosander's terbium had been definitely assigned the name erbium. The introduction of spectral analysis used by Delafontaine confirmed the original findings, and *terbium* (the original erbium) was finally recognized as an element (by Marignac in 1878 and Henry Enfield Roscoe in 1882) forty years after Mosander's initial discovery.[4, 35] Two elements had become six, and the quest of separating these six continued.

Jean-Charles de Marignac (1817-1894) noticed in 1878 some inconsistencies in the erbium salts, yielding both red and colourless crystals, in which he concluded that there were really two elements. The element in the red salts retained the name erbium, whereas the new element was dubbed *ytterbium* (Gadolin's original name for the element yttrium) One verification of de Marignac's ytterbium was made in Uppsala by Lars Fredrik Nilson in a Norwegian mineral called *euxenit*. After a few months, he succeeded finding ytterbium in the mineral, but in parallel experiments yet another unknown earth emerged! It turned out to be a metal with only a few properties separate from ytterbium but with a significantly lower atomic weight. Nilson's suggestion calling the metal *scandium* was based on the fact that the two minerals gadolinite and euxenite only had been discovered on the Scandinavian peninsula.[50] The detection of scandium was at the time more important than those of the lanthanoids, as it confirmed Mendeleyev's prediction of the element he had named *eka-boron* in 1872. With almost frightening prediction, Nilson's scandium added to the confirmation of the periodic table proposed by Mendeleyev (Table 5).

The same year, 1878, Cleve studied the erbium where ytterbium had been removed and managed to separate yet another two elements through spectral analysis – *thulium* (after the old Roman name for the outmost north, Thulia) and *holmium* (after "Holmia" the Latin name for Stockholm, or possibly an attempt of self-immortalization by the person suggesting the name and discoverer of the pure metal, Otto Holmberg)[35, 51].

Table 5. Comparison of a few selected properties between Nilson's scandium and Mendeleyev's eka-boron. The connection between the prediction and the discovery was the work of Per Teodor Cleve.

	Scandium, Sc	Eka-boron, Eb
Year of discovery	1878	1869-71 (prediction)
Relative atomic mass	44.956	~45
Oxide	Sc_2O_3	Eb_2O_3
Specific gravity (oxide)	3.8	~3.5

Indications of holmium had been seen by Marc Delafontaine and Louis Soret in their element erbium-X, and it was later proven that this element was identical with the holmium reported by Cleve. Delafontaine continued his effort, observing that absorption spectra from cerite and another mineral samarskite yielded two different didymium samples. Paul-Émile François Lecoq de Boisbaudran followed up this work and discovered the element which he named *samarium* in 1879. de Marignac also studied samarskite and after retrieving two different oxalates, he consulted Soret who performed a spectral analysis in which both samarium and one more element, *gadolinium*, was found.[4, 35] The metal was duly named in honour of Johan Gadolin, the chemist who started the investigations on the lanthanoids.

Carl Auer von Welsbach continued the work on Mosander's didymium, and, through more than a hundred fractional crystallizations, reached the conclusion that it consisted of two elements.[4] Here, instead of keeping the old name, he questionably gave both metals new names, *praseodymium* (Greek for "green twin") and *neodymium* (Greek for "new twin"), respectively. This sidestep removed Mosander from most lists of recognized discoverers even some of those that favour Swedish chemists.[52] The holmium isolated by Cleve also turned out to be hiding a new element, as Lecoq de Boisbaudran in 1886 found one more lanthanoid in it, and after all the effort suggested the name *dysprosium* (after the Greek word dysprositos meaning "hard to reach"). Before the turn of the century Eugène-Anatole Demarçy had also fractionally crystallized *europium* from Lecoq de Boisbaudran's samarium, named in honour of the continent Europe.[53]

Another naming controversy that arose a few years later was von Welsbach's claim that de Marginac's ytterbium was a mixture of two elements, which he in

1907 also introduced new names for (just like in the case with didymium), cassiopeium for the old ytterbium and aldebaranium for the new element. Georges Urbain performed parallel studies in Paris, and had reached the same conclusion, though instead calling them neo-ytterbium and lutecium. In a third investigation, the American Charles James had retrieved significant amounts of the new element, but never published his results when he heard of Urbain's progress.[4] Urbain was later credited with the discovery, but the honour could have just as easily been belonging solely to James. Today, all three share the credit of the discovery. The outcome was in any case a new element which ended up with a variation of Urbain's name suggestion, *lutetium*.

Along the line of discoveries, there had been no theory behind how many lanthanoids there actually should be, and by 1907 when all thirteen naturally occurring ones hade been detected, the theory was still in the making. When Henry G. J. Moseley introduced a model in 1913 based on high-frequency X-ray spectra,[54, 55] (Fig. 7) and physicist Niels Bohr interpreted this in 1918 as an expansion of the fourth quantum group from 18 to 32 electrons,[56] it was obvious that there was one more lanthanoid still to be discovered, the elusive element 61. The story of the last rare earth element is told in Chapter 4.5.

1.3.2.4 Naming the lanthanoids

As we have seen, finding a new element has never been an easy task, not even in the times when new elements were found on a yearly basis. It should also be obvious that an equally challenging feat is to assign the honour of the *actual* discovery of an element. The criterion for discovery has changed over the years, sometimes to fit personal and national interests. This means that the discoverer could be the first person who recognizes a compound in which the element exists, and not necessarily the scientist that performs the actual isolation of the element itself. The general rule is, however, that the recognition falls upon the first official public statement of a discovery, though independent discoveries are usually given equal amount of respect, at least when it comes to historical findings.[35]

Also, the use of a certain language can contradict a straightforward scientific treatment as seen in the tungsten *vs.* wolfram debate.[29, 57, 58] Additionally, the discoverer often proposes a name for the element, but it is not certain that the name made it over the years. The so-called *erbium/terbium controversy* is not the only name confusion in lanthanoid history. The case with didymium and praseodymium is another example, and a suggestion that *didymium* even should be reinstated as the name for element 59 has been put forth, though it is unlikely to succeed.[4] A list of names of both existing and non-existing lanthanoids is shown in Table 6, and serves as an excellent example of both the discovery and naming problem, partially due to the difficulty with which the elements were obtained.

The lanthanoids can be classified from the different minerals in which they were first found, and Figures 8 and 9 is essentially a pictorial summary of the previous chapter.

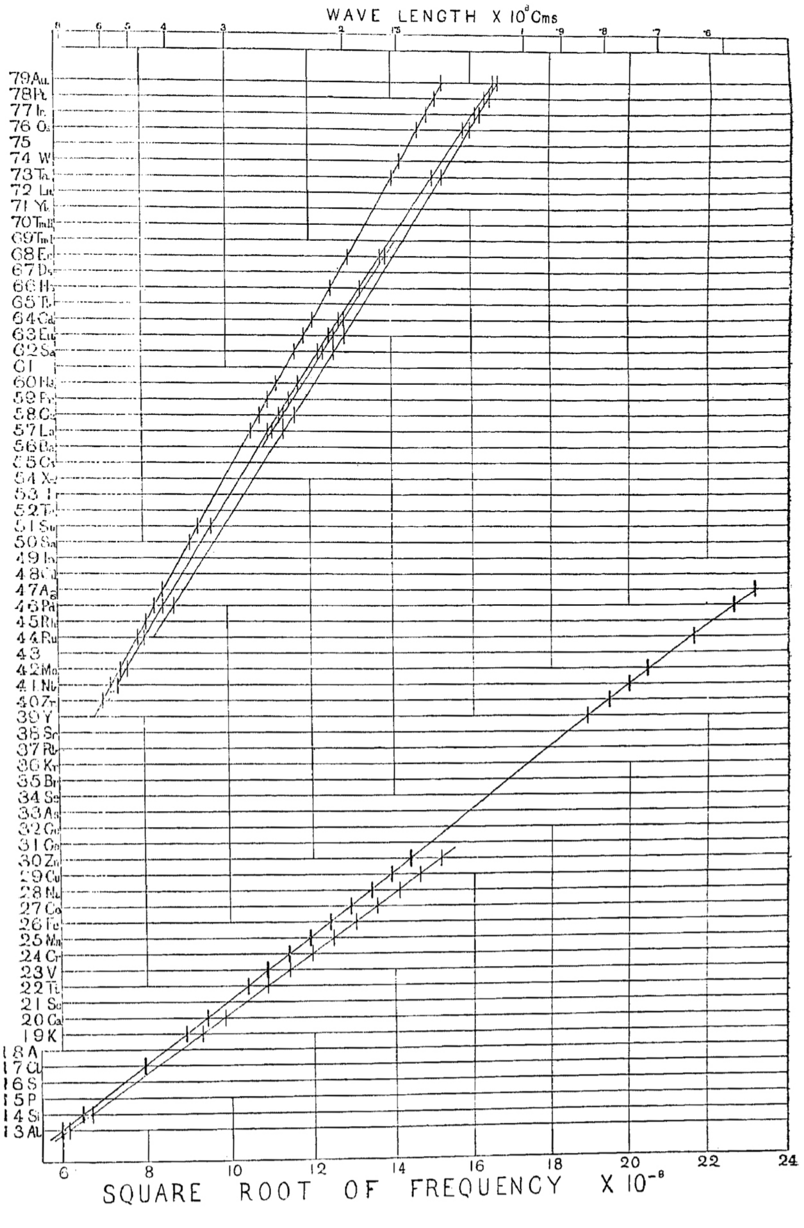


Fig. 7. Moseley's chart of high-frequency spectra. Moseley was able to predict unknown elements, without even having access to them. By measuring the principle lines in X-ray spectra, he could deduce that three elements were missing with atomic numbers 43, 61, and 75 (from ref. 55).

1.3.3 Abundance and usage

The term *rare earth* is an unfortunate one, at least to describe the abundance of the rare earth elements. Even the least common one (except the radioactive element 61, promethium) thulium, is more abundant than iodine (0.5 ppm in the earth's crust).[59] As has been said before, earth refers to the obsolete word for oxide. Finally, rare earth is ambigious from a different point-of-view as well, as it in the beginning included oxides that were not true rare earths, *e.g.* thorium oxide and zirconium oxide.[60] The largest rare earth metal deposits, in the form of bastnäsite and monazite, are found in China and the United States.[60] In-depth descriptions of the original Swedish locations, Ytterby and Bastnäs, are included in larger studies performed by the Geological Survey of Sweden, SGU.[44, 61]

The lanthanoids are often used without separation, for instance in steel to improve strength and workability, and in magnesium alloys in the production of lighter flints. Scandium is extensively used in lasers, and it is worth noting that in 1984 the price for scandium went from 10,000 to 75,000 US dollars per kg when laser research increased demands in the main exporting country Soviet Union, but prices dropped the year after when deposits were found in the United States.[62] Some refined lanthanoids have found their way into the production of permanent magnets, fluorescent screens and high temperature superconductors.[60] Rare earth element trifluoromethanesulfonate salts are used as catalysts in some organic chemical reactions.[63, 64]

Table 6. Some of the original suggestions and alternative names of the lanthanoids. In 1911 Carl Auer von Welsbach reported that it was supposedly possible to split terbium into two elements and thulium into three new elements, which prematurely were named by Josef Maria Eder (denebium, dubhium, eurosamarium, neothulium, and welsium). It turned out that the recorded spectra were merely complex mixtures of already known rare earth elements, and are not included in the list.

Name	Name suggested by	Accepted name today
aldebaranium	Auer von Welsbach	ytterbium
cassiopeium, Cp	Auer von Welsbach	lutetium
cererium	Klaproth	cerium
cyclonium	Quill *et al.*	*
didymium, Di	Mosander	neodymium, praseodymium
decipium, Dp	Delafontaine	samarium
element X	Soret	holmium
erbium	Mosander	terbium
florentium, Fr	Rolla & Fernandes	*
illinium	Hopkins *et al.*	*
mosandrum	Smith	terbium and holmium
neoytterbium, Ny	Urbain	ytterbium
philippium, Pp	Delafontaine	holmium
terbium	Mosander	erbium
ytterbium	Gadolin	yttrium

* The proposed elements cyclonium, florentium, and illinium were all claims of element 61, *promethium*. None of the experiments could be confirmed and the names and claims were therefore rejected.

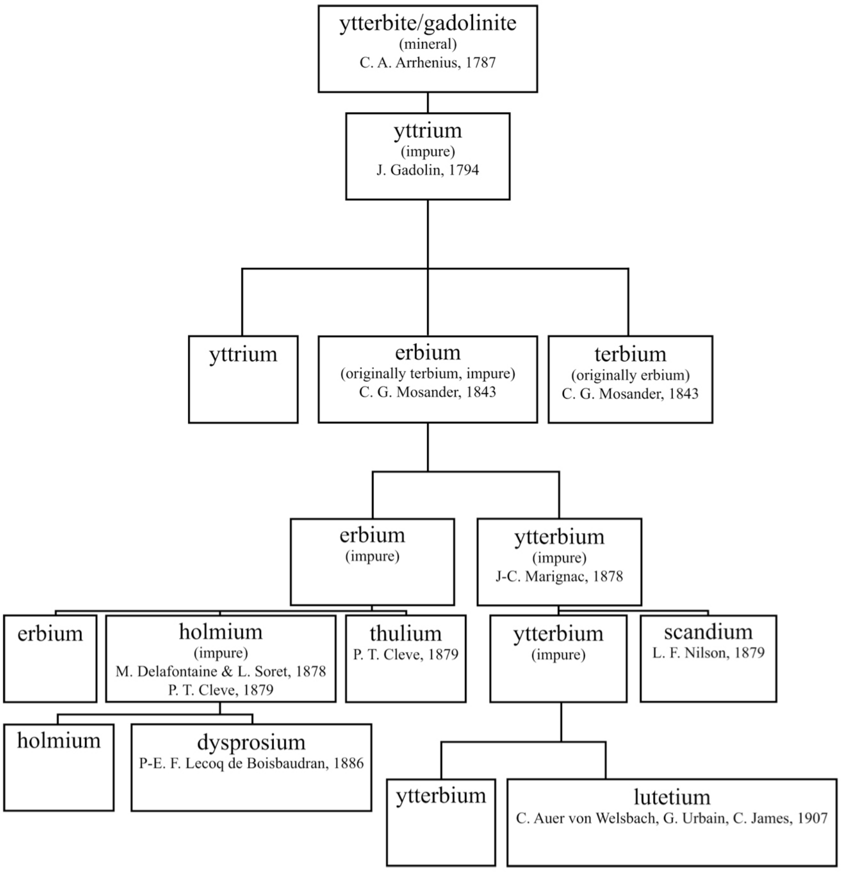
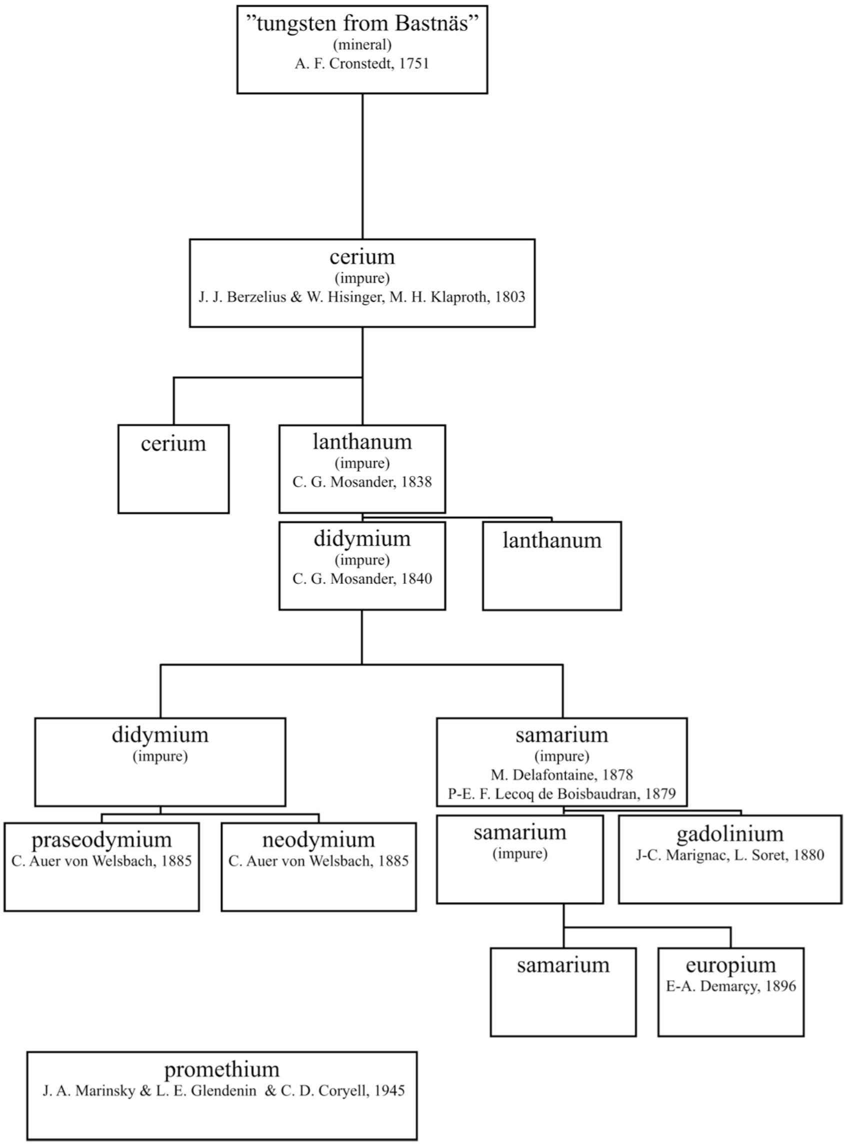


Fig. 8 and Fig. 9. The genealogy of the lanthanoids. The complex compositions of the two starting minerals *gadolinite* (ytterbite) and *cerite* ("tungsten from Bastnäs") is revealed in the flow chart of the discoveries of the elements. Promethium forms a separate line.


”tungsten from Bastnäs”
(mineral)
A. F. Cronstedt, 1751
cerium
(impure)
J. J. Berzelius & W. Hisinger, M. H. Klaproth, 1803
cerium
lanthanum
(impure)
C. G. Mosander, 1838
didymium
(impure)
C. G. Mosander, 1840
lanthanum
didymium
(impure)
samarium
(impure)
M. Delafontaine, 1878
P-E. F. Lecoq de Boisbaudran, 1879
praseodymium
C. Auer von Welsbach, 1885
neodymium
C. Auer von Welsbach, 1885
samarium
(impure)
gadolinium
J-C. Marignac, L. Soret, 1880
samarium
europium
E-A. Demarçy, 1896
promethium
J. A. Marinsky & L. E. Glendenin & C. D. Coryell, 1945

2 Basic Concepts

In the chapters below the chemistry, upon which the collected works in this thesis are built, is explained. The theories and definitions described herein are vital for coordination chemistry, but should not be taken as full descriptions of their respective areas as this falls outside the scope of this thesis.

2.1 Hard and Soft Acids and Bases (HSAB) Theory

Even before Werner formulated his ideas for coordination chemistry, chemists had noticed that certain elements paired up more easily with some elements than others. In the early days, this observation was sometimes mixed up with other properties of the compounds involved, but the need to systematize chemistry has been an integral part of chemistry since Mendeleyev used some of the noted similarities in solving his puzzle for the first proper periodic table of elements.[7]

Systematization attempts in coordination chemistry started in 1958 when a first proposal was put forth to classify various metal complexes by their complex formation stabilities. It was based on the complexes with halide ions (fluoride, chloride, bromide, and iodide), where *class a* and *class b* metal ions formed two separate groups: $F^- >> Cl^- > Br^- > I^-$ (class a) and $F^- << Cl^-, Br^- < I^-$ (class b).[65] An extended view of this way of looking at donor and acceptor atoms was introduced a few years later by Pearson, a model called hard and soft acids and bases or *HSAB theory*,[66] making use of Lewis' definition of an acid (electron-pair acceptors; metal ions and the proton) and a base (electron-pair donors; ligands). The *hard* acids and bases (non-polarizable, or *class a* in the previous terms) are those metal ions and ligands with weak electron-pair acceptor and donor properties forming bonds with mainly electrostatic interactions. The *soft* ones (*class b*) are those classified as strong electron-pair acceptors and donors establishing dominating covalent interactions between each another. There are a number of *borderline* cases, which means that the classification has been used as a guideline rather than law, but the general rule is that hard acids prefer hard bases and vice versa, useful information for many organic reactions.[67]

Hard metal ions have multiple charges and are small, with a high charge density and thus high electrostatic interactions as a consequence. The scandium(III) and aluminium(III) ions serve as good examples for hard Lewis acids, which coordinate best to correspondingly small, electronegative ligands (Lewis bases) coordinating through fluorine or oxygen donor atoms. On the other side of the spectrum, we find that soft metal ions have low charge densities (often singly charged and large ionic radius), among them the noble metal ions gold(I), silver(I) and platinum(II), where the presence of the many *d*-electrons make them easier to polarize. The soft donor atom ligands (including phosphorous and sulfur), have low electronegativity. Table 7 lists the hard/borderline/soft designation for the metal ions and solvent ligands included in this thesis.

Table 7. The hard and soft acids and bases (HSAB) theory. The Lewis acids and bases presented in this thesis are included with a few examples as listed by Pearson (R = carbon chain of undetermined length).

Hard Lewis acids	Borderline Lewis acids	Soft Lewis acids
H^+, Na^+, K^+		Cu^+, Ag^+, Au^+
Be^{2+}, Mg^{2+}, Sr^{2+}	Fe^{2+}, Ni^{2+}, Zn^{2+}	Cd^{2+}, Pd^{2+}, Pt^{2+}
Sc^{3+}, Fe^{3+}, Ln^{3+}		Tl^{3+}

Hard Lewis bases	Borderline Lewis bases	Soft Lewis bases
H_2O, NH_3, R_2O		RSH, R_2S
Cl^-, NO_3^-,	Br^-	I^-, CN^-

2.1.1 Classification of solvents

In addition to the HSAB theory, a number of scales have been constructed for classification of the electron-donor capabilities of solvents. Gutmann's donor number, D_N, was the first one and is perhaps the best known of these scales.[68] It is based on calorimetric measurements and derives its values from the heat of reaction of antimon pentachloride and the ligand under study in benzene solution, $SbCl_5 + L \rightarrow SbCl_5L$. A more relevant scale when dealing with strong electron-pair donors was developed by Sandstöm *et al.*[69], D_S, which takes soft-ligand properties into consideration. The designated D_S value for each solvent is obtained by studying the difference of the symmetric stretching vibration of mercury(II)bromide, v_1(Hg-Br), in gaseous phase and the solvent under study, $D_S = v(HgBr_2)$ (g) - $v(HgBr_2)$ (solv.). The D_N and D_S scales are oftentimes comparable, but there are some examples where they do differ significantly.[70]

2.1.2 Oxygen donor solvents

Ligands including an electron-pair donating oxygen atom are almost all hard, and among them we find some of the most common solvents in chemistry, *e.g.* water, alcohols, ethers, ketones, carboxylic acids, amides and sulfoxides. The physical chemical information available for these solvents, particularly water, is much too broad to be included in this thesis. Therefore, the main focus is an attempt to explain the difference between three main groups: water, other non-space-demanding oxygen electron-pair donor solvents in general (DMSO in particular) and space-demanding oxygen donor solvents (with a focus on DMPU). A brief look at non-oxygen solvents (including DMTF) is included in the end.

2.1.2.1 Water

The most striking property of water is its hydrogen bonding ability. In solid state, water transforms to ice with an intricate system of hydrogen bonds, separating the water molecules at a slightly longer distance than in liquid water. This in turn makes ice less dense, resulting in the chemical abnormity of a solid that floats in its own liquid. Hydrogen bonds are also the reason why water is a liquid at room temperature. This tremendously important physical property is not seen in the related group 16 compounds H_2S, H_2Se, or H_2Te.

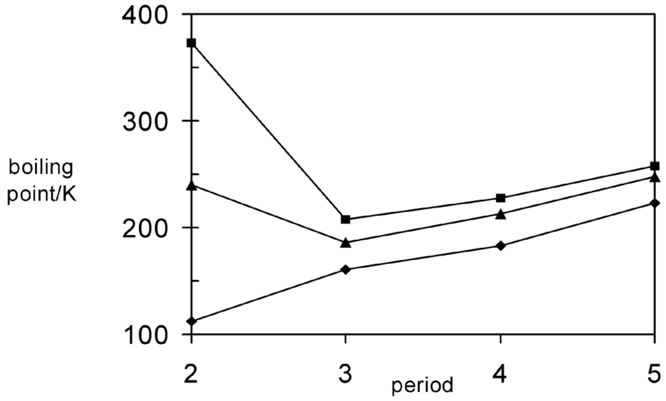


Fig. 10. Boiling points of the hydrogen containing compounds of Group 14 (♦), 15 (▲), and 16 (■). Normally, boiling points increase further down in the same group, but the relatively strong intermolecular hydrogen bonding produces anomalous values for water (H_2O) and ammonia (NH_3).

Similar effects, though much weaker, is seen in hydrogen fluoride and ammonia in the corresponding series for the neighbouring group 14 and 15. A yet weaker effect would be visible for methane in the group 14 analogue, but is non-existing due to the geometry of methane and methane-like compounds (Fig. 10).

The strong hydrogen bonding in water is uniquely reflected in its coordination chemistry, for instance in the hydrates of the early lanthanoids where it reaches stable nine-coordination, a coordination number that remains throughout the remaining lanthanoids, although the occupancy number is reduced across the series.[71] Selected physical chemical properties for water are listed in Table 8.[72]

2.1.2.2 Other non-aqueous oxygen solvents

There are, of course, many other oxygen electron-pair donating solvents. Alcohols, DMF, DMSO, and various urea derivatives are just a few of the most common ones being used in both inorganic and organic chemistry. The alcohols are to some extent intermediates, sharing some of the properties of water but also some of the aprotic solvents (solvents not able to form significant hydrogen bonding). DMSO is a hygroscopic, colourless liquid (at room temperature) with a high dipole moment and permittivity (see Paper IV). Also, DMSO has some hydrogen bonding properties, and is used as a good solvent for electrolyte solutions.[73] It should be mentioned that some very soft metals, for instance palladium(II) and platinum(II) bind to the sulfur atom instead of the oxygen atom. For the metal ions used in this thesis, however, DMSO is solely used as an oxygen electron pair donor.

Table 8. A selection of physical properties of the oxygen donor ligands water and DMPU.

solvent	formula	m.p. [a]	b.p. [a]	D_S [b]	D_N [b]	ε_r [c]	μ [d]
water	H_2O	0.0	100.0	17	18	78.5	1.85
DMPU	$(CH_2)_3(CH_3)_2N_2CO$	-23.8	246.5	34	-	36.1	4.23

[a] Melting point (m.p.) and boiling point (b.p.) given are in °C at atmospheric pressure (1 bar), [b] Donor strength (D_S) and donor number (D_N) are quantitative measures of Lewis basicity. [c] The permittivity (ε_r) listed is relative to that of vacuum, $\varepsilon_0 \approx 8.854 \cdot 10^{-12}$ F/m. [d] The dipole moment is in debye (1 D ≈ $3.335 \cdot 10^{-30}$ C m).

2.1.2.3 DMPU and other space-demanding solvents

N,N'-dimethylpropyleneurea, DMPU is a versatile polar, aprotic solvent with a wide range of uses in the syntheses of pharmaceuticals, dyes and polymers, where it acts as an unreactive co-solvent[74-76] It can also be used for surface cleaning and in hydrocarbon extractions, as the hygroscopic liquid is completely miscible in water. Trichloromethane (chloroform) and dichloromethane (methylene chloride), however, do retain DMPU in the organic phase.[74, 76]

DMPU (CAS no. 7226-23-5) was developed as a less harmful substitute for the carcinogenic substances 1,1,3,3-tetramethylurea, TMU, and hexamethyltriphosphoric amide, HMPA [77, 78], but it is possible that also DMPU may act as a possible chemical mutagen.[79] TMU and HMPA were both used in the many organic and organometallic reactions which needed a dipolar, aprotic co-solvent. Especially HMPA was used extensively, as it is able to strongly solvate cations, but this changed when the carcinogenic activity was noted and the compound was classified as such. Also *N,N'*-dimethylethyleneurea, DMEU (IUPAC name: 1,3-dimethylimidazolidin-2-one) was developed as another safe HMPA substitute, which is effectively used in organic reactions with high basicity.[75]

The first recorded use of DMPU as a coordinating ligand was made by Anderson and Smith in 1990[80], and were followed by a few papers by the Carmalt and Norman research group in the first half of that decade.[81-83] Pure DMPU was studied crystallographically by Armstrong *et al.* in 1992.[84] More recent studies include two Japanese research groups, studying lanthanoid catalysts.[85-87] This thesis and the work surrounding it are part of an extended DMPU study by the Persson group with many publications since the first one appeared in 2000.

The ability to imitate the unreactive, dipolar, and aprotic properties of HMPA was the original justification for developing DMPU (in addition to being non-carcinogenic). This unreactivity is likely caused by the two methyl groups which border the electron donating oxygen atom and a semi-rigid ring structure (Fig. 11). The molecule is said to be *space-demanding (at coordination)*, that is having spatial requirements due to surrounding, non-coordinating atoms (in this case, the methyl groups). These methyl groups have been shown to obstruct the standard coordination chemistry seen in less space-demanding solvents, forming solvates with lower coordination number[1] just like TMU and HMPA.[88, 89]

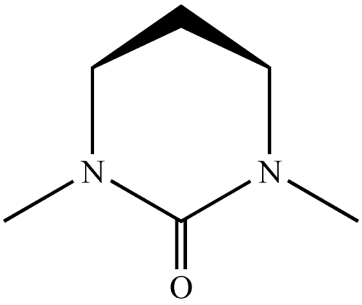


Fig. 11. The chemical structural representation of DMPU. The methyl groups close to the oxygen add hindrance to the coordinating abilities. Hydrogen atoms are omitted for clarity.

Other properties that make DMPU a good solvating agent are its relatively high electron-pair donor ability, high permittivity, high dipole moment, and a wide liquid range (Table 8). Solvates incorporating a space-demanding solvent molecule, such as DMPU, may show a decrease in the coordination number, and a lowering of this kind may alter the chemical reactivity significantly. When compared with their six-coordinated counterparts, five-coordinated solvates, such as nickel(II) in DMPU, show a marked higher ability to form complexes.[1] In spite of their carcinogenic properties, both HMPA and TMU have been thoroughly studied over the years. A search in the *Cambridge Structural Database* (CSD) returns well over 30 structures, both homoleptic and heteroleptic.[90]

2.1.3 Non-oxygen donor solvents

In addition to the many oxygen donating solvents that exist, there are a vast number of other solvent ligands. They are, just like in the case of the oxygen donating ones, often grouped by the actual coordinating atom in each ligand. The following list is by no means complete, but gives an insight into the world of important and common solvents (nitrogen, sulfur, and phosphorus donor ligands) and some of their properties.

2.1.3.1 Non-space-demanding solvents

Among the nitrogen donor solvents, ammonia is a likely candidate for the most studied one. The coordination chemistry of ammonia is well described by Nilsson and the references therein.[70] Other well-known nitrogen donors include acetonitrile and pyridine.[90]

Sulfur donor solvents are often used in parallel studies with oxygen ones, as has been done in the iron(II/III) study in this thesis (Paper IV). This has a natural background, as sulfur belongs to the same group as oxygen which may lead to similar intramolecular binding chemistry, but not necessarily the same coordination chemistry due to the fact that sulfur is much softer and larger than oxygen. The latter property results in sterical hindrance when coordinating to smaller ions. The sulfur coordinating molecules are also much softer bases than the corresponding oxygen ones. The sulfur donor solvent used in Paper IV, *N,N*-dimethylthioformamide, has been thoroughly studied before[91]. Other sulfur coordinating ligands include various thio solvents, *e.g.* thiols and thioethers.

Solvents with phosphorous as the coordinating atom are also available, where alkyl phosphites and phosphines are the most studied types. The uses of these versatile solvents include organic synthesis reactions for production of dyes, pharmaceuticals and flame retardants. A more in-depth introduction has been given elsewhere,[70] and an important physical chemical property of phosphorous ligand solvents is described below.

2.1.3.2 Space-demanding solvents and cone angle

The most familiar examples of space-demanding ligands are probably those of the phosphine family mentioned above. Tolman introduced the term *ligand cone angle* in 1970 as an explanation of steric effects [92] and by 1977 he reviewed the works on the subject "*published through 1975, which best illustrate the basic principles.*"[93] Since then, Tolman's cone angle has been the quantitative measure to describe the space-demanding properties of most common phosphorous ligands. More recently, Müller and Mingos combined the idea of cone angle with the *Cambridge Structure Database*,[90] retrieving a statistical analysis of all reported structures until March 1994.[94] The study revealed that the cone angles were fairly correctly estimated, but the distribution around Tolman's original value was much larger than expected. Similar studies could essentially be performed on any other ligand system (with the same donor atom), where amine ligands were surveyed by Seligson and Trogler.[95] and isocyanides by de Lange *et al.*[96] More recently, Tolman's cone angle idea has been investigated and compared to Platonically perfect sets of angles.[97]

2.2 Solution *vs.* Solvation

Scientific language is very different from the one most of us use on a daily basis. Words like *dissolve* and *melt* are used quite regularly (and in a few different contexts), without the strict scientific definition. To avoid confusion, scientific terms are defined to mean specific occurrences.

2.2.1 Definitions

A *solvent* is any liquid medium which can be used to create a solution. In turn, a *solution* is a homogenous mixture of a *solute* (dissolved substance) and one or several solvents. The most common solvent, though not always thought of as one, is water. *Solvation* takes place when a solid substance is dissolved in a solvent, forming a solution, where the solvated ions or molecules, are surrounded by solvent molecules. In aqueous solutions, solvation is called *hydration*. We can thus see that the systematic and clear notation of thermodynamics is needed to avoid ambiguity. The various expressions including the words *enthalpy* and *entropy* are also a vital part of thermodynamical texts. The full definitions of these terms are covered in most introductory chemistry textbooks, but enthalpy is in simple terms the heat flow in a system and entropy is a measure of the disorder of a system.[98-100] It should be pointed out that usually it is the difference or change (symbolized by Greek letter delta, Δ) in enthalpy or entropy between two conditions that is measured, as it may be hard or even impossible to determine the absolute values.

2.2.2 Solvation energy

For solvation to occur spontaneously, the total enthalpy change (ΔH) and the product of the thermodynamic temperature and the entropy difference ($T\Delta S$) needs to be energetically favourable. The sum is called the *linear Gibbs energy relation*, written $\Delta G = \Delta H - T\Delta S$. The enthalpy change can be determined by comparing the lattice energy with the heat of solvation (Fig. 12).

The entropy portion is slightly harder to visualize. Nature strives towards more disorder (the total entropy increases continuously), which means that a more disordered (chaotic) system is more advantageous. This often promotes solvated ions compared to the precise properties of the solid state.

2.2.3 First and second coordination shell

The first coordination shell is usually the object under study, as the greatest influence of the central ion is found in it. The mean distance between the first coordination shell ligands and the central ion is also the most often quoted value in binding purposes.[101] A second coordination shell is formed if there are strong intermolecular forces present (essentially only hydrogen bonding), where also interactions between the first and second shell are fairly often observed (Fig. 13).

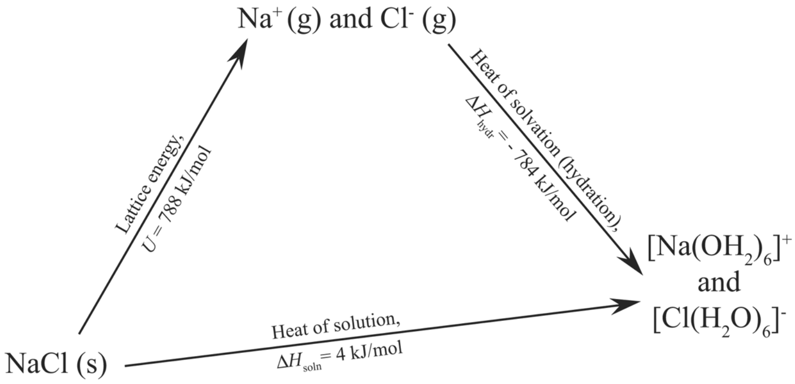


Fig. 12. The enthalpic part of the solution process for table salt, NaCl, shown in thermodynamical terms. The process can be thought to take place in two separate steps, where the outcome is hydrated sodium and chloride ions (after Chang, ref. 99).

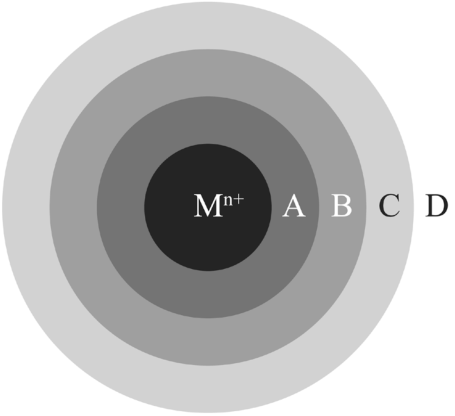


Fig 13. A schematic cross-section of the different regions of solvation for a metal ion M^{n+}. The first solvation (or coordination) shell, A, is well-ordered. The second shell, B, is not as ordered, but for aqueous solutions and multiple charged ions it may be. A disordered region, C, may be present before reaching the bulk solution, D (after Burgess, ref. 102).

A definite second solvation shell, however, is only seen when either well-defined bonds are formed between the molecules in the first and second shell (particularly in aqueous solutions) or in solvents with very low dielectric constants, that inefficiently reduce the charge of the solvated ions (or more often ion pairs). In older theoretical calculations, the effect of a second coordination shell was normally not included, but today thanks to greater computer capabilities they can be. One should keep in mind that this model is based on the situation in very dilute solutions. The true situation in a system should, if possible, be determined in each case.

2.2.4 Bulk Solution

Bulk solution is described as the part of the solvent not involved in the solvation of the solute(s). The solvated clusters, including the coordination shells just described, interact with the bulk solution, in the same sense a solvent molecule would do. The bulk structure observed in water is as we have seen in Chapter 2.1.2.1 somewhat unique with its complex system of hydrogen bonding. For water, with its specific three-dimensional structure, there is sometimes not a smooth transition between the second coordination shell and the bulk solution. In these instances, it may be needed to include a disordered region in the calculations to rectify the mismatch.[102] Essentially only liquid ammonia and methanol comes close to a structure similar to that of water, although a few other solvents show some effects of their hydrogen bonding.

2.2.5 Complex formation

To look at the ability to form complexes has long been a way of determining the reactivity of different compounds. It was used in the classification of HSAB theory and is still used to resolve certain configurational issues not detectable by any other means.[1, 66] The ability to form complexes can be evaluated through equilibrium constants. Large databases on this subject are available.[103]

2.3 The ionic radius

One of the most easily recognized trends in the entire periodic table of elements are the atomic and ionic radii. They are, of course, tightly connected to the electronic configurations of the atom or ion in question and the type of outer-shell electrons that surround it.[101] These electronic properties then in turn are responsible for the chemistry of the element, and is as important to chemists today as they were at the time of the first periodic classifications.

Since very few elements participate in reactions in their elemental form, it is normally the ionic radius that is listed in textbooks and papers. It is usually an ion or at least an "activated" atom in a molecule that form all the compounds we are familiar with, not the element itself. This makes most metals less common than their oxides, halides, *etc.*, where the noble metals (*e.g.* gold, platinum, and silver) are exceptions as their native state in nature is the elemental form.

An ionic radius depends mainly on four properties: the charge of the ion, the coordination and configuration of the ion, the number of electron shells, and whether the ion is in a high or low spin state.[101] In the case of the lanthanoids and other elements with high atomic number, relativistic effects are added to this list, for the lanthanoids called the *lanthanoid contraction*.[104, 105] Most ions have one or two principal oxidation states, though a few have a multitude of options that more or less common. The alkali metals, for instance, are all-in-all positively singly charged, whereas as a manganese ion can vary from manganese(-III) to manganese(VII).[24] The issue of coordination and configuration is described in more detail later in Chapter 2.4. High and low electron spin states occur in transition metal elements, whose electronic structures are described in Chapter 2.6.

2.3.1 Definitions

The radius is probably the most important physical and chemical property of an atom or ion. It is also the one feature that is most frequently reported, in spite of the fact that it cannot be measured directly! One can, however, measure the distance between two nuclei and indirectly establish values also for the radii. The assumptions are that the distance between two atom nuclei is closely related to the sum of atomic/ionic radii involved, and that the distance for a particular species does not change significantly for one element between substances of similar kind (with similar environment, coordination, and geometry). Even this procedure is ambiguous,[27] but has been the main way of determining useful values for radii since the first attempts by Bragg, Pauling and Goldschmidt *et al.*[106-108] One should always keep in mind that radii values, especially older ones, are somewhat flexible and that there is no absolute way of determining where one ion or atom ends and the other starts.

2.3.2 Probable values

When performing extensive studies of the same element, it becomes obvious that certain ionic radii are tightly connected to the element investigated. The papers by Beattie *et al.* and Shannon are two established studies that determined the values for oxygen. In Beattie's article they reached the conclusion that the radii associated with three-coordinated oxygen in water is 1.34 Å, whereas Shannon calculated his corresponding value for the oxide anion (O^{2-}) to 1.40 Å.[101, 109] With these two distances as basis, other scientists have used to create an even vaster catalogue of atomic and ionic radii. There are two large databases available, *Cambridge Structure Database* (CSD) and *Inorganic Crystal Structure Database* (ICSD) both updated several times a year,[90, 110] to keep track of the latest development. As an example from Paper IV, the more than twenty values for hydrated iron(II) ions fall within ±0.02 Å and the ten values for hydrated iron(III) ions fall within ±0.01 Å. A simple search alone makes these large databases virtual goldmines when looking for the bigger picture in a structural study, like Papers II, IV, and V and other similar investigations.[111]

The systematization effort performed by Shannon and Prewitt[112] and later revised by Shannon alone seven years later,[101] and is worth extra attention. The average interatomic distances in chalcogenides and halides (groups 16 and 17 in the periodic table of elements, respectively) are listed, separating the information by element, oxidation state, and coordination number. The averaged data listed makes the collected information a good and valuable tool for any researcher in coordination chemistry, and is even better when supplemented with the databases previously mentioned.

As an example of how the assumed value for a radius has changed over the years, we can take the six-coordinated lithium(I) in lithium fluoride, LiF, as example. Pauling estimated the ionic radius to be $r_{Li^+} = 0.60$ Å, Goldschmidt's value is 0.78 Å, while the actual electron density minimum was determined to be at 0.92 Å from the centre of the lithium nucleus.[107, 108, 113]. Shannon's revised value, which is an average based on many determined structures is 0.90 Å.[101]

Clear differences between the three of the four characteristics mentioned earlier in this chapter can be seen in the different ionic radii for iron(II) and iron(III) in Table 9.

Table 9. Ionic radii for iron(II) and iron(III) for different coordination number (CN) and spin states. Values taken from Shannon (ref. 2).

Iron(II)			Iron(III)		
CN	Radius/Å	Spin state	CN	Radius/Å	Spin state
4	0.63	high	4	0.49	high
6	0.61	low	6	0.55	low
6	0.78	high	6	0.65	high
8	0.92	high	8	0.78	high

2.4 Coordination numbers (CN)

In his presentation speech for the 1913 Nobel Prize in Chemistry, the President of the Royal Swedish Academy of Sciences at the time, Theodor Nordström, explains Alfred Werner's classic coordination theory using Werner's surprisingly simple terms. He tells the audience the true meaning of the *primary valence* and *secondary valence* of a metal, comparing it with van't Hoff's giant leap in organic chemistry when he introduced stereochemistry.[114] As we have already seen in Chapter 1.1.2, Werner's evidence truly "open up new fields" as predicted by the Nobel Prize Committee and was more than convincing in explaining the difference between the dissimilar amminecobalt chlorides despite their similar chemical formulae.

The primary valence, nowadays called *oxidation state*, is equal to the number of negative charges that need to be added to the metal ion to receive a neutral complex. The secondary valence, Werner's *coordination number* not only specified the geometry of the central atom, also included the possibility to bind neutral molecules in addition to the negatively charged ions. These term changes also included moving away from the belief that the secondary valance was tightly connected to certain fixed geometric positions. The full analysis of these terms are elegantly summed up in Werner's Nobel Lecture.[16] The term coordination number can be defined as the number of ligand donor atoms connected to the atom or ion under study, still most often a central metal atom or ion. The term has also separately been used to describe the number of nearest neighbours in a crystallographic structure, but now both definitions are included in the same meaning.[115]

2.4.1 Coordination numbers and HSAB theory

It is useful to divide the different ways of coordination in the HSAB theory terms that were introduced in Chapter 2.1. On one hand, there is coordination between hard acids and hard bases, where electrostatic forces are the predominating factor, which in turn means that the ions can be thought of as hard spheres. The coordination of these complexes can be estimated through trigonometric relationships, where limiting radius ratios (r^-/r^+) can be calculated (Fig. 14).[116] The limiting radius ratio is thus the limit rather on how small (and not how large) the cation can be relative to the anion. Table 10 lists the limiting radius ratios for the most common coordination numbers found in minerals. Conversely, for soft acids binding soft bases, the coordination number is dependent on the molecular orbitals available for binding. Typical soft metal ions like palladium(II) and platinum(II) with a d^8 electron configuration, therefore accepts binding in a square planar fashion.[117, 118] Naturally, there are also examples that fit in between these two extremes.

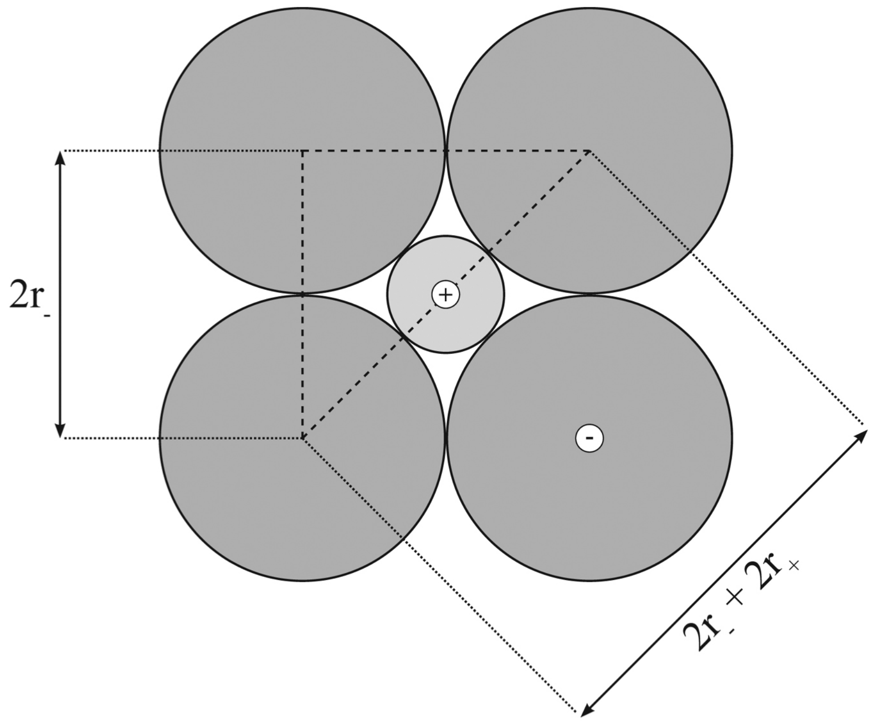


Fig. 14. The limiting radius ratio for hard acid/hard base interactions can be trigonometrically calculated. This figure is simplified to two dimensions (after McBride, ref. 116).

Regardless of how one defines coordination number there is no simple clear definition that is satisfying for all ligands and cases,[119] but for monodentate ligands it is usually easy to determine the coordination number. The solvents studied and discussed in this thesis are all of this kind, and are in addition (with the exception of *N,N*-dimethylthioformamide, DMTF), all oxygen donor ligands. For transition metal ions, coordination numbers can be said to roughly vary between two and nine, where four and six are the most common ones, even though coordination numbers higher than nine have been found. The following description of coordination numbers four to nine include those of interest for the remaining part of this thesis and the individual works appended to it. Some coordination numbers are connected to more than one geometrical configuration, and in those instances those relevant for the discussions in this thesis have been included.

Table 10. Limiting radius ratios for common coordination numbers (CN) and their respective geometries for hard acid/hard base systems (after McBride, ref. 116).

CN	Geometry	Limiting radius ratio
4	tetrahedral	0.225
6	octahedral	0.414
8	cubic	0.732
12	dodecahedral	1.000

2.4.2 Coordination number four (CN = 4)

For compounds binding to four ligand atoms, two geometrical configurations are predominant: the tetrahedral structure and the square planar one. As described below, certain properties are associated with the two arrangements, but there are some compounds where the energy difference is small enough to allow both configurations to form. For the mixed alkylarylphosphine nickel(II)bromide, $[NiBr_2(PEtPh_2)_2]$, even interconversion between the two forms is possible.[117] Structural disputes involving $[ML_2L'_2]$ complex were solved in the early days of coordination chemistry merely by studying if any *cis* and *trans* isomers were formed. For instance, the existence of both *cis*- and *trans*-diamminedichloroplatinum(II) was taken as enough evidence that it was square planar (Fig. 15). This was later proven to be true, though in retrospect and without the fixed geometrical configuration mistakenly ascribed to the secondary valency, it *could* have been another example where both the tetrahedral form and the square planar one are present.[115] Four-coordination is commonly found in both the crystalline state and in solution.

cis-$[PtCl_2(NH_3)_2]$ *trans*-$[PtCl_2(NH_3)_2]$

Fig. 15. The structures of *cis*- and *trans*-diamminedichloroplatinum(II). The designations *cis* and *trans* are taken from Latin, meaning “on the same side (of)” and “on the opposite side (of)”, respectively.

2.4.2.1 Tetrahedron

The tetrahedral structure (T_d) is possibly the most commonly used chemical representation of a molecule, though its extended use may originate from the methane structure in organic chemistry rather than inorganic or coordination chemistry (Fig. 16). The tetrahedron is nevertheless a very common configuration among transition metal complexes, especially those who vary in oxidation state (*e.g.* permanganate, MnO_4^-) or d^5 and d^{10} metal complexes (*e.g.* $[Ni(CO)_4]$ and $[ZnCl_4]^{2-}$, respectively).[115] The tetrahedral angle, 109.5°, was one of the directional modes angles the secondary valance of a chemical compounds could have. A tetrahedron is the preferred four-coordinated arrangement for soft metal ions as copper(I), silver(I), gold(I) and mercury(II), and in complexes with space-demanding ligands such as the larger halides, phosphines, and sometimes (as shown later in this thesis) *N,N'*-dimethylpropyleneurea, as the tetrahedral structure allows maximum distance between the ligands.

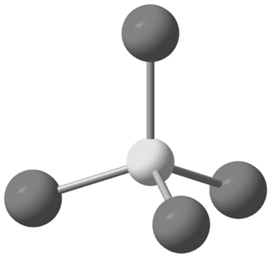


Fig. 16. A tetrahedrally coordinating metal complex forms bond to four ligands, theoretically separated by an angle of 109.5°.

2.4.2.2 Square plane

Square planar (*sqpl*) geometry is frequent in metal complexes with special *d* electron configuration, principally the d^8 elements. The most commonly used examples include the chemistry of palladium(II), platinum(II) and gold(III). The diamminedichloroplatinum(II) complexes, $[PtCl_2(NH_3)_2]$ (Fig. 15), mentioned earlier thus has its coherent counterpart in diamminedichloropalladium(II), $[PdCl_2(NH_3)_2]$.[117] There are also examples of metal ions that at first glance may look square planar, but indeed are more or less severely distorted octahedrons. This behaviour is normally explained with the Jahn-Teller effect (or a pseudo-Jahn-Teller effect).[120, 121] The original theorem proposed by H. A. Jahn and E. Teller, states that certain molecules will reduce its symmetry as an effect of its unstable degenerate electronic state, resulting in split or distorted degenerative orbital energy levels. The pseudo-Jahn-Teller effect involves splitting of non-degenerate electronic states (induced by nuclear displacements), which yield a similar end result.[121] The sliding scale (from a regular octahedron to a heavily distorted one, yielding a Jahn-Teller effect generated pseudo-square planar complex) makes it hard to differentiate them from true square planar complexes.[122] Even so, the commonly cited (square planar) "four-coordination" of tetraamminediaquacopper(II), $[Cu(NH_3)_4]$ (aq) in chemistry textbooks seldom get a satisfying treatment.[123-125] Hopefully this can be ascribed to the respective author's intention and scope of the literature, but a brief footnote of the Jahn-Teller effect could just as easily be included.

2.4.3 Coordination number five (CN = 5)

Five-coordination is a lot more uncommon than four-coordination. One reason for this is the lack of higher symmetry stabilizing many chemical systems, and five-coordination is more often seen in solution where symmetric restrictions are less important. There are two main five-coordinated geometries: the trigonal bipyramid (*tbp*) and the square pyramid (*sqpy*). They are closely related to one another, which can be illustrated with the so-called Berry mechanism or pseudo-rotation for a five-coordinated complex, with its *tbp-sqpy-tbp* interconversion (Fig. 17). As an effect, the energy difference between the two is often small enough to make it difficult to determine which of the two forms that is the principal one in solution.

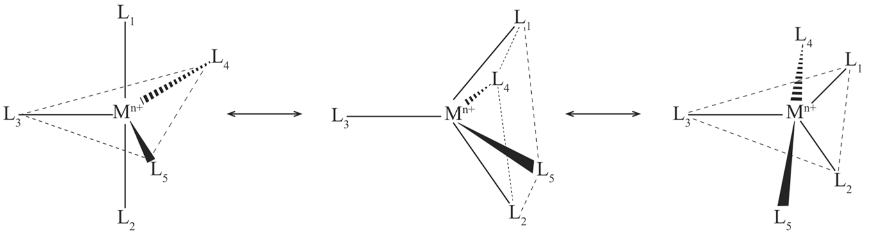


Fig. 17. The so-called Berry mechanism or pseudo-rotation, a *tbp-sqpl-bp* interconversion, is possible for 5 coordinated molecules and complexes (after Cotton *et al.*, ref. 126).

And even if this sometimes is possible to determine with the help of other techniques or observations, many five-coordinated compounds show structures that are transitional between the two forms. It should be stressed that there are other known transitional pathways as well.[126, 127] In any case, five-coordinated compounds do exist in greater numbers than once thought, with examples including elements with the entire range of *d*-electron structure.[115]

2.4.3.1 Trigonal bipyramid

The trigonal bipyramid is often regarded as the more common of the two predominant five-coordinations. A true trigonal bipyramid has its five coordinating positions at the five vertices of the geometric structure, resulting in a D_{3h} symmetry, with the possibility of interconversion as described above. In the case where two bonds are placed in the axial positions and three in the equatorial plane one can speak of a true trigonal bipyramid, but many complexes are slightly distorted and thus hard to classify correctly. The trisbromobis(*N,N'*-dimethyl-propyleneurea)iron(III) compound in Paper III has been crystallographically been determined to be a trigonal bipyramidal structure (as seen on the thesis cover).

2.4.3.2 Square pyramid

A square pyramidal structure, with its C_{4v} symmetry, is the other main option for a five-coordinated structure. In fact, one of the first complexes with five-coordination, $[VO(acac)_2]$, was square pyramidal with the doubly bonded oxygen in the unique apical position.[115] Other examples include the $[InCl_5]^-$ and $[TlCl_5]^{2-}$ ions, but there is no general rule when this or the trigonal bipyramidal structure is preferred.[127] The intermediate state of the Berry pseudo-rotation (Fig. 17) is also a square pyramid, which means that all intraconverting species at least to some extent can be classified as square pyramidal structures. Special cases include $[Ni(CN)_5]^{3-}$, where both geometries are present simultaneously.[127]

2.4.4 Coordination number six (CN = 6)

Six-coordination is commonly found in both the crystalline state and in solution, and it was through this coordination number that Werner had his greatest success.[16] The by far most common geometry is the octahedron or a slightly distorted octahedron, including elongation in a trigonal or tetragonal fashion (Figs. 18 and 19).

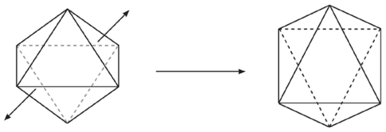


Fig. 18. Trigonal distortion of an octahedral complex (after Greenwood *et al.*, ref. 115).

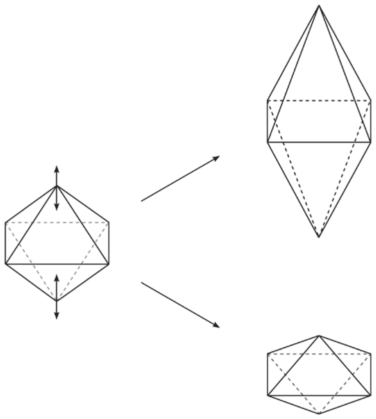


Fig. 19. Tetragonal distortion of an octahedral complex (after Greenwood *et al.*, ref. 115). The effects are exaggerated to visualize the effect. The top result is frequently seen in tetraamminecopper(II) complexes (see Chapter 2.4.2.2).

2.4.4.1 Octahedron

The octahedral arrangement linked to the symmetry O_h is by far the most common one among transition metal ions (Fig. 20). The establishment of the octahedron as *the* six-coordination configuration was, however, not as simple as it may seem. The three likely candidates for hexa-coordination were a planar model, the trigonal prism, and the octahedral structure. A compound with the general structure $[ML_4L'_2]$ would generate different number of isomers depending on which of the configurations that actually existed, where a planar or a trigonal structure would show three, but an octahedron only two (Fig. 20). Even though numerous compounds, mainly including chromium(III) and cobalt(III), were synthesized yielded only two different isomers, this could not be used as indisputable proof to rule out the possibility of the two less likely geometries. It was not until Alfred Werner synthesized the optical isomers of $[Co((OH_2)Co(NH_3)_4)_3]^{6+}$ that the question was fully resolved.

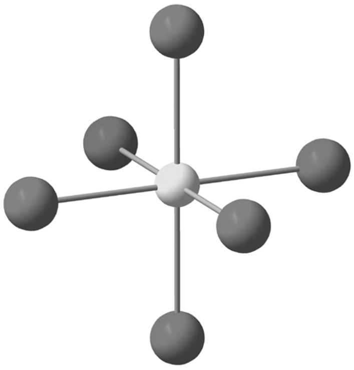


Fig. 20. A octahedrally coordinating metal complex forms bond to six ligands, theoretically with 90° angles from each other.

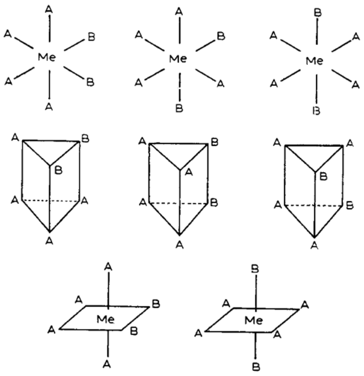


Fig. 21. The structure of six-coordinated complexes. Werner's idea of octahedral complexes solved the problem why only two forms of [$ML_2L'_2$] complexes are seen, where the corresponding planar and trigonal prism structures would yield three isomers (after Werner, ref. 16). Me is the former abbreviation for metal, M.

2.4.4.2 Trigonal prism

The octahedron is not the only configuration for six-coordination, where trigonal prismatic and anti-prismatic structures are also found, even though in smaller numbers. In addition to these two, intermediates are also found with varying twist angle (Fig. 22).[115] The structural differences between octahedral and trigonal structures were explored by Wentworth, discussing examples of trigonal variations (MoS_2, WS_2, and $M[S_2C_2(CN)_2]_3^{2-}$ for M = V, Mo, and Fe).[128]

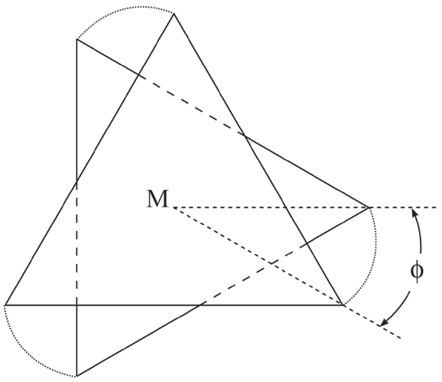


Fig. 22. A trigonal prismatic complex with a twist angle, *Φ*. The angle illustrates the relationship between the trigonal prismatic, anti-prismatic, and intermediate configurations (after Wentworth, ref. 128).

2.4.5 Higher coordination numbers (CN > 6)

There are many instances where the coordination number exceeds six. This is often the case when the central ion involved is large enough to accommodate a high number of less space-demanding ligands such as water or DMSO (see also Chapter 4.3.1). Other instances include stabilization of the ionic charge, which could lead to an increased coordination number, seen in for instance crown-ethers.[102] Very high coordination numbers (CN > 9) are in some instances regarded as nonsense, where the hapticity (*η*) of ferrocene and other *hapto* ligands usually is the target. The coordination number of cyclopentadienyl rings may be looked at in different ways, and the five *η*-attached carbon atoms have been given coordination numbers 2, 5 and 6.[119, 129, 130]

2.4.5.1 Capped trigonal prisms (CN = 7, 8, or 9)

The trigonal prism described in Chapter 2.4.3.2 (Fig. 21) is the base for so-called capped trigonal prisms. The monocapped trigonal prism has an additional ligand attached at one of the rectangular faces of the prism ($[NbF_7]^{2-}$), the bicapped has two and the tricapped has three ($[ReH_9]^{2-}$). There are other geometric forms tied to higher coordination numbers, for instance a capped octahedron and pentagonal bipyramids (both CN = 7). The energy difference between the different shapes is small, which makes prediction of the actual geometry difficult. It has been proposed that it is ultimately the stereochemical properties of the counter ion and ligands available that decides the geometry.[115] The extent of capping is sometimes a question of ionic radius, as has been shown for the hydrated lanthanoid(III) ions in the solid trifluoromethanesulfonate salts.[71] It should be pointed out that all of these lanthanoids have a nine-coordinated structure, where some of the capping positions for the later lanthanoid(III) ions show water deficiency.

2.4.5.2 Square antiprism (CN = 8)

As for the other high coordination numbers, the eight-coordinating square antiprismatic geometry may show a slight distortion. Once again, this makes the separation between it and other configurations, such as a dodecahedron, somewhat hard. In any case, the square antiprism is a fairly well-known structural form, with many examples, including the hafnium(IV) and zirconium(IV) hydrates.[131]

2.4.6 Other coordination numbers

The other coordination numbers, those lower than four and higher than nine, lie outside the realms of this thesis. Often elements are tightly connected with one or a few typical coordination numbers, and it is thus easier to search the literature for the appropriate element, rather than the coordination number itself.

2.5 The crystalline state

A crystal is a solid substance where a repetitive organisation of atoms in space (the unit cell) is duplicated in all three directions over and over again.[132] Based on this repetitiveness, the structure can be elucidated through interference patterns when the crystal is subjected to X-ray radiation with proper equipment and under the right circumstances. The unit cell is what often determines the shape of the crystal and can be classified into one of the seven crystal systems (Table 11). [132] Through mathematical group theory, it is possible to find all symmetric equivalents and through this determine which set of operations, space group, the crystal belongs to. The idea of the crystalline state is tightly connected to the methods used to describe it. Further reading could include the books by Massa and Giacovazzo.[132, 133]

2.6 Electron structure in metal ions

It is the slight variation in the electron structure that at the same time creates the many differences and similarities between the distinct transition metal ions. The same can be said for the lanthanoid ions (also called inner transition metal ions), though the similarities outweigh the differences, as has been seen in the problems of their discovery. For the transition elements, the chemically most important electrons are in the *d* shell, where they are added one by one across the period, thereby affecting the chemical ability of the compound. For the lanthanoids, the filling takes place in the *f* shell, which allows a more stable ionic charge – a threefold positive one – something that is reflected in the similarities of the neighbouring lanthanoid elements.

Table 11. The seven crystal systems and the restrictions on their cell dimensions. For a complete definition of the angles, see Massa (ref. 132).

Crystal system	Cell edge restriction	Cell angle restriction
triclinic	none	none
monoclinic	none	$\alpha = \gamma = 90°$
orthorhombic	none	$\alpha = \beta = \gamma = 90°$
tetragonal	a = b	$\alpha = \beta = \gamma = 90°$
trigonal, hexagonal	a = b	$\alpha = \beta = 90°, \gamma = 120°$
cubic	a = b = c	$\alpha = \beta = \gamma = 90°$

2.6.1 Transition metals (d elements)

The electronic structure of the *d* elements is based on the filling of the *d* shell. By definition set by IUPAC, transition elements are only those that have or form ions with an uncompleted *d* shell, which excludes the d^{10} elements zinc, cadmium, and mercury.[29] This definition is appropriate as an unfilled shell results in several features that are not present in the d^{10} elements. For this thesis it is relevant to also include zinc and cadmium, and they are thus treated together with the transition elements, appropriately grouped as *d* elements. The properties of the transition elements are directly connected to the filling of the *d* shell. The stable ions seen across the first transition metal series is connected to the loss of an appropriate number of electrons from either the 4*s* and or 3*d* shell. This is summarized in Fig. 23., where the preference of a half-filled *d* shell also can be seen. The stability offered by a half-filled shell has been explained by Cann.[134] At the same time, the outmost electrons are those involved in the ionization process, making that the ionic radius is greatly dependent on their presence. This results in the varying ionic radius for the different element at separate ionic states seen in Fig. 1.

				+**7**					
			+**6**	+6	+6				
		+**5**	+5	+5	+5	+5			
	+**4**	+4	+4	+**4**	+4	+4	+4		
+3	+3	+3	+**3**	+3	+**3**	+**3**	+3	+3	
+2	+2	+2	+2	+**2**	+**2**	+**2**	+**2**	+**2**	+**2**
+1		+1		+1	+1	+1	+1	+1	
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	-1	-1	-1	-1	-1	-1	-1		
			-2	-2	-2				
				-3					

Fig. 23. The oxidation states of the first row *d*-elements. The more common oxidation states and metallic form are shown in bold (after Greenwood & Earnshaw, ref. 130).

2.6.2 Lanthanoids

The corresponding situation for the lanthanoids does not take place in the *d* shell. Instead, the lanthanoids follow another regular pattern, where essentially the electron with the lowest energy repeatedly is added in the 4*f* subshell.

	+4	+4						+4						
+3	**+3**	**+3**	**+3**	**+3**	**+3**	**+3**	**+3**	**+3**	**+3**	**+3**	**+3**	**+3**	**+3**	**+3**
+2	+2	+2	+2		+2	**+2**	+2		+2			+2	+2	
							+1	+1						
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

Fig. 24. The oxidation states of the lanthanoids. The more common oxidation states and the metallic form are shown in bold (after Greenwood & Earnshaw, ref. 130)

Generally speaking, the energies of the 4*f* electrons are lower than the corresponding 5*d* electrons, which in effect means that the former are added to a subshell and do not participate as actively in the ionization process (and hence the chemical reactivity) as the *d* electrons for the transition elements.[60] If different chemical behaviour is seen the outermost electrons, and the addition of electrons in the lanthanoid series takes place in a shell *inside* the outermost ones, it becomes clearer why the chemistries of the lanthanoids are so alike. The result is a series of elements that readily form ions with the same ionic charge, commonly written Ln^{3+} (Fig. 24), resulting in a steady decrease in ionic radius (Fig. 2). In addition, as we have seen in the transition elements, some stability is noticeable when a shell is half-filled, even if this cannot explain all the irregularities present in the lanthanoids.[27, 105, 134, 135] The anomalies in the ground electronic state are observable for lanthanum, cerium, gadolinium and lutetium. The electronic configurations for all lanthanoids (and their trivalent ions) are listed in Table 11.

Table 12. The electronic configuration of the lanthanoids in the ground state and their trivalent ions. The electronic configurations for the lanthanoid metals follow the *energy levels* for the respective shell, whereas the configurations for the lanthanoid(III) ions describe the *geometrical arrangement* of the electrons in an attempt to show the similarities in chemical behaviour (identical sets of outer-shell electrons).

Atomic number	Element name, chemical symbol	Electronic configuration	
		Ln	Ln^{3+}
57	lanthanum, La	$\mathrm{[Kr]}5s^2 4d^{10} 5p^6 6s^2 5d^1$	$\mathrm{[Kr]}4d^{10} 5s^2 5p^6$
58	cerium, Ce	$\mathrm{[Kr]}5s^2 4d^{10} 5p^6 6s^2 5d^1 4f^1$	$\mathrm{[Kr]}4d^{10} 4f^1 5s^2 5p^6$
59	praseodymium, Pr	$\mathrm{[Kr]}5s^2 4d^{10} 5p^6 6s^2 4f^3$	$\mathrm{[Kr]}4d^{10} 4f^2 5s^2 5p^6$
60	neodymium, Nd	$\mathrm{[Kr]}5s^2 4d^{10} 5p^6 6s^2 4f^4$	$\mathrm{[Kr]}4d^{10} 4f^3 5s^2 5p^6$
61	promethium, Pm	$\mathrm{[Kr]}5s^2 4d^{10} 5p^6 6s^2 4f^5$	$\mathrm{[Kr]}4d^{10} 4f^4 5s^2 5p^6$
62	samarium, Sm	$\mathrm{[Kr]}5s^2 4d^{10} 5p^6 6s^2 4f^6$	$\mathrm{[Kr]}4d^{10} 4f^5 5s^2 5p^6$
63	europium, Eu	$\mathrm{[Kr]}5s^2 4d^{10} 5p^6 6s^2 4f^7$	$\mathrm{[Kr]}4d^{10} 4f^6 5s^2 5p^6$
64	gadolinium, Gd	$\mathrm{[Kr]}5s^2 4d^{10} 5p^6 6s^2 5d^1 4f^7$	$\mathrm{[Kr]}4d^{10} 4f^7 5s^2 5p^6$
65	terbium, Tb	$\mathrm{[Kr]}5s^2 4d^{10} 5p^6 6s^2 4f^9$	$\mathrm{[Kr]}4d^{10} 4f^8 5s^2 5p^6$
66	dysprosium, Dy	$\mathrm{[Kr]}5s^2 4d^{10} 5p^6 6s^2 4f^{10}$	$\mathrm{[Kr]}4d^{10} 4f^9 5s^2 5p^6$
67	holmium, Ho	$\mathrm{[Kr]}5s^2 4d^{10} 5p^6 6s^2 4f^{11}$	$\mathrm{[Kr]}4d^{10} 4f^{10} 5s^2 5p^6$
68	erbium, Er	$\mathrm{[Kr]}5s^2 4d^{10} 5p^6 6s^2 4f^{12}$	$\mathrm{[Kr]}4d^{10} 4f^{11} 5s^2 5p^6$
69	thulium, Tm	$\mathrm{[Kr]}5s^2 4d^{10} 5p^6 6s^2 4f^{13}$	$\mathrm{[Kr]}4d^{10} 4f^{12} 5s^2 5p^6$
70	ytterbium, Yb	$\mathrm{[Kr]}5s^2 4d^{10} 5p^6 6s^2 4f^{14}$	$\mathrm{[Kr]}4d^{10} 4f^{13} 5s^2 5p^6$
71	lutetium, Lu	$\mathrm{[Kr]}5s^2 4d^{10} 5p^6 6s^2 5d^1 4f^{14}$	$\mathrm{[Kr]}4d^{10} 4f^{14} 5s^2 5p^6$

3 Experimental section and materials

The experimental section of this thesis is concentrated to include the details that are normally not included in the scientific articles, which means that the preparatory work is described in more detail. The exact preparation of the materials used is described the respective papers.

3.1 Metal salts

The trifluoromethanesulfonate (triflate) metal salts were prepared by dissolving an appropriate amount of the respective metal or metal oxide in trifluoromethane-sulfonic acid. The resulting slurry was filtered, put in a ceramic bowl and carefully heated on a hot plate in a hood to boil off the remaining acid and water. The acidic fumes can be highly corrosive, which is why the use of an ordinary oven is not to prefer. The remaining salt was then finely ground several times and dried in an ordinary oven at high temperature, until a very fine (and dry) powder is obtained. The prepared salts are best stored in an oven at high temperature or in a suitable evacuated chamber.

3.2 Solvents

The solvents used in the appended papers consisted of *N,N'*-dimethylpropyleneurea (all papers) and also deionized water , dimethyl sulfoxide, and *N,N*-dimethylthioformamide (Paper IV). Bulk deionized water was used for the preparation of the aqueous samples. Dimethylsulfoxide was distilled in a similar fashion to the one described for DMPU below. DMTF was prepared as previously described.[136]

3.2.1 Distilling DMPU

DMPU is known to be a fairly hygroscopic solvent, and stock purchased solvent is listed as 98% pure.(reagent grade, Aldrich) To remove unwanted amounts of water, the DMPU was distilled under reduced pressure (~6 kPa at temperatures lower than 400 K) shortly before being used using calcium hydride (reagent grade, Merck) as a drying agent. To monitor the effect of this distillation, an analysis of the water content through a modern Karl Fischer method[137] was performed by Mikro Kemi AB, an accredited analytical laboratory in Uppsala, Sweden[138]. The test showed that freshly distilled DMPU contained 0.052 percent water by mass. The water content of older samples was also determined, via (non-distilled) leftover amounts of DMPU approximately three and six months after their distillation (opened a couple of times per month during retrieval of solvent). The water content of these two was 0.088 and 0.19 percent water by mass, respectively. The small amount of water remaining in the freshly distilled DMPU is probably not large enough to cause any serious problems, but proves that ample precautions should be taken during storage. Furthermore, the DMPU has to be stored in dark glass bottles away from sunlight, as it can photochemically react which results in a slightly yellowish tint of the solvent. Pure DMPU is transparent and colourless and is best stored over 3 Å molecular sieves.

3.3 Methods

The methods used for the studies in this thesis all involve X-ray technology: extended X-ray absorption fine structure (EXAFS), large angle X-ray scattering (LAXS), and single crystal X-ray diffraction. The first two are used in the study of solutions, whereas both EXAFS and X-ray diffraction are used for investigations of the solid state (the latter limited to the crystalline state).

3.3.1 EXAFS

Extended X-ray absorption fine structure (EXAFS), first reported by Sayers *et al.*,[139] has become a much used technique in many areas in chemistry and biology.[140] Structural data (in gas, solution, or solid state) can satisfactorily be obtained by means of EXAFS, and has served as the foremost method in the data included in this thesis together with single crystal X-ray diffraction. The compound or solution under study is subjected to high-energy X-rays (photoelectrons), which excite core electrons creating an electromagnetic wave with specific properties tied to the host element of the excited electrons. Through interference with back-scattered waves from neighbouring atoms, a unique pattern (an EXAFS wave) for the compound is created and recorded. Vital information about the compound's bonds (distance and geometry) can be extracted from this X-ray absorption spectrum wave with the help of specially developed computer programs on the subject.

The EXAFS measurements in this thesis were performed at three different locations: Stanford Synchrotron Radiation Laboratory (SSRL) in the USA, European Synchrotron Radiation Facility (ESRF) in Grenoble, France, and MAX-lab at Lund University, Sweden. Two different software packages were used to extract and refine the EXAFS data: EXAFSPAK (including FEFF7)[141, 142] and GNXAS[143].

3.3.2 LAXS

Large angle X-ray scattering (LAXS) is a much lesser used technique than EXAFS. It can be used when studying complexes in solution just like EXAFS, but also gives valuable insights in the structure of glass and other non-crystalline compounds.[144-146] LAXS measurements scan a wide range of angles, which yield a continuous scattering curve for all atoms in the solution, not only including the complex investigated, but also the counter ions and the bulk solution. By modelling the contribution from the two latter parts using properly standardized curves, the structure of the complex in solution can be extracted. The main drawback with the LAXS technique is the requirement of fairly high concentrations of the desired complex. This imposes some limitations to which systems that are to be investigated.

3.3.3 Single crystal X-ray diffraction

The most utilized technique to investigate the structural phenomenon in coordination chemistry is probably single crystal X-ray diffraction. What used to be a magnificent feat – the definitive determination of all atomic positions within a crystal – is nowadays done on almost a daily basis in chemistry labs all around the globe. Single crystal X-ray diffraction has been thoroughly described in the literature, and is thus left out of this thesis. Two good sources for an introduction to the technique are the books by Massa and Giaccovazzo.[132, 133]

3.3.4 Advantages and disadvantages

The different techniques used in this thesis all have their own set of advantages and disadvantages. The last one mentioned, single crystal X-ray diffraction, is normally regarded as the one technique to prefer if one can obtain crystals that are good enough for measurements. Under the best conditions, the atomic coordinates of all non-hydrogen atoms can be resolved. There is, however, a certain limit to the quality of the crystal or rather the homogeneity of the crystal, under which it is not possible to obtain sufficiently good data. In addition, the crystal lattice can (under specific conditions) impose a higher degree of symmetry on a complex with lower (true) symmetry. The most famous example is probably the copper(II) hydrates, where the Jahn-Teller effect (see Chapter 2.4.2.2) does not seem to be present. Solid state EXAFS data clearly shows that it *is* present, however, an effect of the lattice independence in such measurements. EXAFS data has no requirement of perfect crystals or any crystals for that matter, which indeed is advantageous. EXAFS measurements can also be performed on solutions, thereby allowing comparisons of the structures in solid state and solution. The EXAFS data is non-directional, but still yields fundamental structural information, where the usual outcome is the distance between a central atom and the nearest backscattering atoms. The availability of the synchrotron radiation needed for EXAFS is restricted to certain research facilities. If EXAFS gives information of the first coordination shell conditions surrounding a central atom, LAXS can be said to be superior in determining the structure of the outer coordination spheres and the structure of the bulk solvent, which makes data from solution EXAFS and LAXS complementary. The main drawback with LAXS is that it requires very concentrated solutions to yield informative data. The information gathered is also the total absorbance of all ions and the bulk solvent, which may sound somewhat complicated, but is nonetheless useful if it can be interpreted correctly.

4 Results and discussion

The results and discussion in this chapter is based on the data reported in Papers I-V. For an in-depth look at the specific data for each structure, the reader is advised to read the appropriate article in the appendix.

4.1 Structures of solvated iron(II) and iron(III) ions

Iron is essential to all forms of life on the planet, where perhaps the most famous example is the presence of iron in haemoglobin, the oxygen transporting protein in blood. A greater understanding of the coordination chemistry of iron is therefore of interest. The coordination chemistry of aqueous systems (and other similar solvents without spatial demands) has been studied for a long time, but little is known about the chemical behaviour in space-demanding solvents.

4.1.1 DMPU solvated iron(III) bromide

Iron bromide complex formation in aqueous solutions and DMSO is very weak[103]. In DMPU, however, the calorimetric study showed that iron(III) in *N,N'*-dimethylpropyleneurea forms about 1,000 times stronger bromide complexes (Paper III). This strengthening in the stability constants is smaller than observed for the nickel(II) bromide system in DMPU (roughly 10,000 stronger than in aqueous solution). In the nickel(II) case, a coordination switch from square pyramidal to tetrahedral configuration takes place already at the formation of the first complex, seen in the radical colour change from red to blue.[1] This colour change is not noticed in the iron(III) case and an indication that it most probably does not undergo any configuration change in solution. It is therefore likely that the complex retains its geometry throughout the entire complex formation, where solvent ligand molecules are exchanged for bromide ions.

The hydrated and DMSO solvated iron(III) ions are six-coordinated in solution. In DMPU, based on the bond distances seen keeping the space-demanding properties of the solvent in mind, it is most probably five-coordinated, most likely in a trigonal bipyramidal configuration.(Paper IV) The strengthening of the complex formation seen in DMPU has been attributed to the relatively low stability of the five-coordinated solvated iron(III) ion. Another assisting property is the effect of desolvation since the bulk of the aprotic solvent DMPU, where the intermolecular forces are relatively weak, is much less well-ordered than an aqueous solution, where hydrogen bonding adds structural restraints in the bulk. The five-coordination is confirmed in the crystallographic determination of tribromobis(*N,N'*-dimethylpropyleneurea)iron(III), seen on the cover of this thesis. The bromide ions lie in the same plane as the iron(III) ion, but one is more strongly bound than the other two (based on the shortened Fe-Br bond distance, 2.37 and 2.44 Å, respectively). The Br-Fe-Br angles display a very unusual pattern with the largest angle between the longest Fe-Br bonds, while the angles between the short and one long Fe-Br bond are much smaller. The mean Fe-O bond distances are

1.98 Å, and the O-Fe-O angle is 169.0°, yielding a slightly distorted trigonal bipyramid, with the DMPU ligand molecules in the apical positions.

The crystallographic structure is also supported by EXAFS data, where the best fit is obtained using two different bromide distances. This behaviour in the solid complex is believed to be an effect of covalent contribution in the Fe-Br bonds, where the bromides bind through the most favourable orbitals. In solution, however, EXAFS and LAXS measurements on the tribromoiron(III) complex can only distinguish one Fe-Br distance, and weak or no Fe-O interaction suggesting that the neutral complex is basically three-coordinated. In Chapter 3.2.4 it was mentioned that such differences can be explained (imposed) by symmetry elements integrated in crystal lattice energies, where additional stability is offered by the two capping DMPU molecules. In solution, with no stabilizing lattice energies, the reduced charge on the successive iron(III)bromide complexes (to neutrality) evidently removes the need for any of the DMPU molecules to bind strongly to the complex. Comparing to the configuration change seen in the nickel(II) bromide case in DMPU, the iron(III) bromide takes a different path (Fig. 25)

$Ni(dmpu)_5^{2+}$ *sqpy* (5)	$NiBr(dmpu)_3^{+}$ *tetr* (4)	$NiBr_2(dmpu)_2$ *tetr* (4)	
$Fe(dmpu)_5^{3+}$ *tbp* (5)	$FeBr(dmpu)_4^{2+}$ ”*tbp* (5)”	$FeBr_2(dmpu)_3^{+}$ ”*tbp* (5)”	$FeBr_3$ *trig* (3)

$$\longrightarrow$$

increasing bromocomplexation

Fig. 25. The bromo complexes of nickel(II) and iron(III) in DMPU. The penta(*N,N'*-dimethylpropyleneurea)nickel(II) complex undergoes a coordination and configuration change at the attachment of the first bromide. The corresponding change for the iron(III) system is believed to not take place until completion of the tribromo complex.

4.1.2 Hydrated and DMSO solvated iron(II) and iron(III) ions

The behaviour of the iron(III) bromide in DMPU was partially explained by the results of the study of iron(II) and iron(III) in solvents with different coordination properties (Paper IV). In order to establish a firm ground to base new results on, a literature search among iron hydrates and iron solvates was performed and reported in the paper. From the study it was concluded that the iron(II) and iron(III) ions are octahedrally coordinated both in aqueous solutions and the solid hydrates, results in this study are in complete agreement with data in the literature. Similarly, for the DMSO solvated iron(II) and iron(III) ions, the crystallographic structure of hexakis(dimethylsulfoxide)iron(III) perchlorate and the EXAFS data for solid state and solution tells us that the iron ions bind six DMSO molecules in an basically octahedral geometry. It is thus safe to say that the configuration is the same in both solution and solid state for all these complexes.

4.1.2 DMPU solvated iron(II) and iron(III) ions

In DMPU, the solvated iron(II) and iron(III) ions were found to be five-coordinated. This is somewhat unusual, but perhaps not unexpected. The reduction in coordination number is caused by the sterical hindrance of the two methyl groups close to the oxygen donor atom of the *N,N'*-dimethylpropyleneurea molecule, and has previously been reported for a corresponding TMU complex[89] and for nickel(II) in DMPU[1]. The reasoning to reach the conclusion of five-coordination for the two species is slightly different. For iron(II) the reduction of the coordination number in DMPU seems to stop at a five-coordinated complex. The experimental bond distances found in the EXAFS data treatment for the DMPU solvated iron(II) ion fall within those expected for a five-coordinated complex, supporting a coordination change. Furthermore, the ionic radius of the iron(II) ion is also large enough to allow the coordinating DMPU ligands to reduce their bond distances (compared to a six-coordinated compound) with a significant value (ΔR = 0.05 Å), similar to the bond shortening seen for nickel(II).[147] This reduction in bond distance is not seen in the corresponding data for the smaller iron(III) ion, but the complex is nevertheless believed to be five-coordinated. The overcrowded setting around the iron(III) ion simply does not allow the DMPU molecules to get closer, but the five-coordination still is favourable (and supports the situation in the iron(III) bromide complex formation). Similar strained bond elongation effects have been reported before in the highest complexes of copper(I), silver(I) and gold(I) with triphenyl phosphite, another space-demanding ligand.[148] Furthermore, the difference between the EXAFS wave in solution and solid state is small, which is taken as a strong indication that the structures of the complex in solution and solid state are the same.

4.1.3 DMTF solvated iron(II) and iron(III) ions

The DMTF solvated iron(II) and iron(III) ions are reduction/oxidation chameleons. If ample precautions are taken, it is possible to crystallize solid iron(III) DMTF solvates. These have, based on the Fe-S bond distance, been determined to be four-coordinated in a tetrahedral fashion. The crystals have to be stored in sub-zero temperatures, and are then stable for weeks. During preparation it is possible to end up with the iron(II) solvate, as DMTF has reducing properties. And once reduced to iron(II), the ionic radius is large enough to host six DMTF solvent molecules.[136] The difference between the crowdedness seen in DMPU (space-demanding ligand) and DMTF (large donor atom) thus affects the reduction in coordination number. This is further enhanced by sulfur (in DMTF) being a softer donor than oxygen (in DMPU).

There is no literature value for the coordinating sulfur atom in sulfur donor molecules in the same sense Beattie *et al.* and Shannon provides a value for oxygen.[101, 109] Based on the calculated bond distances for the iron(II) and iron(III) ions, a reasonable value for the sulfur radius is 1.75 Å. This is confirmed by other metal ions, as long as not too much covalency is part of the coordination bond. Comparing the iron values with those for four other ions: four-coordinated *N,N*-dimethylthioformamide solvated zinc(II)[149] and copper(II)[150] ions, and the six-coordinated *N,N*-dimethylthioformamide solvated cadmium(II)[150] and nickel(II)[147] ions, the value 1.75 Å fits very well using the appropriate metal ion radii from Shannon's paper.

4.2 Structures of DMPU solvated zinc(II) and cadmium(II) ions

A better understanding of the fundamental chemical properties of cadmium(II) and zinc(II) ions is valuable. Insight in the coordination chemistry of the zinc(II) ion is important, for instance, as it could help explain the role the ion plays in some of the enzymes that are essential to life.[151] Conversely, the cadmium(II) ion is highly toxic, as it easily binds to sulfhydryl groups (-SH) in proteins and enzymes. Once taken up in the human body, the cadmium level stays high, with a half-life of up to 30 years.[152]

4.2.1 DMPU solvated zinc(II) ion

The crystalline structure of DMPU solvated zinc(II) ion shows a tetrahedral complex. Even though the hydrate is octahedrally coordinated, it is not unusual for zinc(II) to revert to four-coordinated complexes when space-demanding solvent molecules are used, *e.g.* in TMU.[88, 89] In solution on the other hand, a mean bond distance elongation suggests that there is a fair amount of the five-coordinated complex. The zinc(II) ion is certainly large enough to accommodate five DMPU molecules around it. This signifies once again that the situation in the crystalline state may not be the same as in the corresponding solution. It also suggests that the transitional ligand exchange mechanism for the zinc(II) DMPU solvate is an associative one. The fifth ligand molecule can attach itself to the zinc(II) ion and stay there for a significant amount of time, before one DMPU molecule is lost re-forming the four-coordinated complex.

4.2.2 DMPU solvated cadmium(II) ion

The crystal structure of DMPU solvated cadmium(II) ion verifies a six-coordinated complex. There are clear indications that the structure is severely strained, again due to the space-demanding properties of DMPU, and the crystals were also very sensitive to heat and moisture. The crystal packing is also noteworthy, where multiple twinning effects are observed. In solution, the DMPU solvated cadmium(II) exhibits a bond shortening. This is taken as evidence for the existence of a transitional five-coordinated species, making the ligand exchange mechanism dissociative. This means that one ligand molecule must leave the cadmium(II) ion, before a sixth DMPU molecule can restore the octahedral configuration. Transitional structures have also been reported for water and DMSO, but in those instances they include a six/seven-coordination. The structure of bis[1,3-dimethyl-3,4,5,6-tetrahydropyrimidin-2(1H)-one-*κ*O]diiodocadmium(II) reported in Paper I was the second ever four-coordinated cadmium(II)iodide complex (and the first one with crystal coordinates).[153] The tetrahedral structure is the energetically favourable one, permitting enough space for the large iodide ions, and at the same time highly symmetrical. This has previously been proposed for similar systems in DMSO.[154, 155]

4.3 Structures of solvated lanthanoid(III) ions

As was described in the scope of this thesis (Chapter 1.1), the lanthanoid series is unique when it comes to certain properties. Nowhere else in the periodic table can we find such a long sequence of elements where the chemical properties are so similar. This is reflected in their troublesome history of discovery, but can also be used as an advantage when performing for instance an in-depth coordination chemistry study. It should be mentioned that when studying the *entire* lanthanoid series (probably also including scandium and yttrium), it is unavoidable to end up with massive amounts of data, but in return the results are likely worth more than two dozen investigations without the systematic order offered. Nevertheless, the interest in the lanthanoid(III) coordination chemistry has increased lately, as their trifluoromethanesulfonate salts have been found to be useful catalysts in organic syntheses.[63, 64] This creates a demand for increased knowledge about the coordination chemistry of the ions. And since DMPU also is frequently used in organic syntheses, the interest is two-fold.

4.3.1 Coordination numbers and the lanthanoid(III) ions

For the lanthanoids the coordination numbers are, in general, in the range from seven to nine. There are instances where higher numbers have been reached, usually involving small bidentate ligands (*e.g.* NO_3^-) and the larger, early lanthanoid(III) ions. Hydrates of lanthanoid(III) trifluoromethanesulfonate salts have recently shown water deficiency across the series as the ions get smaller.[71] Other examples in the literature report that a change in coordination number takes place, or even a configuration shift, but the they do not include any studies of water deficiency.[156-160] Clearly water is small enough to allow high numbers (nine-coordination), and a similar picture is seen for DMSO, where the coordination number has been determined to be eight (square anti-prismatic) in both solution and solid state.[161] Furthermore, the coordination number six is unusual but occurs in the hexabromo- and hexachlorolanthanoid(III) complexes. Numbers lower than six are only obtained with extremely bulky and space-demanding ligands, such as $N(Si(CH_3)_3)_2$.[60]

4.3.2 DMPU solvated lanthanoid(III) ions in solid state

All lanthanoid(III) iodides are octahedrally coordinated in the solid state (Paper V). The values are in very good agreement with previous listed ones, where the typical lanthanoid slope is seen (Fig. 26). Crystallographically, six-coordination has been observed in two structures of salts including DMPU solvated lanthanoid(III) ions, samarium(III)[87] and ytterbium(III)[85] and for the two rare earth ions, scandium(III)[162] and yttrium(III).[163] The EXAFS spectra for the studied DMPU solvated lantanoid(III) ions in the solid state show essentially the same function, which is a strong indication that they have the same coordination number (Fig. 27). Once again, the crowding around the metal ion due to the spatial demands of DMPU reduces the possibility for more than six DMPU molecules to bind to the central atom in a crystal lattice. For the early lanthanoid(III) ions (lanthanum to neodymium), the values obtained are more or less equal to those reported by Shannon[101]. The middle section (samarium to dysprosium) differ slightly (up to 0.01 Å) and the late lanthanoids (holmium to lutetium) by as much as more than 0.02 Å. The trend observed in this study is more regular than the one Shannon proposes (Table 13).

4.3.3 DMPU solvated lanthanoid(III) ions in solution

In solution, the DMPU solvated the lanthanoid(III) ions all have the same coordination number, with the exception in lutetium(III). The EXAFS function of the solvated lutetium(III) ion in the solid state is the same as in solution, something that is not seen in the remaining part of the series (Fig. 28), confirming what is seen in Fig. 26. This is extremely strong evidence that DMPU solvated lutetium(III) is six-coordinated. In addition, for the remaining ions, the contribution of multiple scattering within the metal-oxygen sphere is severely reduced and the mean Ln-O bond distance is long enough to exclude the possibility of a six-coordinated complex, but also sufficiently short to rule out an eight-coordinated complex. Therefore, the rest of the series must be seven-coordinated in solution.

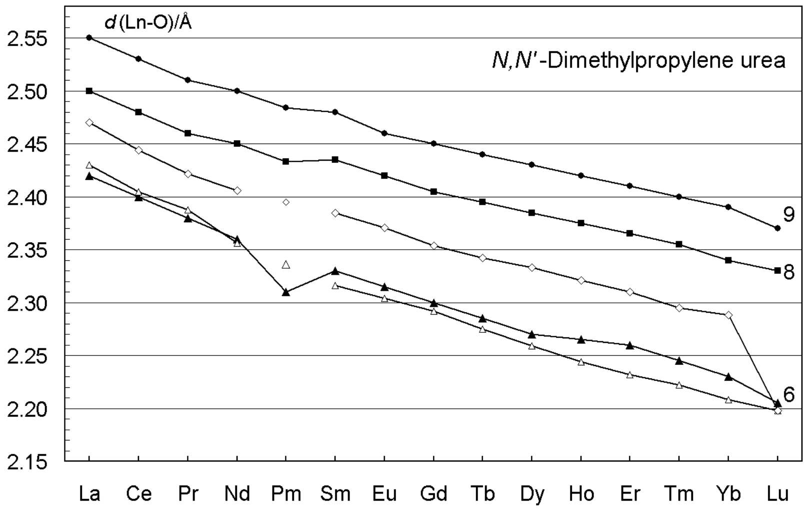


Fig. 26. The results of the EXAFS study of the DMPU solvated lanthanoid(III) ions. The middle series (◊) is from measurements on solutions and the bottom one on solid state (Δ). Shannon's values for six- (▲), eight- (■), and nine-coordination (●) are included for reference. The results show that DMPU solvated lutetium(III) has the same coordination number in both solution and solid state. The Pm-O bond distance has been estimated to 2.395 Å seven-coordination and 2.336 Å for six-coordination.

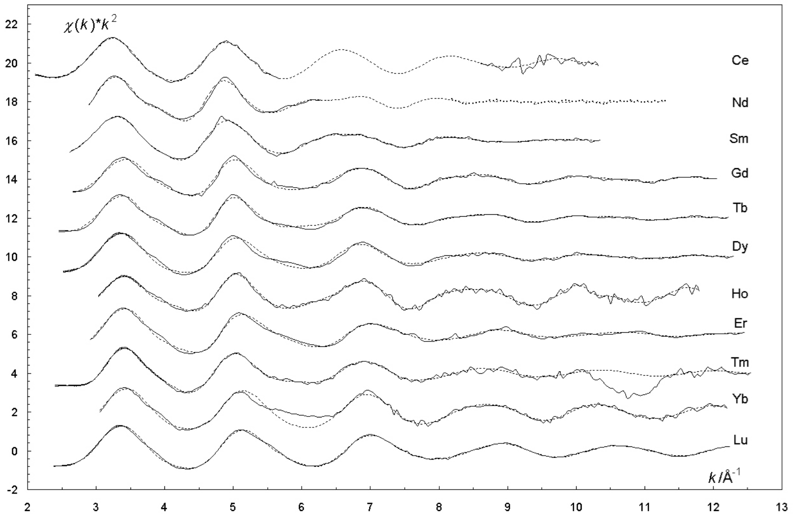


Fig. 27. The near-identical solid state EXAFS spectra for the DMPU solvated lanthanoid(III) ions. This is a strong indication that they have the same coordination number, in this case an octahedral symmetry.

Table 13. The ionic radii for the six- and seven-coordinated lanthanoid(III) ions. The values are based on the oxygen radius value (1.34 Å) from Beattie *et al.* (ref. 109).

	Ionic radius/Å	
Element	CN = 6	CN = 7
lanthanum	1.090	1.120
cerium	1.065	1.094
praseodymium	1.048	1.072
neodymium	1.016	1.056
promethium	[a]	[a]
samarium	0.976	1.035
europium	0.964	1.021
gadolinium	0.952	1.004
terbium	0.935	0.992
dysprosium	0.919	0.983
holmium	0.904	0.971
erbium	0.892	0.960
thulium	0.882	0.945
ytterbium	0.868	0.938
lutetium	0.858	0.858

[a] See chapter 4.5.2 for suggested values.

When performing EXAFS measurements at the K edge, rather than the lower L_3 edge, most of the backscattering (multiple) contribution is lost. This is depicted in the Fourier transform (Fig. 29). This artefact underestimates the importance of multiple scattering, but is not a problem if dealt with appropriately.

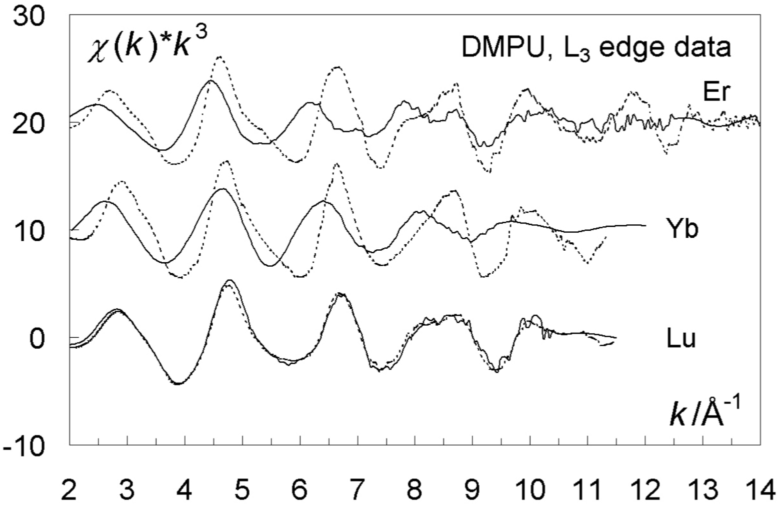


Fig. 28. A comparison between the EXAFS spectra for the DMPU solvated erbium(III), ytterbium(III), and lutetium(III) ions in solution (dotted line) and solid state (solid line). The identical spectra for lutetium(III) proves that the ion has the same coordination and configuration in solution and solid state.

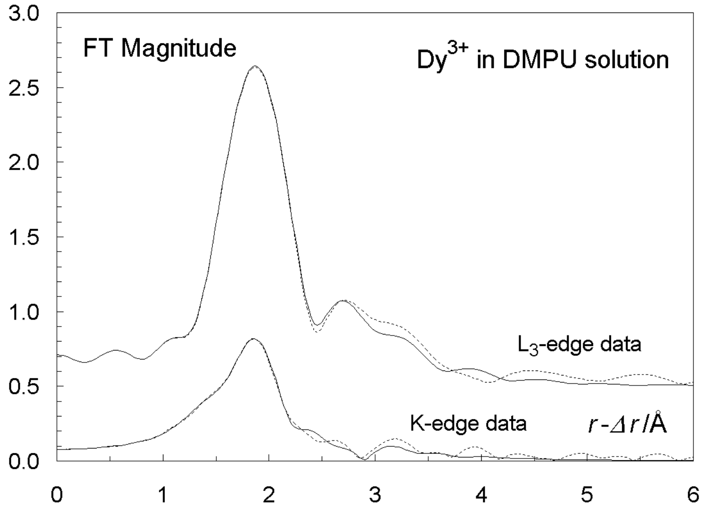


Fig. 29. A comparison between K-edge and L3-edge EXAFS data for the DMPU solvated dysprosium(III) ion in solution. Contributions outside the Dy-O sphere is lost in the high energy K-edge spectra.

4.4 Preferred coordination number

The papers included in this thesis and the works within its larger project include many examples that show that for hard metal ions a higher coordination number is observed in solution than in corresponding solid solvate, which often forces ions to settle with a lower coordination number, probably due to symmetry restrictions. For the DMPU solvated lanthanoid(III) ions this is seen in the varying coordination number in solution from seven to six, whereas the crystalline structures all are six-coordinated. This ultimately means that in all instances, in the corresponding solution, must exist a fraction of the six-coordinated species, albeit sometimes very small. The lattice forces are more favourable for highly symmetric complexes which causes precipitation of solvate complexes with this higher symmetry. The fashion with which the ligand exchange takes place can be observed in the mean M-O bond distance if the life-time of the transient species is sufficiently long, causing a significant increase or decrease in the M-O bond distance in comparison to observations in well-defined complexes in the solid state.

4.5 Element 61, promethium

Element 61 was the last of the lanthanoids to be discovered, in retrospect not strange at all since all of its isotopes are radioactive. Just like the other lanthanoids, it played tricks on numerous chemists, and there were several failed attempts to prove the existance of it. In the end, a trio of American scientists Jacob Marinsky and Lawrence E. Glendenin, led by Charles D. Coryell at Clinton Laboratories in Oak Ridge, Tennessee, found it among other rare earth elements eluted from radioactive samples. The political situation and the implication of the find, a new element in fission products of uranium, delayed the report of the discovery by a few years, but after a meeting with American Chemical Society in 1947 it was announced that element 61 had been found.[164] Suggestions for the name of element 61 included *phoenicium* (after the bird Phoenix, who rose from the ashes) and *clintonium* (after the laboratory in which it was found). Grace Mary Coryell, professor Coryell's wife, suggested prometheum (later changed to *promethium*) after Prometheus, the titan who stole the fire from the gods and gave it to humans.[4]

4.5.1 Physical chemical properties and usage of promethium

Promethium is formed as uranium decays, but is unstable and decays further into more stable elements. This means that the amount of promethium in the earth's crust at any given time is very low, in fact as low as $5{\cdot}10^{-20}$ g/ton (a rare earth in the true sense of the word!), too low to be able to be detected by conventional methods. With the help of spectral analysis, there have been indications that promethium is present on the surface of the star HR^{465} in the Andromeda galaxy.[8]

Naturally, the unstable nature of promethium limits the studies performed on and uses of the element, but there have been a few reports in addition to the original discovery publication.[165-167] Promethium has been used as a β emitter power cell in pacemakers, but the longevity was determined to be to limited.[168]

4.5.2 The coordination chemistry of promethium

Though there has been no investigation of the promethium(III) ion in this study, it is still possible to interpolate the coordination chemistry properties of the element through the characteristics the lanthanoid(III) ions display. These predictions are not as spectacular as those performed by Mendeleyev and later proven by Nilson and others, but rather using the same approach as Moseley did, which shows that the periodic trends of chemistry is still a valid method for predicting chemical behaviour. Based on studies parallel to this thesis performed by Abbasi *et al.*, the hydrated promethium(III) ion should be nine-coordinated, and the DMSO solvated eight-coordinated.[73] Based on the results in the work included in this thesis the DMPU solvate is seven-coordinated in solution, but the solid state reverts to a six-coordination as has been seen for many of the other lanthanoid(III) ions. The Pm-O bond distances and ionic radii for these coordination numbers are presented in Table 13 and the graphical verification is found in Figure 26. The value that Laubereau and Burns, who synthesized tricyclopentadienylpromethium(III) in 1969, suggested the value 0.979 Å as the promethium(III) ionic radius.[165] This is very close to the suggested value for six-coordinated promethium(III), and adds to the notion that cyclopentadienyl rings' pentahapticity corresponds to a regular bidentate ligand.

Table 14. Revised Pm-O bond distances and ionic radii for promethium(III) for coordination numbers (CN) six, seven, eight, and nine. Shannon's values are listed for comparison. The value for the oxygen radius (1.34 Å) is taken from from Beattie *et al.* (ref. 109).

CN	$d_{\text{Pm-O}}$/Å	IR/Å	IR/Å
6	2.34	1.00	0.97
7	2.38	1.04	n/a
8	2.44	1.10	1.093
9	2.48	1.14	1.144

5 Highlights

As we have seen in the different studies including DMPU, both previous ones reported and those part of this thesis, it is clear that the space-demanding ligand frequently creates a chemistry unlike the one we normally see in aqueous systems. The structure of the ligand molecule itself and its spatial demands are of utmost importance, unlike large donor atoms in ligand molecules such as sulfur, and further research will without any doubt reveal more structures with different reactivity and coordination preference.

We have established several structures where the behaviour of complexes in solution and solid state is notably different, which, in the case of iron(III) and other metal ions, changes the complex formation ability significantly. A greater understanding of such changes is needed to be able to understand reactions taking place in *e.g.* organic syntheses and to use this knowledge to perform reactions which are not possible to carry out in in the solvents normally used today.

The ionic radii given by Shannon for the six-coordinated lanthanoid(III) ions have been revised, and values for seven-coordination for the same have been supplied. Also, expected values for Pm-O bond distances for promethium(III) are made for six-, seven-, eight-, and nine-coordination.

The second four-coordinated cadmium(II) iodide, the first one with crystal coordinates, was structurally determined.

6 Future aspects

There are still many unexplored paths within the project of DMPU coordination chemistry. Completing the lanthanoid(III) study was a big leap forward, as the number of described DMPU structures doubled in number. The next project could possibly include the remaining first row transition metals, with special attention to manganese and cobalt. After a few more large-scale studies have been performed, it may be possible to determine what makes a certain metal ion choose its coordination number. The main factor the ionic radius, but are there other more factors involved? Comparisons with other cyclic ureas and ordinary urea may be needed to finetune the selectivity in coordination numbers. For the cyclic ureas, the five-membered *N,N'*-1,3-dimethyl-ethyleneurea and the non-methylated propyleneurea would be two prime candidates. Once the research has reached this far, it is probably a good idea to return to the lanthanoid series for a thorough beginning. The minute discrepancies between the different lanthanoids will surely come in handy, just as they did for Gadolin in the end of the 18th century.

7 Acknowledgment

First of all, naturally, I would like to thank my supervisor, **Ingmar Persson**. Ingmar, you gave me the chance of a lifetime and I have never felt like I made a bad choice. You have shown me more of the world than most other people I know – and what a journey it has been! I guess we have circled the globe a few times, if only we had not been so set on returning every time. Our mutual visits to, for me, both new and familiar places (Umeå, San Francisco, Stockholm, Grenoble, Lund, and Rome), have shown me that there is more to chemistry than just the facts. Nevertheless, it is as an inorganic chemist you excel best, (though you do have certain skills in innebandy as well). At least to me, it is not a coincidence that your name anagrams into *man in progress*.

Secondly, my graditude goes to my assistant supervisor, **Lars Eriksson**. Lasse, I can only speculate what you would have done if I had not asked you to be my assistant supervisor, but I know for a fact that you would have had a lot more time on your hands! Then again, you probably would have helped someone else instead. I have had very many stimulating conversations with you covering essentially all subjects possible, and I think you enjoyed them as well. I like the idea of us writing a book together sometime. It would be completely pointless, but still attract the wild minds I know exist out there! Our mutual trips were not as long as the ones I took with Ingmar, usually to the nearest cafeteria or the occasional trip to MAX-Lab, but they were just as interesting.

Special mention also goes to **Paola D'Angelo**, who explained why EXAFS works and what to do when it does not behave! *Che palle!* The time we spent in Uppsala, Malmö, and Rome will remain a permanent memory engram. I hope we have a chance to meet on a regular basis, so I can teach you some more Swedish and the art of drinking (real Swedish) coffee.

For help with the thesis and other scientific discussions, I recognize the support and insight from **Ingmar Persson** (for innumerable fruitful suggestions), **Vadim Kessler** (an expert crystallographer who, together with **Gulaim Seisenbaeva**, helped me with the Russian abstract in this thesis – in the wintertime, who has the time to be *snegative*?), **Ida Widnersson** (who assisted in the layout and proof-reading), **Tobias Lauer** (who helped me with the translation of the German abstract and some non-chemist proof-reading), and **Anton Pohanka** (who dares to criticize me when he thinks I am wrong!)

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The innebandy people should also get some of the glory. I know I will miss the Friday sessions a lot, but I will try to keep playing (if possible). For all of you interested, the only time I failed to score more than twice was that famous why-did-you-lift-your-stick-**Henrik** -when-I-tried-to-jump-over-it time and I had to leave the game prematurely. The pain in my leg went away, but the blemish in the scoring sheet remains. For those of you still playing when I leave, may I remind you of an old Klingon saying: *”If winning is not important, why keep score?”*

My room mates over the years, **Leif Häggman** (the Timrå fan from up north), **Pavel Smirnov** (I still use your miniature Russian-English dictionary!), **Joanna Krakowiak** (who introduced me to Polish rock!), **Krzystof Lyzcko**, (always happy!), **Gunnar** and **Anton** (the rest of the trio con brio) should all receive their well-earned credit. Together, you put up with the same type of music over and over again and very rarely complained – I guess I did not play loud enough.

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On a more personal level I want to thank a different set of people, those who made me excel as a person during my time as a Ph.D. student. Firstly, **Julia**, who has been there all the time. Thanks for all those samovars of tea! I don’t know what else to say. Secondly, **Johan Kuikka**, who is never more than a phone call away (except when he is changing provider – silly you!) and **Olof Widmark**, always ready to do something fun. A special thanks goes to **Elin Ahldén**, **Jonas Östlund** and **Cecilia** (Ceci) and **Tobias Lauer** for hosting me and pleasant discussions about life *as such*. And I would not be who I am if it was not for my parents **Bengt** och **Ingrid**, my brothers **Patric**, **Joacim**, and **Alexander**, and the rest of the family lines (seven generations up and seven generations down). Tack!

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If you have not figured it out yet, besides creating crosswords, I find nothing more soothing than listening to **Erasure**, **Lindemän** or **Owe Thörnqvist**, watching *Mystery Science Theater 3000*, *Star Trek* or *Dead Men Don’t Wear Plaid*, solving *Rätselrennen* (thanks **CuS**!), laughing and joking, or just enjoying a cup of coffee or tea while doing nothing. What do you do to relax?

However, I will miss *you* most of all, **Scarecrow**.

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Abbreviations and symbols used

acac = 2,4-pentanedione (acetylacetone)
C_{4v} = trigonal bipyramidal symmetry
CN = coordination number
Δ = change (Greek letter delta)
DMF = *N,N*-dimethylformamide
DMPU = *N,N'*-dimethylpropyleneurea
DMSO = dimethylsulfoxide
DMTF = *N,N*-dimethylthioformamide
EXAFS = extended X-ray absorption fine structure
G = Gibbs energy
GNXAS = data analysis software for EXAFS data
H = enthalpy
HMPA = hexamethyltriphosphoric amide
HSAB = hard and soft acids and bases (theory)
IUPAC = International Union of Pure and Applied Chemistry
L, L' = ligand (atom, ion, or molecule)
LAXS = large angle X-ray scattering
M = metal atom or ion (if charged)
O_h = octahedral symmetry
S = entropy
sqpl = square planar
sqpy = square pyramid
tbp = trigonal bipyramid
T_d = tetrahedral symmetry
TMU = 1,1,3,3-tetramethylurea
trig = trigonal

IUPAC names of solvents

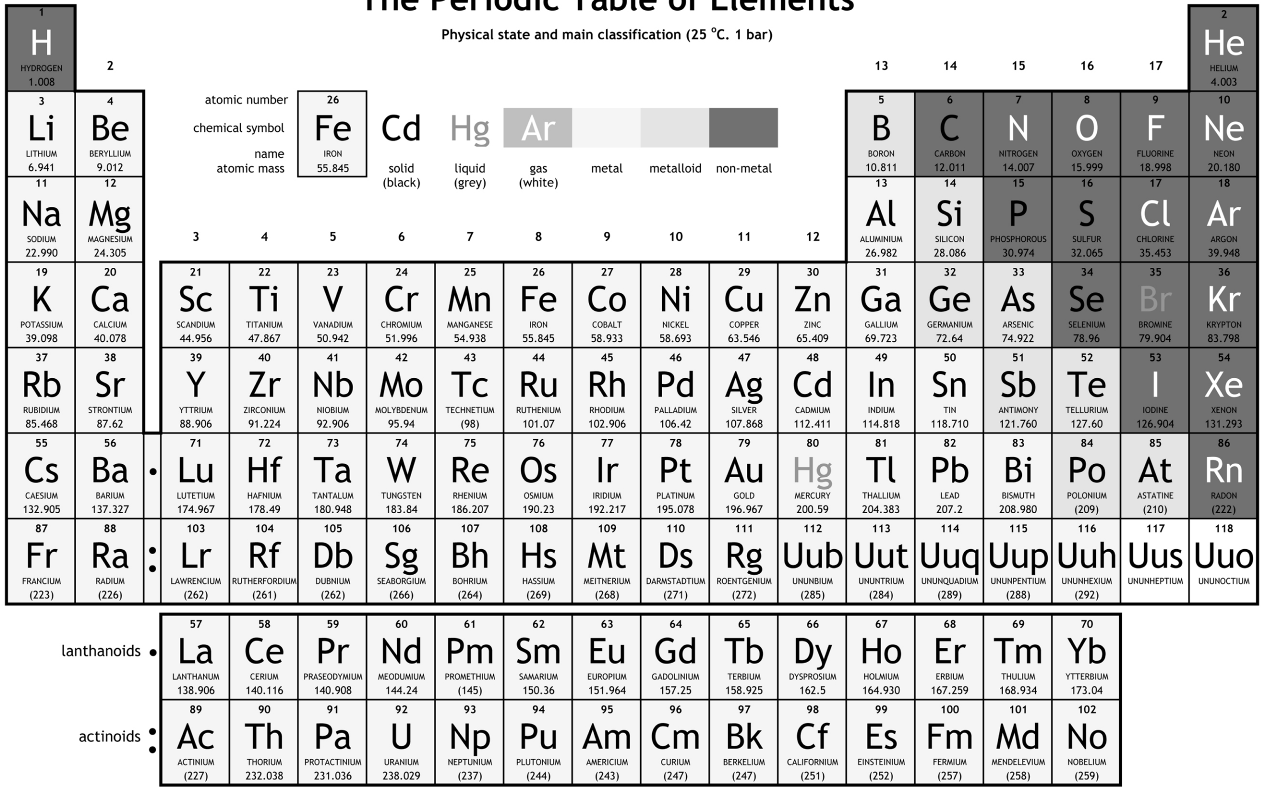
DMF = *N,N*-dimethylmethaneamide
DMPU = 3,4,5,6-tetrahydro-1,3-dimethyl-2(1*H*)-pyrimidin-2-one
DMSO = methylsulfinylmethane
DMTF = *N,N*-dimethylmethanethioamide
HMPA = *N*-bis(dimethylamino)phosphoryl-*N*-methylmethanamine
TMU = 1,1,3,3-tetramethylurea

The Periodic Table of Elements

Physical state and main classification (25 °C. 1 bar)

atomic number — 26
chemical symbol — Fe
name — IRON
atomic mass — 55.845

Cd	Hg	Ar			
solid (black)	liquid (grey)	gas (white)	metal	metalloid	non-metal



1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H HYDROGEN 1.008																		2 He HELIUM 4.003
3 Li LITHIUM 6.941	4 Be BERYLLIUM 9.012												5 B BORON 10.811	6 C CARBON 12.011	7 N NITROGEN 14.007	8 O OXYGEN 15.999	9 F FLUORINE 18.998	10 Ne NEON 20.180
11 Na SODIUM 22.990	12 Mg MAGNESIUM 24.305												13 Al ALUMINIUM 26.982	14 Si SILICON 28.086	15 P PHOSPHOROUS 30.974	16 S SULFUR 32.065	17 Cl CHLORINE 35.453	18 Ar ARGON 39.948
19 K POTASSIUM 39.098	20 Ca CALCIUM 40.078		21 Sc SCANDIUM 44.956	22 Ti TITANIUM 47.867	23 V VANADIUM 50.942	24 Cr CHROMIUM 51.996	25 Mn MANGANESE 54.938	26 Fe IRON 55.845	27 Co COBALT 58.933	28 Ni NICKEL 58.693	29 Cu COPPER 63.546	30 Zn ZINC 65.409	31 Ga GALLIUM 69.723	32 Ge GERMANIUM 72.64	33 As ARSENIC 74.922	34 Se SELENIUM 78.96	35 Br BROMINE 79.904	36 Kr KRYPTON 83.798
37 Rb RUBIDIUM 85.468	38 Sr STRONTIUM 87.62		39 Y YTTRIUM 88.906	40 Zr ZIRCONIUM 91.224	41 Nb NIOBIUM 92.906	42 Mo MOLYBDENUM 95.94	43 Tc TECHNETIUM (98)	44 Ru RUTHENIUM 101.07	45 Rh RHODIUM 102.906	46 Pd PALLADIUM 106.42	47 Ag SILVER 107.868	48 Cd CADMIUM 112.411	49 In INDIUM 114.818	50 Sn TIN 118.710	51 Sb ANTIMONY 121.760	52 Te TELLURIUM 127.60	53 I IODINE 126.904	54 Xe XENON 131.293
55 Cs CAESIUM 132.905	56 Ba BARIUM 137.327	•	71 Lu LUTETIUM 174.967	72 Hf HAFNIUM 178.49	73 Ta TANTALUM 180.948	74 W TUNGSTEN 183.84	75 Re RHENIUM 186.207	76 Os OSMIUM 190.23	77 Ir IRIDIUM 192.217	78 Pt PLATINUM 195.078	79 Au GOLD 196.967	80 Hg MERCURY 200.59	81 Tl THALLIUM 204.383	82 Pb LEAD 207.2	83 Bi BISMUTH 208.980	84 Po POLONIUM (209)	85 At ASTATINE (210)	86 Rn RADON (222)
87 Fr FRANCIUM (223)	88 Ra RADIUM (226)	:	103 Lr LAWRENCIUM (262)	104 Rf RUTHERFORDIUM (261)	105 Db DUBNIUM (262)	106 Sg SEABORGIUM (266)	107 Bh BOHRIUM (264)	108 Hs HASSIUM (269)	109 Mt MEITNERIUM (268)	110 Ds DARMSTADTIUM (271)	111 Rg ROENTGENIUM (272)	112 Uub UNUNBIUM (285)	113 Uut UNUNTRIUM (284)	114 Uuq UNUNQUADIUM (289)	115 Uup UNUNPENTIUM (288)	116 Uuh UNUNHEXIUM (292)	117 Uus UNUNHEPTIUM	118 Uuo UNUNOCTIUM
	lanthanoids	•	57 La LANTHANUM 138.906	58 Ce CERIUM 140.116	59 Pr PRASEODYMIUM 140.908	60 Nd MEODUMIUM 144.24	61 Pm PROMETHIUM (145)	62 Sm SAMARIUM 150.36	63 Eu EUROPIUM 151.964	64 Gd GADOLINIUM 157.25	65 Tb TERBIUM 158.925	66 Dy DYSPROSIUM 162.5	67 Ho HOLMIUM 164.930	68 Er ERBIUM 167.259	69 Tm THULIUM 168.934	70 Yb YTTERBIUM 173.04		
	actinoids	:	89 Ac ACTINIUM (227)	90 Th THORIUM 232.038	91 Pa PROTACTINIUM 231.036	92 U URANIUM 238.029	93 Np NEPTUNIUM (237)	94 Pu PLUTONIUM (244)	95 Am AMERICIUM (243)	96 Cm CURIUM (247)	97 Bk BERKELIUM (247)	98 Cf CALIFORNIUM (251)	99 Es EINSTEINIUM (252)	100 Fm FERMIUM (257)	101 Md MENDELEVIUM (258)	102 No NOBELIUM (259)		

The names and symbols of the elements are those approved by the International Union of Pure and Applied Chemistry (IUPAC). After years of dispute, IUPAC resolved the issue with naming elements 104-109 (*Pure & Appl. Chem.* . **1997.** 69. 2471-2473) in 1997. The atomic masses listed have been limited to three decimals. Elements with their atomic mass in parentheses do not have any stable isotopes. This is also the case with thorium, protactinium and uranium, but they have a natural composition which is listed here. The placements of the lanthanoids and actinoids is explained in W.B. Jensen "The positions of lanthanum (actinium) and lutetium (lawrencium) in the periodic table". (*J. Chem. Ed* .. **1982.** 59. 634-636). Francium could be the third liquid element at 25 °C, a fact supported extrapolation of the melting point alkali metal series (Group 1). **Layout: D. Lundberg, 2006.**