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Stability of europium(II) in aqueous nitrate solutions

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Electronic supplementary information (ESI) available: Background information and supporting CV measurements, UV-VIS spectra, magnetic susceptibility data and XANES spectra.

AbstractView Article Online
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In the lanthanide series, Eu^{3+} is the most easily reduced to its divalent state. Reduction of Eu^{3+} has been studied extensively in aqueous media that are insensitive to reducing conditions. Recently, it was reported that reduction of Eu^{3+} is also feasible in aqueous nitrate solutions, and that Eu^{2+} remained sufficiently stable in these media to conduct separation experiments. However, additional fundamental research on the reduction efficiency of Eu^{3+} and stability of Eu^{2+} in these media has not been reported yet. In this paper, cyclic voltammetry, magnetic susceptibility measurements, UV-Vis absorption spectroscopy and X-ray absorption near edge structure (XANES) were used to gain more insight in the reduction of Eu^{3+} in aqueous nitrate media. Within the parameters used in this work, near-quantitative reduction of Eu^{3+} could be achieved within 120 min in highly concentrated nitrate salt solutions, using both chemical and electrochemical reduction techniques. Moreover, Eu^{2+} was remarkably stable in these solutions, showing just a few percent of back-oxidation after 5 h in a sealed measurement cell.

Keywords: Divalent europium; lanthanides; XANES; magnetic susceptibility; electrochemistry

Introduction

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Lanthanides are crucial elements in lamp phosphors and permanent magnets, and several radiolanthanides have found their application in nuclear medicine.¹⁻⁴ For some of these applications, a very high level of purity is required. In the past, europium had a high supply risk because of its use in lamp phosphors.⁴⁻⁶ A lot of research was conducted to obtain europium from various resources, including both primary (by-product in ores, *e.g.* monazite) and secondary (end-of-life products, *e.g.* fluorescent lamps) ones. In these resources, europium is always found together with other lanthanides. However, separation of europium from other lanthanides by ion-exchange and solvent extraction is very challenging. The lanthanide ions possess very similar electronic structures ([Xe] 4f⁰⁻¹⁴) with a predominant trivalent oxidation state (Ln³⁺). The 4f subshell is filled with electrons across the lanthanide series, which are shielded by the electrons in the filled 5s and 5p subshells. As a consequence, the 4f electrons show a core-like behavior, *i.e.* they do not participate in bond formation or ligand interactions.^{7,8} This results in very similar chemical properties across the lanthanide series.

Changing the oxidation state induces significant changes in chemical properties, which opens perspectives for the development of efficient separation technologies. Ce³⁺ ($E^0(\text{Ce}^{4+}/\text{Ce}^{3+}) = +1.72 \text{ V}$) and Tb³⁺ ($E^0(\text{Tb}^{4+}/\text{Tb}^{3+}) = +3.10 \text{ V}$) can be oxidized to the +IV oxidation state, by which they are stabilized by an empty 4f subshell ([Xe] 4f⁰) and by a half-filled 4f subshell ([Xe] 4f⁷), respectively. Sm³⁺ ($E^0(\text{Sm}^{3+}/\text{Sm}^{2+}) = -1.55 \text{ V}$), Eu³⁺ ($E^0(\text{Eu}^{3+}/\text{Eu}^{2+}) = -0.34 \text{ V}$) and Yb³⁺ ($E^0(\text{Yb}^{3+}/\text{Yb}^{2+}) = -1.05 \text{ V}$) can be reduced to the +II oxidation state because of a stabilizing effect of a near-half filled ([Xe] 4f⁶), a half-filled ([Xe] 4f⁷) and a filled 4f subshell ([Xe] 4f¹⁴), respectively. However, Sm²⁺ and Yb²⁺ in aqueous solutions tend to be

very short-lived because of their high oxygen-sensitivity and their high tendency to reduce water. Eu^{2+} is known to have a reasonably long lifetime in aqueous solutions, despite its

reduction potential lying outside the stability region of water.

Eu^{3+} can be selectively reduced using chemical, electrochemical or photochemical techniques.⁹⁻¹⁵ Oxidizing agents, such as dissolved oxygen ($E^0(\text{O}_2/\text{H}_2\text{O}) = +1.23 \text{ V}$), H^+ ($E^0(\text{H}^+/\text{H}_2) = 0.00 \text{ V}$) or nitrate anions ($E^0(\text{NO}_3^-/\text{NO}) = +0.95 \text{ V}$, in presence of H^+), are usually avoided because of the high possibility for back-oxidation of Eu^{2+} . Consequently, reduction of Eu^{3+} is usually performed in media that are insensitive to reducing conditions, most often containing chlorides.^{9,11,14-19} Nevertheless, our research group recently observed that Eu^{3+} could also be successfully reduced in nitrate media at quasi-neutral pH.^{20,21} Reducibility of Eu^{3+} in aqueous nitrate media opens new perspectives to isolate europium from other trivalent lanthanides. The ability of trivalent lanthanide ions to form extractable nitrate complexes, whereas divalent lanthanide ions cannot, is important with respect to development of efficient separation and purification techniques.²²⁻²⁴ We have shown that Eu^{2+} is sufficiently stable in deaerated aqueous solutions with high nitrate salt concentrations to perform solvent extraction, leading to a very efficient method to separate samarium and europium.²⁰ The formation of europium in its divalent state was evident from a color change of the aqueous solution upon reduction, *i.e.* from a colorless solution to a yellow-orange solution. The colored solutions showed to be stable over time in an inert atmosphere, but gradually lost their color upon contact with air (with O_2 as oxidizing agent) or upon acidification (addition of H^+ as oxidizing agent).

In this paper, additional fundamental research was conducted to investigate the reducibility of Eu^{3+} and the stability of Eu^{2+} in aqueous nitrate media. Chemical and

electrochemical reduction of Eu^{3+} in nitrate aqueous media were demonstrated and investigated by using various techniques. The influence of the nitrate salt concentration in solution on the reducibility of Eu^{3+} was elucidated, and the time needed to reach maximum reduction of Eu^{3+} was determined. The relative amounts of Eu^{2+} and Eu^{3+} as a function of reduction time were determined by X-ray absorption near-edge structure (XANES) measurements using the europium L_{III} -edge.²⁵⁻³¹ More detailed quantification of the reduction rate using electrochemical reduction techniques is subject of current investigations.

Experimental

Materials

$\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%) was purchased from Strem Chemicals, Inc. (Newburyport, USA). LiNO_3 (anhydrous, 99%) was purchased from Alfa Aesar (Karlsruhe, Germany). $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%) and granular zinc (30 mesh, $\geq 99.7\%$) were purchased from Acros Organics (Geel, Belgium). LiCl (99%) was purchased from Sigma-Aldrich (Overijse, Belgium). Europium and zinc standard solutions ($\geq 99.99\%$, $1000 \mu\text{g mL}^{-1}$, 2-5% HNO_3 , Plasma HIQU), $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ($>99\%$), NH_4NO_3 ($>99\%$) and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ($>99.5\%$) were purchased from Chem-Lab (Zedelgem, Belgium). All products were used as received, without any further purification. Aqueous samples were prepared with MilliQ water ($18.2 \text{ M}\Omega \text{ cm}$ at 25°C).

Methods

Chemical reduction of europium was performed by using a large excess of granular metallic zinc, *i.e.* at least hundred stoichiometric equivalents. The solutions contained

various concentrations of europium (0.66, 6.6 and 66 mmol L⁻¹) and nitrate salt (0.1, 3.6 or 9 mol L⁻¹ NO₃⁻). Analogous chloride solutions were studied for comparison. The aqueous solutions were purged with argon before and during reduction of Eu³⁺ to remove aerial and dissolved oxygen to prevent back-oxidation of Eu²⁺ by O₂. The pH of the aqueous feed solution was kept between 4.5 and 6.5. This way, the pH of the final feed solution remained sufficiently high to avoid back-oxidation of Eu²⁺ by H⁺ or NO₃⁻ (in the presence of H⁺), and sufficiently low to prevent precipitation of Eu³⁺ as europium hydroxide. The majority of Zn²⁺ formed during reduction of Eu³⁺ was found to precipitate as the white, highly insoluble zinc(II) hydroxide in these conditions. The pH was measured before and after reduction of Eu³⁺ by means of a Hamilton Slimtrode pH electrode coupled to a Mettler-Toledo SevenCompact pH meter. The solutions were filtered after chemical reduction through a syringe filter with a pore size of 0.45 µm before being analyzed.

Electrochemical reduction of europium was performed in a three-electrode electrochemical cell. The potential at the working electrode was controlled by a Metrohm Autolab PGSTAT302N potentiostat in potentiostatic mode, operated by Nova 2.1.2 software. *Cyclic voltammetry* (CV) experiments were performed in a custom-made glass electrochemical cell with a 50 mL inner volume. The solution was purged by argon gas prior to the measurements. A constant argon flow was maintained over the solution while cyclic voltammograms were recorded, providing an inert gas blanket. Dissolved oxygen (O₂) might slow down the kinetics of Eu³⁺ reduction because of the possible competition with O₂ reduction at the cathode.³² This is especially likely if protons are available, leading to the production of H₂O. A glassy carbon electrode (ϕ = 4 mm) served as the working electrode, and a coiled platinum wire (ϕ = 1 mm) served as the counter electrode. Platinum working

electrodes are less efficient for the reduction of Eu^{3+} because of their low overpotential for hydrogen generation. The reference electrode consisted of a Ag/Ag^+ redox couple in a 3 mol L^{-1} KCl solution ($E^0 = +0.2225$ V vs. SHE at 25 °C).³³ A scan rate of 50 mV s^{-1} was used, unless stated differently. Solutions containing 10 mmol L^{-1} of Eu^{3+} and various concentrations of nitrate and chloride salts (0, 1, 3, 6 and 9 mol L^{-1} NO_3^- or Cl^-) were studied. Electrolytic reduction of Eu^{3+} was performed in a BASi bulk electrolysis cell at a constant potential of -0.7 V vs. Ag/Ag^+ . A BASi MF-2077 reticulated vitreous carbon electrode (RVC, surface area: 10.5 cm^2 effective/ cm^2 geometric) was used as working electrode. The BASi MF-2052 reference electrode consisted of a Ag/Ag^+ redox couple in a 3 mol L^{-1} KCl solution. A BASi MW-1033 coiled platinum wire auxiliary electrode ($\phi = 0.5$ mm, 23 cm), separated from the electrolysis solution by a sintered glass frit (pore size: 4-5 μm), served as a counter electrode in these experiments.

UV-VIS absorption spectra were recorded to investigate the change in absorbance upon reduction of Eu^{3+} . Reduction of Eu^{3+} in aqueous nitrate media yielded a yellow-orange solution, whereas the start solutions were colorless. The reduction of Eu^{3+} in aqueous nitrate medium was compared to the reduction of Eu^{3+} in aqueous chloride medium. Chemical reduction was performed by stirring the solutions with zinc grains for 2 h in an inert atmosphere. Matching quartz cuvettes with a path length of 1 mm were used for Eu^{2+} samples, whereas matching quartz cuvettes with a path length of 10 mm were used for Eu^{3+} samples. Absorption spectra were recorded in the 200–800 nm range using an Agilent Cary 6000i UV-VIS-NIR spectrophotometer in double beam mode, operated by Cary WinUV software. Source changeover occurred at 350 nm. A scan rate of 150 nm min^{-1} and a resolution of 0.5 nm were used. The blank solutions consisted of a 3 mol L^{-1} $\text{Ca}(\text{NO}_3)_2$ and a

3 mol L⁻¹ CaCl₂ solution for measurement in aqueous nitrate and chloride media, respectively. These blank solutions were used to account for the broad absorption band of nitrate, ranging from 200 to 320 nm.³⁴ Spectra of the solutions containing europium were recorded in duplicate before and after reduction. A europium concentration of 6.6 mmol L⁻¹ was used in solutions containing 3 mol L⁻¹ Ca(NO₃)₂ and a 3 mol L⁻¹ CaCl₂.

Magnetic susceptibility measurements were performed to monitor the chemical and electrochemical reduction of Eu³⁺ in aqueous nitrate solutions containing 3 mol L⁻¹ Ca(NO₃)₂ at room temperature as a function of time. The magnetic susceptibility of the solution was measured every 15 min using a Sherwood Scientific MSB-AUTO magnetic susceptibility balance. Polished quartz sample tubes with an inner diameter of 4 mm were used to load the sample into the magnetic susceptibility balance. These quartz sample tubes were measured immediately after filling, and remained open during the short measurement. A sample tube sealed with Parafilm® was used to monitor the stability of Eu²⁺ in solution for 2.5 h after reduction.

X-ray absorption spectroscopy (XAS) was used to determine the Eu²⁺/Eu³⁺ ratios in the nitrate solutions containing different europium (0.66, 6.6 and 66 mmol L⁻¹) and nitrate (0, 3 and 6 mol L⁻¹) concentrations as a function of reduction and oxidation time in steps of 15 min. The XAS spectra were collected at room temperature at the Dutch-Belgian Beamline (DUBBLE, BM26A) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The energy of the X-ray beam was tuned by a double-crystal monochromator operating in fixed-exit mode using a Si(111) crystal pair. The energy was calibrated by means of a metallic iron foil. The measurements were performed in transmission mode using Ar/He-gas-filled ionization chambers at ambient pressure. A brass sample holder with Kapton® windows and

a flexible polymeric spacer (VITON) with a thickness of 2 mm was used as a sample holder.

The spectra were recorded by scanning through the europium L_{III} absorption edge (ca. 6977 eV), from 6775 to 7000 eV, focusing on the region in the spectrum near the edge. High-energy resolution (<0.5 eV) was used when scanning the region of 6964 to 6995 eV.

Deconvolution of the spectra by fitting procedures allowed spectral analysis.³⁵ The ratio between the integrated peaks allows calculation of the relative amount of Eu^{2+} and Eu^{3+} in the samples ($Eu^{x+}/(Eu^{2+} + Eu^{3+})$, with $x = 2$ or 3). The white line transition was approximated by fitting with a pseudo-Voigt function, whereas an arctangent background function for each oxidation state was used to fit the absorption edge step. The arctangent background function for both oxidation states had to be accounted for and the relative amounts of Eu^{2+} and Eu^{3+} changed as a function of the reduction time. Therefore, construction of the arctangent functions and peak deconvolution were solved iteratively in Origin 2016 (v9.3) (see ESI for the steps followed). Additionally, a correction factor for Eu^{2+} had to be taken into account, as it was observed in previous studies that the technique is not equally sensitive for both oxidation states.^{25,26,36,37} Peak amplitudes almost twice as high for Eu^{3+} compared to Eu^{2+} were already reported. In our work, the correction factor was determined to be 1.5, based on the peak amplitudes and peak areas. As mentioned by Moreau *et al.*, a very weak peak at slightly higher energy than the white line might appear in the spectrum, which is commonly attributed to multiple-scattering effects.³⁷ These effects, however, were not accounted for when calculating the relative amounts Eu^{2+} and Eu^{3+} in the samples.

Results and discussion

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Chemical reduction of europium

Reduction of Eu^{3+} to Eu^{2+} changes the chemical properties of the europium ion significantly, leading to different characteristics and ligand interactions.³⁸ The structural properties of Eu^{2+} are very similar to the ones of alkaline earth metals, *i.e.* the ionic radius of Eu^{2+} (1.25 Å) is similar to that of Sr^{2+} (1.26 Å).^{37,39} The approach of altering chemical properties of Eu^{3+} by reduction has been studied frequently to improve the isolation of europium from other trivalent lanthanides.^{9,11,16,20} Eu^{3+} can be reduced either chemically, electrochemically or photochemically.^{11-14,40} Chemical reduction of Eu^{3+} typically involves the use of metallic zinc or zinc amalgam (Zn(Hg) , Jones reductor, $E^0(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$):

Despite the efficient reduction of Eu^{3+} , Eu^{2+} is relatively sensitive towards back-oxidation. Therefore, oxidizing agents, such as dissolved oxygen (O_2) protons (H^+) or nitrate anions (NO_3^-) have to be avoided:

Consequently, reduction of Eu^{3+} is usually performed only in media that are insensitive to reducing conditions. For example, reduction of Eu^{3+} in an aqueous chloride media is already well established.^{11,14,16,32,41,42}

Taking into account the reduction potential of nitrate, the redox behavior of europium in aqueous nitrate media has not been intensively studied in literature yet. Only the work of Holleck in the 1940s,^{43,44} and a more recent study of Zelic in 2003 report electrochemical experiments on europium in aqueous nitrate media.²¹ Nevertheless, the formation and existence of Eu^{2+} in aqueous nitrate media in our experiments was clearly indicated by a change in color of the solution, *i.e.* the solution containing 6.6 mmol L^{-1} europium changed from colorless to yellow upon formation of Eu^{2+} . At higher europium concentrations (*ca.* 66 mmol L^{-1}), the solution turned orange (Figure 1). In contrast, reduction of Eu^{3+} in chloride media did not result in a colored solution.

Figure 1: Colored solutions of Eu^{2+} in aqueous solution containing $6 \text{ mol L}^{-1} \text{ LiNO}_3$ after chemical reduction for 2 h. The color changes as a function of the Eu^{2+} concentration in the solution, *i.e.* orange ($66 \text{ mmol L}^{-1} \text{ Eu}^{2+}$), bright yellow ($6.6 \text{ mmol L}^{-1} \text{ Eu}^{2+}$), pale yellow ($0.66 \text{ mmol L}^{-1} \text{ Eu}^{2+}$) and colorless ($0.066 \text{ mmol L}^{-1} \text{ Eu}^{2+}$).

The colored solutions remained stable over time when stored in a sealed vial under inert atmosphere (Ar or N₂). Our previous studies also showed that the colored solutions remained stable during solvent extraction and extraction chromatography processes, where Sm³⁺ could be efficiently separated from Eu²⁺.²⁰ The Eu²⁺-rich aqueous phases retained their yellow color after these separation experiments, indicating stabilization of Eu²⁺ species in these concentrated nitrate media.

Nevertheless, the Eu²⁺ nitrate solutions lost their color gradually upon exposure to oxygen in air (Eq. 2). Fast back-oxidation of Eu²⁺ by contact with oxygen was already observed by Jelinek *et al.* in aqueous chloride media.³² In order to achieve efficient reduction of Eu³⁺, it is important to remove all oxygen from the solution by purging with an inert gas prior to reduction. The solutions also lost their color instantly upon acidification (addition of H⁺, Eq. 3-4). An excess of H⁺ in the solution before reduction is not considered problematic as the excessive H⁺ will be efficiently reduced by Zn⁰ or Eu²⁺, producing H₂. This automatically results in an increase of pH, leading to more neutral pH, so that Eu²⁺ is not further back-oxidized. The presence of H⁺ in the initial solution will result only in slightly longer reduction times and H₂ generation. Nevertheless, a minimal acidity is required to avoid precipitation by hydrolysis of Eu³⁺ (at pH >6.5). Additionally, it is known that reactions of nitrogen-oxygen compounds are generally slow at ambient temperatures and low acidity, which is beneficial for the lifetime of Eu²⁺ in nitrate salt solutions.

Remarkably, solutions with low nitrate salt concentrations (<3 mol L⁻¹) did not change color upon reduction, indicating that a minimum nitrate salt concentration is required to reduce Eu³⁺ and stabilize Eu²⁺. Presumably, the lower nitrate salt concentrations, and consequently lower ionic strengths, were insufficient to stabilize Eu²⁺ species in solution

(*vide infra*). A change in counter ion of the inert nitrate salt (*i.e.* NH_4NO_3 , $\text{Ca}(\text{NO}_3)_2$ or LiNO_3)

did not influence these observations. The behavior of a 3 mol L⁻¹ $\text{Ca}(\text{NO}_3)_2$ blank solution and a 3 mol L⁻¹ $\text{Ca}(\text{NO}_3)_2$ solution containing another Ln^{3+} , *i.e.* Sm^{3+} , in contact with Zn^0 were tested as well. No color change was observed after vigorous stirring for >2 h. Therefore, it can be concluded that yellow coloring of the solution only occurs in case Eu^{2+} is present.

Electrochemical reduction of europium

Electrochemical techniques are very helpful to investigate reactions involving electron transfer. This way, the flow of electrons can be related to chemical changes. In this respect, cyclic voltammetry was used to investigate the reduction of Eu^{3+} to Eu^{2+} in aqueous media containing different nitrate salt concentrations (1 to 9 mol L⁻¹). The redox behavior of $\text{Eu}^{3+}/\text{Eu}^{2+}$ in analogous aqueous chloride media was studied for comparison.

The formal reduction potential of a redox compound is affected by the interaction with ligands, *i.e.* the coordination of Eu^{3+} and Eu^{2+} , and is a function of the ligand dissociation constants.⁴⁵ Changing the electrolyte concentration leads to a considerable variation in activity, ionic strength and hydration of the ions in solution, also changing their inner coordination sphere significantly. Additionally, the ionic conductivity and the viscosity of the solution change significantly with increasing salt concentrations.

Different counter ions, *i.e.* Li^+ , Ca^{2+} and NH_4^+ , were used to investigate the effect of the origin of the supporting electrolyte on the redox behavior of the europium ions (Figure 2). The total nitrate concentration in these experiments was held constant at 6 mol L⁻¹. The reduction of Eu^{3+} in a solution containing 6 mol L⁻¹ LiCl was conducted for comparison. Measurements of the blank solutions can be found in the ESI (Figure S1), as well as a

measurement of a solution containing 10 mmol L⁻¹ Sm³⁺ in 3 mol L⁻¹ Ca(NO₃)₂ (Figure S2). View Article Online
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These results show that the reduction and oxidation signals solely originate from the Eu³⁺/Eu²⁺ redox couple (Figure S4 and Figure S5). Only minor differences were observed when using Ca²⁺ or Li⁺ as counter ion in the nitrate salt. Both resulted in similar reduction potentials for Eu³⁺ ($E_{p,c}$ = -0.65 V and -0.68 V vs. Ag/Ag⁺, respectively). Calcium nitrate (1290 g L⁻¹ at 20 °C for Ca(NO₃)₂·4H₂O), however, has a higher solubility in water, and was therefore preferred over lithium nitrate (522 g L⁻¹ at 20 °C for LiNO₃) for subsequent experiments. Reduction of Eu³⁺ in ammonium nitrate shows slightly different behavior, with a larger current density and slightly more negative reduction potential. Additionally, hydrogen generation is more pronounced, which can be attributed to the acidity of NH₄⁺, leading to a less negative cathodic limit potential. NH₄NO₃ is therefore not the preferred nitrate salt for electrochemical reduction of Eu³⁺ ($E_{p,c}$ = -0.73 V vs. Ag/Ag⁺). Reduction of Eu³⁺ in a LiCl solution ($E_{p,c}$ = -0.78 V vs. Ag/Ag⁺) resulted in a more negative reduction potential compared to reduction of Eu³⁺ in a solution containing Ca(NO₃)₂ or LiNO₃, with a slightly smaller current density. This indicates that reduction of Eu³⁺ occurs more efficiently in aqueous nitrate media.

Figure 2: Cyclic voltammograms (second cycle) of solutions containing 10 mmol L⁻¹ europium and 6 mol L⁻¹ nitrate or chloride anions. Different counter ions (Li⁺, Ca²⁺, NH₄⁺) for the nitrate salts were investigated for comparison. WE: glassy carbon, RE: Ag/Ag⁺, CE: Pt wire, scan rate: 50 mV s⁻¹.

The influence of the concentration of the supporting electrolyte on the reduction of Eu³⁺ was investigated in both nitrate (Figure 3) and chloride media (Figure 4). The *peak potentials* E_p are presented in Figure 5 (Tables S3 and S4 in ESI) as function of the supporting electrolyte concentration for reduction of Eu³⁺ and oxidation of Eu²⁺. In aqueous nitrate media, the cathodic ($E_{p,c}$) and anodic ($E_{p,a}$) peak potentials shifted from -0.66 V to -0.53 V (vs. Ag/Ag⁺) and 0.08 to 0.12 V (vs. Ag/Ag⁺), respectively, when the nitrate concentration in solution was increased from 1 to 9 mol L⁻¹. In his studies making use of a mercury drop electrode, Holleck also observed a shift in reduction potential with changing nitrate salt concentration.^{43,44} In aqueous chloride media, $E_{p,c}$ and $E_{p,a}$ were shifted from -0.67 V to -0.55 V (vs. Ag/Ag⁺) and 0.17 to 0.32 V (vs. Ag/Ag⁺), respectively, upon increasing the chloride concentration from 1 to 9 mol L⁻¹. Thus, it is clear that the shift in peak potential is

directly proportional to the supporting electrolyte concentration, for both nitrate and chloride media, and that the reduction of Eu^{3+} is more favorable in aqueous solutions containing higher supporting electrolyte concentrations. It is also clear that the reduction of Eu^{3+} and the oxidation of Eu^{2+} were consistently more efficient in nitrate aqueous media compared to chloride aqueous media. On average, reduction of Eu^{3+} in nitrate aqueous media occurred at a potential ± 25 mV less negative than reduction of Eu^{3+} in similar aqueous chloride media. Oxidation of Eu^{2+} in aqueous nitrate media occurred at more negative potentials compared to oxidation of Eu^{2+} in aqueous chloride media (± 60 mV on average). Consequently, *peak separation potentials* (ΔE_p) were consistently lower in aqueous nitrate media. The peak separation potentials also increased with increasing supporting electrolyte concentration in both media. The change in peak separation potential with changing supporting electrolyte concentration indicates the dependency of the quasi-reversible system on the viscosity of the solution. The increase in peak separation potential was found to be higher in aqueous chloride media.

The change of peak current density as a function of viscosity was studied in more detail, and is discussed in the ESI (Section 1.2). From these measurements, it is clear that the current density is inversely proportional to the supporting electrolyte concentration, *i.e.* an increasing supporting electrolyte concentration results in an increasing viscosity and a change in capacitive contribution of the electrochemical double layer. In a (quasi-)reversible electrochemical system, the *peak current density* j_p is inversely proportional to the square root of the viscosity.⁴⁶ This relation also holds for the systems studied here.

Figure 3: Cyclic voltammograms (second cycle) of a solution containing 10 mmol L⁻¹ europium and different concentrations of Ca(NO₃)₂ (1 to 9 mol L⁻¹ NO₃⁻). WE: glassy carbon, RE: Ag/Ag⁺ in 0.1 mol L⁻¹ KCl, CE: Pt wire, scan rate: 50 mV s⁻¹.

Figure 4: Cyclic voltammograms (second cycle) of a solution containing 10 mmol L⁻¹ europium and different concentrations of CaCl₂ (1 to 9 mol L⁻¹ Cl⁻). WE: glassy carbon, RE: Ag/Ag⁺ in 0.1 mol L⁻¹ KCl, CE: Pt wire, scan rate: 50 mV s⁻¹.

Figure 5: Change of the peak potential (vs. Ag/Ag^+ in $0.1 \text{ mol L}^{-1} \text{ KCl}$, second cycle) for reduction (solid symbol, solid line) and oxidation (open symbol, dashed line) of europium (10 mmol L^{-1}) in nitrate (black, squares) and chloride (red, circles) aqueous solution as function of the supporting electrolyte concentration. Scan rate: 50 mV s^{-1} .

From the presented cyclic voltammograms it can be concluded that an increase in supporting electrolyte concentration results in a shift of reduction and oxidation potential to less negative values. A similar trend was observed for reduction/oxidation in both nitrate and chloride media, by which these shifts in reduction and oxidation potentials can be attributed to the strong change in ionic strengths and entropy. This indicates that formation and stability of Eu^{2+} at higher nitrate salt concentrations are based on thermodynamic principles. After all, the redox potential is dependent on the Gibbs free energy change and the equilibrium constants of the reduction-oxidation reactions. Consequently, the redox potential is highly dependent on the thermodynamic activity of the redox active species (Nernst equation, Eq. 5).

$$E = E^0 + \frac{RT}{nF} \ln \frac{a_{\text{Eu}^{3+}}}{a_{\text{Eu}^{2+}}} = E^0 + \frac{RT}{nF} \ln \frac{\gamma_{\text{Eu}^{3+}} [\text{Eu}^{3+}]}{\gamma_{\text{Eu}^{2+}} [\text{Eu}^{2+}]} \quad (5)$$

Here, E^0 is the standard reduction potential, R the universal gas constant, T the temperature, n the number of electrons exchanged, F the Faraday constant, a the activity and γ the activity coefficient of the europium species.

An increasing ionic strength with increasing supporting electrolyte concentration causes the mixture of chemical species to deviate more from thermodynamic ideal behavior, by which the activity coefficients of the chemical species become increasingly important. The increase of the ionic strength of the medium alters the ionic atmosphere and changes the charge densities around the ions. As a consequence, the rate constants increase for higher ionic strengths.

Europium ions are strongly hydrated in aqueous media because of their high charge densities, with the highest charge density for Eu^{3+} . Consequently, Eu^{3+} and Eu^{2+} possess very negative hydration enthalpies, *i.e.* $-3501 \text{ kJ mol}^{-1}$ and $-1458 \text{ kJ mol}^{-1}$, respectively. Eu^{3+} is known to be coordinated by 8 to 9 water molecules, whereas Eu^{2+} is coordinated by 7 to 8 water molecules.^{37,39,47} Chloride and nitrate ions (with $\text{Cl}^- < \text{NO}_3^-$) show only modest levels of association with lanthanide ions in aqueous solutions, mostly in the form of double-solvent-separated ion pairs.⁴⁸ Therefore, they are found to predominantly form outer-sphere complexes, even at high salt concentrations.⁴⁹⁻⁵¹ Thus, Eu^{3+} and Eu^{2+} ions in aqueous media can be considered fully hydrated ions. However, the increasing supporting electrolyte concentration in solution leads to a significant decrease of the solvent activity and significant

increase in entropy, resulting in lower hydration of the europium ions in solution and affecting the thermodynamics and stability constants of the complexes. After all, the oxidation of Eu^{2+} is dependent on the hydration enthalpies of both europium species to overcome the third ionization energy I_3 (2404 kJ mol^{-1}) and the activation energy E_a . The shift towards less negative reduction potentials with increasing salt concentration in solution indicates higher stability of the Eu^{2+} species. In general, reduction is favored in case a more stable species is formed when the metal ion is present in the lower oxidation state of the redox couple, resulting in a more positive reduction potential.⁵²

Holleck stated in his work that the ion fields of the nitrate ions deform with increasing nitrate concentration when Eu^{3+} is reduced, leading to a change in polarization and, consequently, a change in charge distribution.^{44,53} As a result, the nitrate ions show transitions from a planar to a pyramidal structure, enhancing a polar binding character that increases the stability of the Eu^{2+} aqua ion. Whether or not (catalytic) amounts of reduction products of nitrates are formed to increase Eu^{2+} stability remains unclear to date. Detection of such species is not straightforward because of the high nitrate concentration in solution. Nevertheless, investigation of the inner- and outer-coordination spheres of Eu^{3+} and Eu^{2+} in more detail would provide more information about the change in hydration as a function of the supporting electrolyte concentration and the nature of the coordinating ligands.

UV-VIS absorption measurements

Reduction of Eu^{3+} in concentrated aqueous nitrate media yielded a yellow-orange solution (Figure 1), whereas aqueous chloride media remained colorless after reduction of Eu^{3+} . Therefore, UV-VIS absorption measurements were performed to compare the

absorbance of Eu^{2+} in aqueous media containing high nitrate and chloride salt

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concentrations. Solutions containing low nitrate salt concentrations remained colorless upon reduction of Eu^{3+} , and were therefore not measured by UV-VIS absorption spectroscopy. XANES measurements on these samples showed that almost no Eu^{2+} is formed in solutions containing lower nitrate salt concentrations (*vide infra*).

Most solutions containing trivalent lanthanide ions are only weakly colored as their transitions in the visible region of the spectrum are symmetry-forbidden f-f transitions. Moreover, the 4f subshells are positioned relatively deep inside the electron shell, shielded by the fully occupied 5s and 5p orbitals, so that the f-f transitions are only very weakly influenced by the surrounding ligands. Sharp emission bands can originate from these transitions.⁵⁴ UV-VIS absorption spectra of the Eu^{3+} solutions show absorption bands originating from the weak f-f transitions from the ground state, $^7\text{F}_0$, and the first excited multiplet, $^7\text{F}_1$, to the multiplet manifolds $^5\text{D}_0$, $^5\text{D}_1$ and $^5\text{D}_2$ and higher lying excited states.⁵⁵ The characteristic fine structure of Eu^{3+} with very low molar absorptivity was observed in UV-VIS spectra when using a longer path length (10 mm), and showed to be very similar in both nitrate and chloride media (Figure S11, ESI).

Eu^{2+} possesses different photophysical properties, stemming from the lowest-energy (4f^7) and first excited-state ($4\text{f}^6 5\text{d}^1$) configurations.³⁸ $4\text{f} \rightarrow 5\text{d}$ transitions become more likely for Eu^{2+} because crystal and ligand field effects reduce the energy of the 5d states.⁵⁶ Inclusion of 5d levels implies broadband transitions, as the ground and excited states differ as a function of the distance of the electrons from the core. The 4f orbitals of Eu^{2+} remain largely unaffected by the presence of ligands, whereas the 5d orbitals are readily affected by ligand interactions. Characteristic spectra arise from the splitting by the crystal field of the

five-fold degenerate 5d orbital into double degenerate 5d(e_g) and triple degenerate 5d(t_{2g}) orbitals.^{57,58} Consequently, the luminescence properties of Eu²⁺ can be changed with different coordinating compounds, and its use has been investigated intensively.^{38,54,59}

Solutions of Eu²⁺ in aqueous chloride media are known to be colorless and non-luminescent, as was also observed in our experiments and confirmed by UV-VIS absorption measurements in a 3 mol L⁻¹ CaCl₂ solution (Figure 6). The affinity of chloride ions for Eu²⁺ is low, forming very unstable complexes.³² Therefore, Eu²⁺ is predominantly coordinated by solvent molecules only, *i.e.* H₂O, which have a quenching effect on the luminescence. Absorption occurred only in the UV region of the spectrum, with two absorption maxima at 252 nm (39682 cm⁻¹) and 322 nm (31056 cm⁻¹). This is similar to what was reported previously on the electro-reduction of Eu³⁺ in 0.1 mol L⁻¹ HCl by Jelinek *et al.*³² After deconvolution, four Gaussian-shaped absorption bands at 240, 270, 317 and 350 nm were attributed to the Laporte-allowed 4f⁷ → 4f⁶ 5d¹ transition, where the 5d orbitals are split by the ligand field. Analogous with Eu³⁺, Jelinek *et al.* reported that Eu²⁺ is probably coordinated by eight to nine water molecules, depending on the pH of the aqueous solution. Moreau *et al.*, however, determined *via* EXAFS (*vide infra*) that Eu²⁺ is predominantly coordinated by seven water molecules.^{37,39}

A comparable absorption spectrum was recorded for Eu²⁺ in a 3 mol L⁻¹ Ca(NO₃)₂ solution (Figure 6), indicating a similar behavior of Eu²⁺ in both media.⁵⁶ The part of the UV region at shorter wavelengths could, however, not be investigated because of the high UV absorption by the nitrate ions, causing an unreliable detector signal. Compared to the Eu²⁺ absorption spectrum in chloride media, the broad absorption bands originating from the 4f⁷ → 4f⁶ 5d¹ transition are slightly shifted to longer wavelengths. Additionally, the molar

absorptivity of the Eu^{2+} species is higher in nitrate media. As a consequence, absorption occurs partially in the blue region of the visible spectrum, and explains the yellow to orange color of Eu^{2+} in aqueous nitrate media. In addition, it was observed that the absorption bands are also shifted to longer wavelengths with increasing europium concentration (Figure S9 and Figure S10, ESI). It remains unclear if any ligand interactions occur to increase stability of Eu^{2+} in aqueous nitrate media. In-depth structural analysis is required to further investigate the nature of the inner coordination sphere of Eu^{2+} in concentrated nitrate media.

Figure 6: UV-VIS absorption spectra of Eu^{2+} (6.6 mmol L^{-1}) in aqueous nitrate and chloride media ($3 \text{ mol L}^{-1} \text{ CaX}_2$, with X NO_3^- or Cl^-). Blank solutions of the respective aqueous media were used for background correction. Lamp changeover occurred at 350 nm . A path length of 1 mm , a resolution of 0.5 nm and a scan rate of 150 nm min^{-1} were used.

Magnetic susceptibility measurements

Eu^{3+} ($[\text{Xe}] 4f^6$) is moderately paramagnetic as a consequence of the occupation of its thermally accessible first excited state (7F_1 , more information on the magnetic properties of Eu^{3+} can be found in the ESI).⁶⁰ By contrast, Eu^{2+} ($[\text{Xe}] 4f^7$) is strongly paramagnetic ($\mu_B = 7.63 - 8.43$) in its ground state (${}^8S_{7/2}$, *i.e.* similar to Gd^{3+}) because of its seven unpaired electrons.⁶¹ Therefore, a change in oxidation state, *i.e.* a change in electron configuration, induces a strong change in magnetic properties. The change in *effective magnetic moment* (μ) as a consequence of the change in oxidation state can be followed by means of *magnetic susceptibility* (χ) measurements.^{62,63} The applicability of this technique was already demonstrated in various crystallographic and geological studies.^{63,64}

Magnetic susceptibility measurements at room temperature were conducted to monitor the reduction of Eu^{3+} to Eu^{2+} in aqueous nitrate media ($3 \text{ mol L}^{-1} \text{ Ca}(\text{NO}_3)_2$) for both chemical (Zn^0 grains) and electrochemical ($-0.7 \text{ V vs. Ag/Ag}^+$) reduction. The results of these measurements are presented in Figure 7, and clearly show a change in volume magnetic susceptibility as a function of the reduction time. The result clearly shows the ability to (electro-)chemically reduce Eu^{3+} in aqueous nitrate media. Reduction of Eu^{3+} reached an equilibrium after *ca.* 120 min of reduction for both reduction methods. A comparison with the chemical reduction of Eu^{3+} in chloride media ($6 \text{ mol L}^{-1} \text{ LiCl}$) can be found in Figure S12 (ESI). Chemical reduction of Eu^{3+} in chloride media proceeded slightly faster, reaching an equilibrium situation after *ca.* 90 min using similar experimental parameters. The plateau value for the volume magnetic susceptibility with respect to the reduction of Eu^{3+} in both media is somewhat different, and can be attributed to the high sensitivity of the magnetic

susceptibility balance to the composition of the samples. First, the total europium concentration in both media was not exactly the same. Second, different species with various effective magnetic moments were present in both samples, originating from the nature of Eu^{3+} and the salts used in this study.

Nevertheless, different parameters can influence the reduction rate of Eu^{3+} to Eu^{2+} for both reduction methods. Therefore, conclusions on reduction efficiency for Eu^{3+} should be treated with caution. The reduction rate in the electrochemical reduction method is highly dependent on the current, which is determined by the applied potential, the surface area and type of the working electrode and the conductivity of the solution. The particle size of the zinc grains, *i.e.* the specific surface area, and the zinc oxide surface layer covering the zinc grains are of high importance in the chemical reduction method. The influence of the zinc grains on the reduction of Eu^{3+} was reported by Sayed *et al.*¹⁴

After reduction, a sealed sample tube was measured every 30 min for a period of 2.5 h (Figure S13, ESI). These measurements did not result in large variations in volume magnetic susceptibility, again indicating the relatively high stability of Eu^{2+} in these solutions when an inert atmosphere is maintained.

Figure 7: Magnetic susceptibility measurements of aqueous solutions containing 66 mmol L^{-1} europium and $3 \text{ mol L}^{-1} \text{ Ca}(\text{NO}_3)_2$ upon electrochemical (black) and chemical (red) reduction. A fresh aliquot was measured every 15 min for a period 4 h at room temperature.

XANES measurements

X-ray absorption near-edge structure (XANES) measurements have already been proven successful in determining valence states of europium in several mineralogical and crystallographic studies, making use of its high sensitivity and selective detection of target elements.^{25-29,65,66} The strong absorption resonances, *i.e.* white lines, at the europium L_{III} edge in the X-ray absorption spectra yield information on the electronic structure of the absorbing species. The divalent and trivalent oxidation state can be easily distinguished because the XANES spectra for Eu^{2+} and Eu^{3+} have distinct resonance peaks separated by *ca.* 8 eV, at 6971.3 and 6979.3 eV, respectively. These resonance peaks originate from the electron transitions between $2p_{3/2}$ and $5d$ electronic states. Deconvolution of the XANES

spectra yields information on the relative ratio of Eu^{2+} and Eu^{3+} present in the samples. The steps followed for deconvolution of the XANES spectra can be found in the ESI.

The XANES spectra of the chemical reduction of Eu^{3+} in steps of 15 min are presented in Figure 8. A solution containing 66 mmol L^{-1} europium and 6 mol L^{-1} LiNO_3 was used to record these spectra. Li^+ was used as the counter ion for nitrate because of the low absorbance of this light element, limiting the interference in the XANES spectra. An indication of the relative amounts of Eu^{2+} and Eu^{3+} after deconvolution of the XANES spectra is presented in Figure 9 (parameters of the exponential fit are listed in Table S5). A trend similar to the one observed for the magnetic susceptibility measurements can be distinguished, *i.e.* a plateau value is reached after *ca.* 120 min. Small deviations from the trend can be attributed to the partial back-oxidation of Eu^{2+} as a result of the filling of the measurement cell. Short contact with air (oxidation by O_2 , Eq. 2) could not be avoided during this operation. Additionally, a high conversion rate of Eu^{3+} to Eu^{2+} by chemical reduction can be observed, *i.e.* >95% after 120 min. Measurements on solutions containing lower europium and nitrate salt concentrations can be found in the ESI (Figures S17-S19). These spectra, however, contain much more noise because of the significantly lower europium content (6.6 mmol L^{-1}), for which the XANES technique is less sensitive. Relatively concentrated samples are needed for good quality XANES spectra. Notwithstanding the lower quality of the spectra, general trends that support previous statements in this research can be distinguished. Firstly, the reduction of Eu^{3+} appears to remain equally efficient for lower europium concentrations in solutions containing the same nitrate salt concentration (6 mol L^{-1}). Secondly, the reduction of Eu^{3+} is much less efficient and Eu^{2+} is less stable at lower nitrate salt concentrations. Thus, sufficiently high nitrate salt

concentrations, resulting in higher ionic strengths, are needed to ensure high reducibility of

Eu^{3+} and to obtain a higher stability for the Eu^{2+} species.

Figure 8: Normalized XANES spectra of the reduction of europium (66 mmol L^{-1}) in a $6 \text{ mol L}^{-1} \text{ LiNO}_3$ aqueous solution as a function of time. Spectra were recorded every 15 min. The solution contained 100% Eu^{3+} at 0 min.

Figure 9: Relative amounts of Eu^{2+} and Eu^{3+} in a $6 \text{ mol L}^{-1} \text{LiNO}_3$ aqueous solution upon chemical reduction with zinc grains as a function of the reduction time. The data were fitted with an exponential function.

After chemical reduction of europium (66 mmol L⁻¹) in aqueous nitrate media (6 mol L⁻¹ LiNO₃) for 180 min, the stability of Eu²⁺ in these media was investigated by recording a XANES spectrum every 60 min for a period of 5 h. The sample remained in the measurement cell, which was closed with Kapton® tape to avoid contact with oxygen in the air. Results of these measurements can be found in the ESI (Figure S20-S21). From these data, it is clear that Eu²⁺ remains remarkably stable over time, and is not readily oxidized after removal of the reducing agent. Over the course of 240 min, only a few percent of Eu²⁺ was re-oxidized to Eu³⁺. Therefore, it can be concluded that Eu²⁺ remains fairly stable in concentrated aqueous nitrate media if contact with any oxidizing agent is excluded. Because of their relatively high stability, Eu²⁺ solutions containing high nitrate salt concentrations are suitable for manipulations. Its use can be tested in different types of applications.

The XAS studies were limited to the near-edge region of the spectrum to be able to follow the reduction as a function of time. A spectrum of a new aliquot was recorded every 15 min, cutting off the measurements at 7000 eV. Consequently, the EXAFS region was not recorded. Therefore, no structural information on the coordination of Eu²⁺ in aqueous nitrate media could be derived, and is topic of future investigations.

Conclusion

The chemical and electrochemical reduction of Eu³⁺ in aqueous media containing high nitrate salt concentrations was monitored by magnetic susceptibility and XANES measurements. Maximum reduction, reaching high relative amounts of Eu²⁺ (>95%), was achieved after 120 min of reduction. Moreover, it was proven by these techniques that Eu²⁺ in these media is stable for several hours when kept in an inert atmosphere. Cyclic

voltammetry studies showed that the reduction potential for Eu^{3+} becomes less negative with increasing supporting electrolyte concentrations. The increase in ionic strength causes a change in solution thermodynamics ensuring a higher stability of Eu^{2+} species by which the reduction reaction is favored. Cyclic voltammetry studies also showed that the reduction of Eu^{3+} and oxidation of Eu^{2+} in aqueous nitrate solutions occurs at slightly less negative potentials compared to similar chloride media. Aqueous solutions containing high nitrate salt concentrations colored yellow-orange upon reduction of Eu^{3+} to Eu^{2+} , whereas similar reduction in aqueous chloride media remained colorless. UV-Vis absorption studies revealed a small shift towards longer wavelengths and broadening of the Eu^{2+} absorption band in nitrate media. This causes Eu^{2+} to absorb in the blue region of the visible light spectrum in nitrate media, whereas absorption of Eu^{2+} in chloride media is restricted to the UV region. From the experiments conducted in this study, it is evident that high ionic strengths are required for an efficient reduction of Eu^{3+} and high stabilization of Eu^{2+} in nitrate media.

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Conflicts of interest

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There are no conflicts to declare.

References

1. M. Van de Voorde, K. Van Hecke, T. Cardinaels and K. Binnemans, *Coord. Chem. Rev.*, 2019, **382**, 103-125.
2. A. J. Amoroso, I. A. Fallis and S. J. A. Pope, *Coord. Chem. Rev.*, 2017, **340**, 198-219.
3. K. Binnemans, *Coord. Chem. Rev.*, 2015, **295**, 1-45.
4. K. Binnemans, P. T. Jones, T. Müller and L. Yurramendi, *J. Sustain. Met.*, 2018, **4**, 126-146.
5. D. Dupont and K. Binnemans, *Green Chem.*, 2015, **17**, 856-868.
6. *Report on Critical Raw Materials for the EU - Report of the Ad hoc Working Group on defining critical raw materials*, European Commission, 2014.
7. J.-C. G. Bünzli, *J. Coord. Chem.*, 2014, **67**, 3706-3733.
8. W. W. Lukens, M. Speldrich, P. Yang, T. J. Duignan, J. Autschbach and P. Kögerler, *Dalton Trans.*, 2016, **45**, 11508-11521.
9. T. Hirai and I. Komasa, *J. Chem. Eng. Jpn.*, 1992, **25**, 644-648.
10. T. Hirai, N. Onoe and I. Komasa, *J. Chem. Eng. Jpn.*, 1993, **26**, 64-67.
11. L. Jelinek, Y. Wei, T. Arai and M. Kumagai, *J. Alloy. Compd.*, 2008, **451**, 341-343.
12. B. Van den Bogaert, D. Havaux, K. Binnemans and T. Van Gerven, *Green Chem.*, 2015, **17**, 2180-2187.
13. B. Van den Bogaert, L. Van Meerbeeck, K. Binnemans and T. Van Gerven, *Green Chem.*, 2016, **18**, 4198-4204.
14. S. Sayed, K. Rabie and I. Salama, *Sep. Purif. Technol.*, 2005, **46**, 145-154.
15. C. A. Morais and V. S. T. Ciminelli, *Sep. Sci. Technol.*, 2002, **37**, 3305-3321.
16. L. Jelinek, Y. Z. Wei, T. Arai and M. Kumagai, *Solvent Extr. Ion Exc.*, 2007, **25**, 503-513.
17. T. Hirai and I. Komasa, *Min. Proc. Ext. Met. Rev.*, 1997, **17**, 81-107.
18. C. A. Morais and V. S. T. Ciminelli, *Hydrometallurgy*, 1998, **49**, 167-177.
19. C. A. Morais and V. S. T. Ciminelli, *Hydrometallurgy*, 2001, **60**, 247-253.
20. M. Van de Voorde, K. Van Hecke, K. Binnemans and T. Cardinaels, *RSC Adv.*, 2018, **8**, 20077-20086.
21. M. Zelic, *Croat. Chem. Acta.*, 2003, **76**, 241-248.
22. B. Onghena, E. Papagni, E. R. Souza, D. Banerjee, K. Binnemans and T. Vander Hoogerstraete, *RSC Adv.*, 2018, **8**, 32044-32054.
23. K. Larsson and K. Binnemans, *Hydrometallurgy*, 2015, **156**, 206-214.
24. K. Larsson and K. Binnemans, *J. Sustain. Met.*, 2017, **3**, 73-78.
25. M. R. Cicconi, G. Giuli, E. Paris, W. Ertel-Ingrisch, P. Ulmer and D. B. Dingwell, *Am. Mineral.*, 2012, **97**, 918-929.
26. Y. Takahashi, G. R. Kolonin, G. P. Shironosova, I. I. Kupriyanova, T. Uruga and H. Shimizu, *Mineral. Mag.*, 2005, **69**, 179-190.
27. J. M. Karner, J. J. Papike, S. R. Sutton, P. V. Burger, C. K. Shearer, L. Le, M. Newville and Y. Choi, *Am. Mineral.*, 2010, **95**, 410-413.
28. N. Avci, K. Korthout, M. A. Newton, P. F. Smet and D. Poelman, *Opt. Mater. Express*, 2012, **2**, 321-330.
29. K. Korthout, K. Van den Eeckhout, J. Botterman, S. Nikitenko, D. Poelman and P. F. Smet, *Phys. Rev. B*, 2011, **84**, 1-7 (085140).
30. J. Rakovan, M. Newville and S. Sutton, *Am. Mineral.*, 2001, **86**, 697-700.

31. C. K. Shearer, J. J. Papike, P. V. Burger, S. R. Sutton, F. M. McCubbin and M. Newville, *Am. Mineral.*, 2011, **96**, 1418-1421.
32. L. Jelinek, T. Arai, W. Yuezhou and M. Kumagai, *J. Rare Earth.*, 2007, **25**, 1-5.
33. R. G. Bates and J. B. Macaskill, *Pure Appl. Chem.*, 1978, **50**, 1701-1706.
34. L. Lépine, R. Gilbert and G. Belanger, *Anal. Chem.*, 1986, **58**, 1152-1156.
35. D. A. Outka and J. Stöhr, *J. Chem. Phys.*, 1988, **88**, 3539-3554.
36. M. R. Antonio, L. Soderholm and I. Song, *J. Appl. Electrochem.*, 1997, **27**, 784-792.
37. G. Moreau, L. Helm, J. Purans and A. E. Merbach, *J. Phys. Chem. A*, 2002, **106**, 3034-3043.
38. J. Garcia and M. J. Allen, *Eur. J. Inorg. Chem.*, 2012, **2012**, 4550-4563.
39. G. Moreau, R. Scopelliti, L. Helm, J. Purans and A. E. Merbach, *J. Phys. Chem. A*, 2002, **106**, 9612-9622.
40. A. G. Atanasyants and A. N. Seryogin, *Hydrometallurgy*, 1995, **37**, 367-374.
41. S. Z. Islami-Rad, M. Shamsaei, R. Gholipour-Peyvandi and M. Ghannadi-Maragheh, *Radiochemistry*, 2011, **53**, 642-645.
42. D. F. Peppard, E. P. Horwitz and G. W. Mason, *J. Inorg. Nucl. Chem.*, 1962, **24**, 429-439.
43. L. Holleck, *Z. Elektrochem.*, 1943, **49**, 496-496.
44. L. Holleck, *Z. Elektrochem.*, 1940, **46**, 69-71.
45. G. Tabbì, A. Giuffrida and R. P. Bonomo, *J. Inorg. Biochem.*, 2013, **128**, 137-145.
46. A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, John Wiley & Sons, Inc., United States of America, Second Edition edn., 2001.
47. S. Andersson, K. Eberhardt, C. Ekberg, J.-O. Liljenzin, M. Nilsson and G. Skarnemark, *Radiochim. Acta*, 2006, **94**, 469-474.
48. S. Friesen, S. Krickl, M. Luger, A. Nazet, G. Hefter and R. Buchner, *Phys. Chem. Chem. Phys.*, 2018, **20**, 8812-8821.
49. P. J. Breen and W. D. Horrocks, *Inorg. Chem.*, 1983, **22**, 536-540.
50. H. Kanno and H. Yokoyama, *Polyhedron*, 1996, **15**, 1437-1441.
51. G. R. Choppin, *Pure Appl. Chem.*, 1971, **27**, 23-41.
52. P. Atkins, T. Overton, J. Rourke, M. Weller and F. Armstrong, *Shriver & Atkins' Inorganic Chemistry*, Oxford University Press, Fifth Edition edn., 2010.
53. L. Holleck, *Z. Elektrochem.*, 1943, **49**, 400-406.
54. J. Jiang, N. Higashiyama, K.-i. Machida and G.-y. Adachi, *Coord. Chem. Rev.*, 1998, **170**, 1-29.
55. J. B. Gruber, U. V. Valiev, G. W. Burdick, S. A. Rakhimov, M. Pokhrel and D. K. Sardar, *J. Lumin.*, 2011, **131**, 1945-1952.
56. J.-C. Rybak, M. Hailmann, P. R. Matthes, A. Zurawski, J. Nitsch, A. Steffen, J. G. Heck, C. Feldmann, S. Götzendörfer, J. Meinhardt, G. Sextl, H. Kohlmann, S. J. Sedlmaier, W. Schnick and K. Müller-Buschbaum, *J. Am. Chem. Soc.*, 2013, **135**, 6896-6902.
57. C. Dujardin, B. Moine and C. Pedrini, *J. Lumin.*, 1993, **54**, 259-270.
58. E. Loh, *Physical Review*, 1968, **175**, 533-536.
59. K. Binnemans, *Chem. Rev.*, 2009, **109**, 4283-4374.
60. *Systematics and the Properties of the Lanthanides*, D. Reidel Publishing Company, Dordrecht, 1983.

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DOI: 10.1039/C9DT03139A

61. V. Kachkanov, M. J. Wallace, G. van der Laan, S. S. Dhesi, S. A. Cavill, Y. Fujiwara and K. P. O'Donnell, *Sci. Rep.*, 2012, 1-5. [View Article Online](#)
DOI: 10.1039/C9DT03139A
62. I. R. Rodrigues, L. Lukina, S. Dehaeck, P. Colinet, K. Binnemans and J. Fransaer, *J. Phys. Chem. Lett.*, 2017, **8**, 5301-5305.
63. S. Kern, R. Kosteletzky and C. M. O'Donnell, *Phys. Lett.*, 1970, **33A**, 27.
64. Y. Misawa, Y. Doi and Y. Hinatsu, *J. Solid State Chem.*, 2011, **184**, 1478-1483.
65. J. J. Joos, K. Korthout, S. Nikitenko, D. Poelman and P. F. Smet, *Opt. Mater. Express*, 2013, **3**, 1338-1350.
66. K. Korthout, A. B. Parmentier, P. F. Smet and D. Poelman, *Phys. Chem. Chem. Phys.*, 2013, **15**, 8678-8683.

Table of contents graphic

Investigation on the reduction of Eu^{3+} and the stability of Eu^{2+} in aqueous solutions containing high nitrate salt concentrations