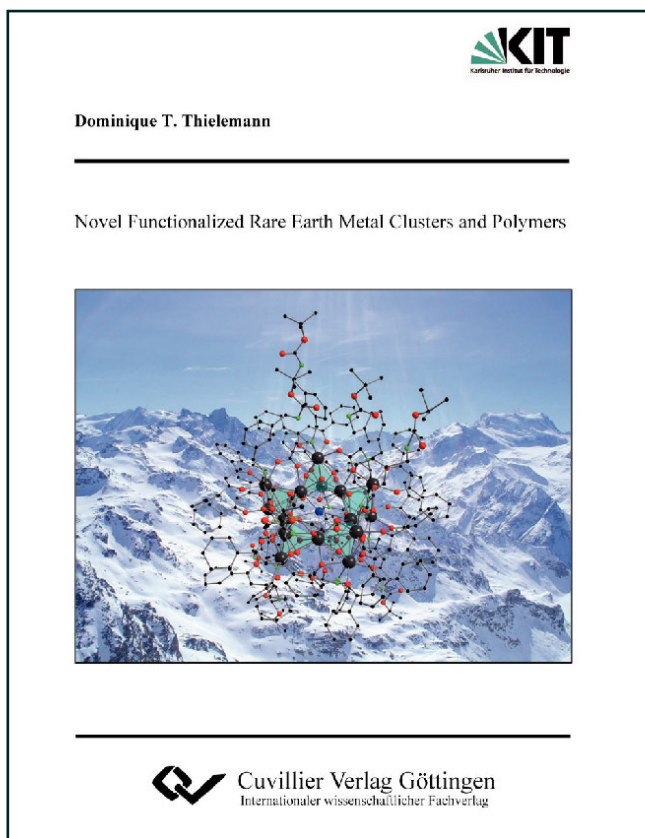




Dominique Tobias Thielemann (Autor)

Novel Functionalized Rare Earth Metal Clusters and Polymers

Neuartige Funktionalisierte Seltenerdmetallcluster und Polymere



<https://cuvillier.de/de/shop/publications/419>

Copyright:

Cuvillier Verlag, Inhaberin Annette Jentsch-Cuvillier, Nonnenstieg 8, 37075 Göttingen, Germany

Telefon: +49 (0)551 54724-0, E-Mail: info@cuvillier.de, Website: <https://cuvillier.de>

1. INTRODUCTION

1.1 The Rare Earth Elements

The rare earth elements comprise 17 metals, starting from scandium (Sc) and yttrium (Y), to be complemented by the 15 lanthanoids ranging from lanthanum (La) to lutetium (Lu). The group three elements scandium, yttrium and lanthanum show a similar chemical behaviour which is derived from the related valence electron configurations $[\text{Ar}]3d^14s^2$ (Sc), $[\text{Kr}]4d^15s^2$ (Y) and $[\text{Xe}]5d^16s^2$ (La).^[1] The term “lanthanoid” arises from the chemical similarity compared to lanthanum as its first representative, giving reason for their common occurrence in nature. Generally, the lanthanoids can be classified into two sections: the lighter lanthanoids can be found in the cerite earths and are assigned to the cerite earth elements (*currently abbreviated as Ct*), whereby they include the atomic numbers from 57 to 64 from lanthanum to gadolinium. The heavier lanthanoids exhibiting atomic numbers from 65 to 71 from terbium to lutetium were discovered in the ytter earths and are thus called the ytter earth elements (*currently abbreviated as Yt*). The denotation “rare earths” is assigned to the oxides of the corresponding elements, and the term “rare” is actually not justified as it solely arises from the late discovery compared to most other elements. The term “rare” is misleading, since some of the rare earth metals show a higher occurrence than some transition metals. For example, tin and cobalt are more rare than cerium, lead is more rare than neodymium and also the three precious metals silver, gold and platinum are more rare than europium and thulium.^[2]

Pacing from the left to the right in the lanthanoid series, the $4f$ -shell is consecutively filled from cerium ($[\text{Xe}]4f^15d^16s^2$) to lutetium ($[\text{Xe}]4f^{14}5d^16s^2$). The low spatial extension of the $4f$ -electrons and their close proximity to the nucleus obstructs a participation in chemical bond synergism. They can only be removed in rare cases. The more distant $5d^1$ - and $6s^2$ -electrons exhibit much lower ionization energies than the $4f$ -electrons, hence, they can be removed much easier and are mainly responsible for the lanthanoids' similar reactivities. By removing the $5d^1$ - and $6s^2$ -electrons, the stable octet ($5s^25p^6$) is achieved to give the most common oxidation state +3 of the lanthanoids. As the $5s$ - and $5p$ -electrons additionally shield the $4f$ -electrons efficiently, the chemical reactivity of the latter is further minimized. Thus, any chemical bonding involving Ln^{3+} species is based on electrostatic interactions and only an insignificant contribution arises from covalent interactions. This issue discloses a large scope of coordination numbers and the energy barriers between different coordination geometries are comparably low.

Since the occupation of lanthanum's $5d$ -orbital with one electron is followed by the filling of the $4f$ -orbitals of the remaining 14 lanthanoids prior to continuation of the filling of the $5d$ -orbitals in hafnium, the lanthanoid series is quasi embedded into the $5d$ -series of the transition metals. In contrast to the conventional periodic table (Fig. 1.1) in which the lanthanoids are positioned below together with the actinoids, the extended periodic table of the elements visualizes this embedding more demonstratively.

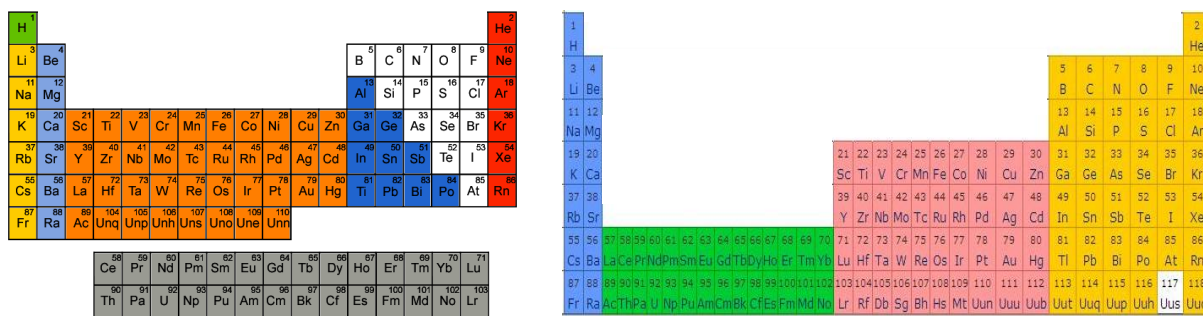


Figure 1.1. Lanthanoid and actinoid series set apart from main periodic table (left) and optional inclusion of lanthanoids and actinoids between the s - and d -block elements (right).

The lanthanoids' $4f$ -orbitals exhibit a shape which is fairly odd compared to its s -, p - and d -analogues, *i.e.* they possess a large surface due to their complex wave functions. In conjunction with the low spatial extension of the $4f$ -orbitals, this aspect effectuates a strikingly shielded of the $5s$ - and $5p$ -electrons, as the $4f$ -orbital geometry is not capable of efficiently compensating the nuclear charge. As a result, by increasing the nuclear charge from cerium (58 protons) to lutetium (71 protons), the effective nuclear charge Z_{eff} increases as well, *i.e.* the ionic radii steadily decrease from the early to the late lanthanoid elements (Fig. 1.2).^[3] Concomitantly, the effective nuclear charge Z_{eff} of the ion tors increases. This effect is called the “lanthanide contraction”,^{[4]-[5]} making each of the element pairs zirconium and hafnium, niobium and tantalum, as well as molybdenum and tungsten almost chemically indistinguishable. Despite the described electrostatic reasons, additional relativistic effects have been reported in literature as another origin of this contraction.^[6]

| Ln^{3+} | Ionic radius [Å] | Ln^{3+} | Ionic radius [Å] |
|------------------|------------------|------------------|------------------|
| La | 1.216 | Tb | 1.095 |
| Ce | 1.196 | Dy | 1.083 |
| Pr | 1.179 | Y | 1.075 |
| Nd | 1.163 | Ho | 1.072 |
| Pm | 1.144 | Er | 1.062 |
| Sm | 1.132 | Tm | 1.052 |
| Eu | 1.120 | Yb | 1.042 |
| Gd | 1.107 | Lu | 1.032 |

Table 1.1. Ionic radii of trivalent nine-coordinate rare earth metal ions.^[3]

1.2 Occurrences and Processing

In nature, there are numerous minerals from which rare earth metals can be gained. The cerite earth elements are mainly present in two minerals: firstly, there is the monazite which is composed of a binary silicate/phosphate host lattice accommodating both cerite earth elements and thorium $(\text{Ce,Th})[(\text{P,Si})\text{O}_4]$, whereby those cerite earth elements having even atomic numbers (cerium, neodymium, samarium and gadolinium) make up the major fraction, as required by Harkins' rule. Monazite can primarily be found in Brazil, in South India, in Sri Lanka, in Western Australia, in the USA and in granitic pegmatites in South Norway. The second mineral, bastnaesite, is primarily present in Kongo and New Mexico, but also countries like *e.g.* Hungary, Greece, the Balkan region, Norway, Mongolia, Malawi and Canada have certain occurrences.^[7] It displays a carbonate/fluoride containing host lattice which mainly contains cerium, lanthanum and dysprosium, whereby the molar fractions of all the rare earth elements depend on the individual deposits. In contrast, the ytter earth elements are primarily available in minerals like thalenite $\text{Yt}_2[\text{Si}_2\text{O}_7]$, thortveitite $(\text{Yt,Sc})_2[\text{Si}_2\text{O}_7]$, gadolinite $\text{Be}_2\text{Fe(II)Yt}_2\text{O}_2[\text{SiO}_4]_2$ and xenotime YtPO_4 , whereby their consistencies once more agree well with Harkins' rule. However, about 70 % of the world total rare earth reserves are placed in china, comprising almost all the minerals described.^[1]

Purposing to separate the rare earth metals from each other to make them chemically applicable, the purified minerals are dissolved in either very basic or very acidic milieu. Initially, advantage was taken from the different solubilities of the corresponding nitrates or hydroxides applying fractional crystallization.^[8] Another possibility is to utilize the different affinities of the individual rare earth elements to form the corresponding tris(*n*-butylphosphate) (TBP) complexes *via* solvent extraction.^[9] However, this method is

unfeasible since several hundreds of separation steps are necessary. Nowadays, industrial separation of rare earth elements is performed *via* ion exchange.^[8-9] Therefore, the corresponding minerals or ores are grinded and dissolved in a hot sodium hydroxide solution. The sparingly soluble hydroxides are separated, dissolved in nitric acid and then charged on an organic ion exchange column. The stationary phase of the column is a resin which is preferably ammonium(polystyrene sulfonate). The adsorbed hydroxides exhibit different binding affinities to this resin, which is based on different hydrodynamic radii originating from individual ionic radii of the Ln³⁺-ions. The smallest Ln³⁺-ion Lu³⁺ possesses the highest charge density and the highest degree of hydration, hence, it has the largest hydrodynamic radius. Consequently, the hydrated Lu³⁺-ion provides the loosest bond to the resin of all the Ln³⁺-ions and is eluted as the first rare earth metal. The principle is *vice versa* valid for the largest Ln³⁺-ion La³⁺, hence, it is the last rare earth element to leave the column. The resulting order ranging from lutetium to lanthanum is further enhanced by addition of complexing agents such as *e.g.* EDTA (ethylene diamine tetraacetate) or α -hydroxy acetic acid and a suitable pH-value.^[8-10] Once the rare earth elements are entirely separated from each other, they can be easily converted to various starting materials like *e.g.* the corresponding trichloride hydrates [LnCl₃·(H₂O)_n] (n = 6, 7) for continuative reactions.

Regarding potential applications, the main significance of the rare earth elements arises from their unique photophysical^[11] and magnetic properties,^[4-5] as well as their comparably low toxicity for cellular organisms.^[11a, 11d] Based on these characteristics, they have successfully found applications as laser materials (*e.g.* YAG-lasers, yttrium-aluminium-garnet),^[12] luminescent devices (erbium doped optical fibres for telecommunication),^[13] permanent magnets^[4] and MRT contrast agents.^[14]

1.3 Rare Earth Metal Luminescence

The described shielding of the *4f*-electrons by the *5s*- and *5p*-electrons permits ligand-induced crystal field splitting only to a low extent. As a result, narrow emission lines are observed for all the rare earth elements, and the wavelengths of emission position are not influenced by individual ligand systems. The only energy split of *4f*-electrons occurs within a range of approximately 100 cm⁻¹ as a function of site symmetry, affording the so called “Stark sublevels”.^[11e] Nevertheless there is one exception with respect to spectrochemical sensitivity towards changes in the metal-ion environment, as *e.g.* the hypersensitive ⁵D₀ → ⁷F₂ transition

in europium(III) compounds which varies its wavelength notably upon changes of ligands and site symmetry.^[15]

The $4f$ -electrons in Ln^{3+} -ions are capable of undergoing $4f$ - $4f$ -transitions which are Laporte forbidden, *i.e.* the sum of the angular momenta of the electrons in the initial and final state do not change by an odd integer.^[11e] As a result, Ln^{3+} -ions exhibit low extinction coefficients upon direct excitation. Besides, this is not valid for divalent Ln^{2+} -ions, since they possess Laporte allowed $4f$ - $5d$ -transitions providing much larger extinction coefficients. Nevertheless, all the rare earth metal atoms provide a certain luminescence, after relevant excited states have once been populated. In this context, the Laporte forbiddance of the $4f$ - $4f$ -transitions even provides one crucial advantage supporting rare earth metal luminescence: the long lifetimes of their excited states which are directly correlated to low probabilities of forbidden transitions. This adds a certain value to the forbiddance of relaxation *via* $4f$ - $4f$ -transitions, since the luminescence of rare earth metal species persists much longer than *e.g.* the autoluminescence of cells. In this context, time resolved luminescence measurements of *e.g.* cellular systems incubated with certain rare earth metal complexes facilitate a reliable localization of the compound *in vivo* and *in vitro*.

The most remarkable representatives are europium and terbium emitting in the visible range of light (360 nm – 760 nm). Neodymium, erbium and ytterbium are capable of emitting luminescence efficiently in the near infrared (NIR) range (760 nm – 2500 nm). The remaining rare earth metal atoms do not provide notable luminescence properties, hence, their applicability as luminescent devices is confined to a minimum.

The discrepancy of the low extinction coefficients can be circumvented by *e.g.* tethering an electronically suitable ligand on a rare earth metal atom to induce a ligand-to-metal energy transfer (LMCT). This process is capable of populating the corresponding excited states of the rare earth metal atoms from which relaxation occurs upon emission of luminescence. Depending on the individual purposes of application, the ligand of choice might be organic like *e.g.* multiply substituted 8-hydroxyquinoline derivatives or inorganic like *e.g.* an oxo ligand. The latter one is currently utilized in europium doped yttrium oxide lattices,^[16] which depicts the origin of the phosphors for cathode-ray tubes and fluorescent lamps.^[17] For the organic ligands, high energy vibrators like O-H and C-H moieties should be absent to avoid quenching of the luminescence. In this context, usage of perfluorinated ionic liquids instead of standard solvents supports higher quantum yields, as previously shown by several groups.^[11d] In addition, three-dimensional molecular networks in terms of *e.g.* metal organic frameworks (MOF) further prevent quenching of luminescence by “swallowing” scaffold

vibrations *via* resonance coupling. This effect can also be achieved upon utilization of multidentate ligands which allocate as much donor atoms as possible to facilitate a high degree of chelation and/or bridging. The latter issues imply the following relation: the lower the vibrational and rotational flexibility of the ligands and of the whole molecular scaffold, the less degrees of freedom are allocated for luminescence quenching.^[11d]

1.4 Rare Earth Metal Magnetism

Except Sc^{3+} , Y^{3+} , La^{3+} and Lu^{3+} , all the trivalent rare earth metal ions possess unpaired $4f$ -electrons and are thus paramagnetic. The magnetic properties of the rare earth metal ions are given by the ground states,^[18] because the rare earth metal ions' excited states are thermally inaccessible. In analogy to the aforementioned lack of spectrochemical sensitivity, the magnetic moments μ_{eff} (given in $[\mu_{\text{B}}]$, Bohr magneton) of rare earth metal ions are essentially not influenced by their chemical environment. In consequence, the magnetic properties are not modified upon a change of the ligand or the coordination geometries, as observed for transition metal compounds. μ_{eff} is given by the equation:

$$\mu_{\text{eff}} = g_J [J(J + 1)]^{1/2}$$

J is the quantum number and the Landé factor g_J is given by the following relation:

$$g_J = 3/2 + [S(S + 1) - L(L + 1)]/2J(J + 1)$$

S is the spin quantum number and L is the quantum number of angular momentum.

In general, the magnetic moments μ_{eff} is larger for the second half than for the first half of the lanthanoid series, since a more than half-filled $4f$ -shell underlies the relation $J = L + S$ and not $J = L - S$, as for the less than half-filled $4f$ -shell of the cerite earth elements.^[18] Consequently, the heavier homologues such as dysprosium gain more relevance for potential applications.^[19] In contrast to the other trivalent rare earth metal ions, Sm^{3+} and Eu^{3+} exhibit spin-orbit coupling to a much lower extent, allowing low-lying paramagnetic excited states to give a contribution to μ_{eff} . This aspect makes the ground state ${}^7\text{F}_2$ in Eu^{3+} thermally accessible and leads to magnetic moments of $3.5 \mu_{\text{B}}$ at room temperature, compared to its diamagnetic ${}^7\text{F}_0$ analogue. The same case is valid for Sm^{3+} , in which the thermally populated ${}^6\text{H}_{7/2}$ ground

state provides paramagnetic behaviour with a magnetic moment of $1.6 \mu_B$, in contrast to the corresponding ${}^6H_{5/2}$ analogue with only $0.85 \mu_B$.

Dysprosium also exhibits low-lying excited states in terms of Stark sublevels within its ${}^6H_{15/2}$ ground state,^[20] providing a very large magnetic moment of $\mu_{\text{eff}} = 10.60 \mu_B$. Moreover, the Dy^{3+} -ion is not spherical in shape, as the $4f^9$ -configuration offers an ensemble of both paired and unpaired electrons ($S = 5/2$). This aspect is associated with a distinct anisotropy, which is in addition to the low-lying excited states essential as a requirement for single-molecule-magnet (SMM) behaviour.^[20-21] Furthermore, SMMs have a certain blocking temperature being usually in the lower Kelvin scale. Below this temperature, the magnetized SMM compounds show a deceleration of relaxation of magnetization, *i.e.* the magnetization is maintained for up to several years.^[22] If an earlier relaxation is purposed, a reversed field is required to bring magnetization back to zero, which makes the magnetism of such compounds switchable and thus flexible on the molecular scale. In this context, the resulting hysteresis below this temperature is of pure molecular origin. Thus, collective long-range magnetic ordering of magnetic moments is not necessary and makes the magnetic spins much more flexible, compared to conventional bulk magnets.

These aspects let SMMs appear as a first approach towards nanomagnets, in which each molecule might serve as the smallest feasible unit for *e.g.* magnetic storage. Optimization of these compounds might further gain applications in fields like quantum computing, high-density information storage and magnetic refrigeration.^[23]

1.5 Rare Earth Metal Clusters

Beyond the mononuclear compounds providing the valuable properties above described, the utilization of oligo- to polynuclear rare earth metal compounds promise to enhance all the desired effects. Therefore, rare earth metal based clusters appear as a suitable approach, since they represent molecular intermediates linking molecular and solid state chemistry and they help to understand size-dependent photophysical properties of electronic materials.^[24] The chemistry of rare earth metal clusters is by far not as developed as the cluster chemistry of the transition metals (especially of molybdenum,^[25] copper,^[26] silver^[27] and gold^[28]), which is surprising since oligomeric lanthanoid structures are proposed to play a key role in some catalytic transformations.^{[29],[30],[31]}