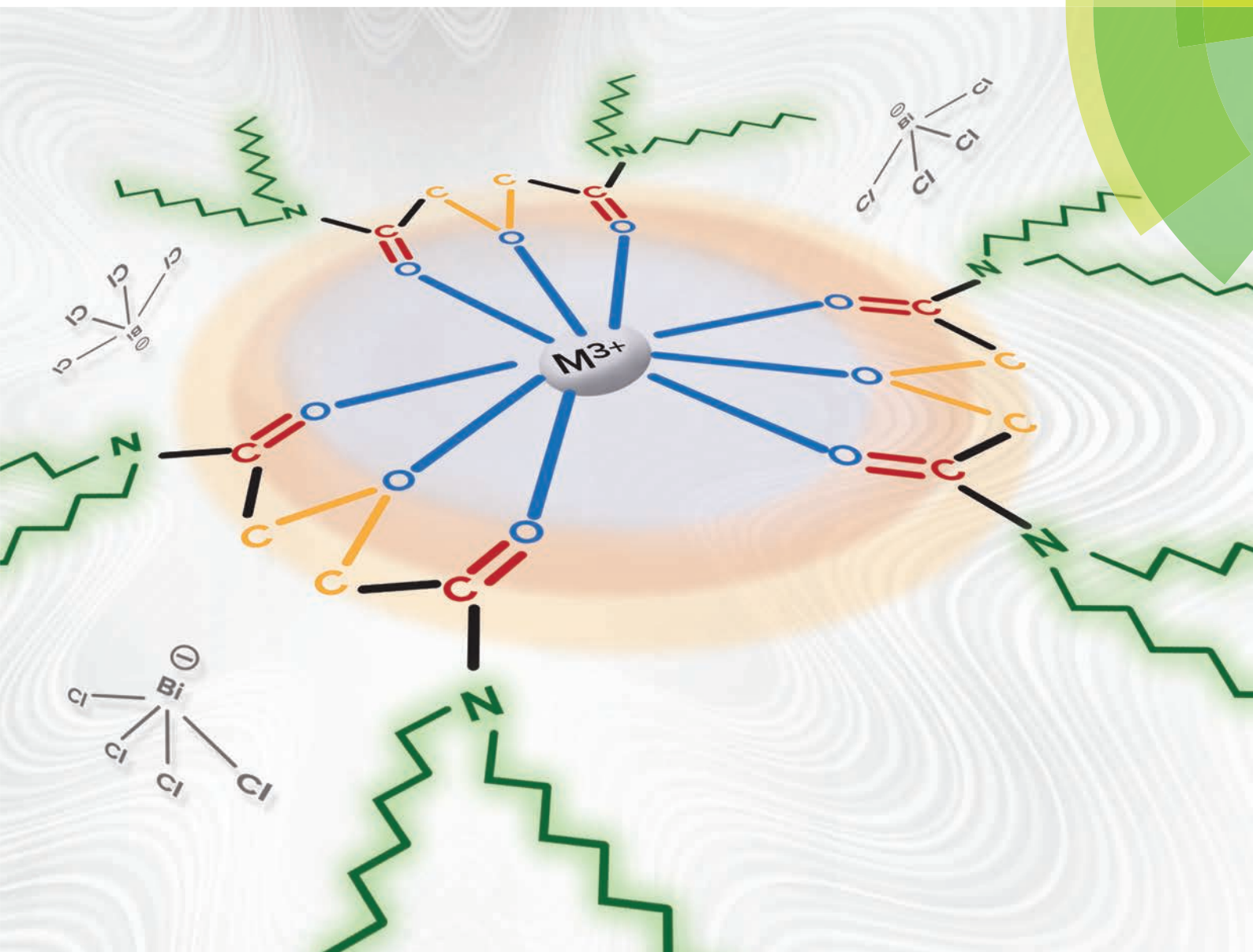


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An europium(III) diglycolamide complex: insights into the coordination chemistry of lanthanides in solvent extraction

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The synthesis, stoichiometry, and structural characterization of a homoleptic, cationic europium(III) complex with three neutral tetraalkyldiglycolamide ligands are reported. The tri(bismuth tetrachloride)tris-(*N,N,N',N'*-tetra-*n*-octyldiglycolamide)Eu salt, [Eu(TODGA)₃][(BiCl₄)₃] obtained from methanol was examined by Eu L₃-edge X-ray absorption spectroscopy (XAS) to reveal an inner-sphere coordination of Eu³⁺ that arises from 9 O atoms and two next-nearest coordination spheres that arise from 6 carbon atoms each. A structural model is proposed in which each TODGA ligand with its O=C_a-C_b-O-C_b-C_a=O backbone acts as a tridentate O donor, where the two carbonyl O atoms and the one ether O atom bond to Eu³⁺. Given the structural rigidity of the tridentate coordination motif in [Eu(TODGA)₃]³⁺ with six 5-membered chelate rings, the six Eu-C_a and six Eu-C_b interactions are readily resolved in the EXAFS (extended X-ray absorption fine structure) spectrum. The three charge balancing [BiCl₄][−] anions are beyond the cationic [Eu(TODGA)₃]³⁺ cluster in an outer sphere environment that is too distant to be detected by XAS. Despite their sizeable length and propensity for entanglement, the four *n*-octyl groups of each TODGA (for a total of twelve) do not perturb the Eu³⁺ coordination environment over that seen from previously reported single-crystal structures of tripositive lanthanide (Ln³⁺) complexes with tetraalkyldiglycolamide ligands (of the same 1 : 3 metal-to-ligand ratio stoichiometry) but having shorter *i*-propyl and *i*-butyl groups. The present results set the foundation for understanding advanced solvent extraction processes for the separation of the minor, tripositive actinides (Am, Cm) from the Ln³⁺ ions in terms of the local structure of Eu³⁺ in a solid state coordination complex with TODGA.

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Introduction

The hydrometallurgy of the rare-earth elements as well as the separation of lanthanide and actinide elements from used nuclear fuel are of strategic importance to global economies and energy initiatives. In one of the newest of these, a process dubbed ALSEP (actinide lanthanide separation)¹ exploits a neutral diglycolamide extractant, either TODGA (*N,N,N',N'*-tetra-*n*-octyldiglycolamide) or T2EHDGA (*N,N,N',N'*-tetra-(2-ethylhexyl)diglycolamide) illustrated in Fig. 1(a), and an acidic organophosphorous extractant for separating the lanthanides from the minor actinides (*i.e.*, Am, Cm). In particular, the separation of tripositive lanthanide ions and tripositive actinide ions (abbreviated hereafter as Ln³⁺ and An³⁺, respectively) by TODGA from hydrochloric acid has been shown to significantly increase with the addition of metal ions that form anionic

chloride complexes (MCl₄[−], M = Fe³⁺, Ga, In, Tl³⁺, Bi).^{2,3} In some cases, the extraction can increase by five orders of magnitude. Solvent extraction data and infrared spectroscopy suggest that Ln³⁺ and An³⁺ are complexed by the basic oxygen atoms (two carbonyl O and one ether O) of the TODGA extractant with the anionic metal chloride complexes acting as counter ions to form neutral complexes. The relatively large metal chloride complexes are incompatible with the highly hydrogen-bonded structure of H₂O in the aqueous phase, making their extraction into the organic phase more energetically favorable than the smaller chloride anion. The objective of this study is to further elucidate the structure of the complexes formed by Ln³⁺ and An³⁺, TODGA, and anionic metal chlorides by examining a selected representative complex Eu(TODGA)₃(BiCl₄)₃ by X-ray absorption spectroscopy (XAS).

Despite the unusually high extractability of Ln³⁺ and An³⁺ ions by TODGA in nitrate and chloride media,^{4–6} the structural aspects of their coordination chemistry are largely unknown. Solvent extraction of tracer concentrations of Ln³⁺ and An³⁺ has been shown to involve 2, 3, or 4 TODGA extractant molecules, with the polarity of the organic phase diluent and the

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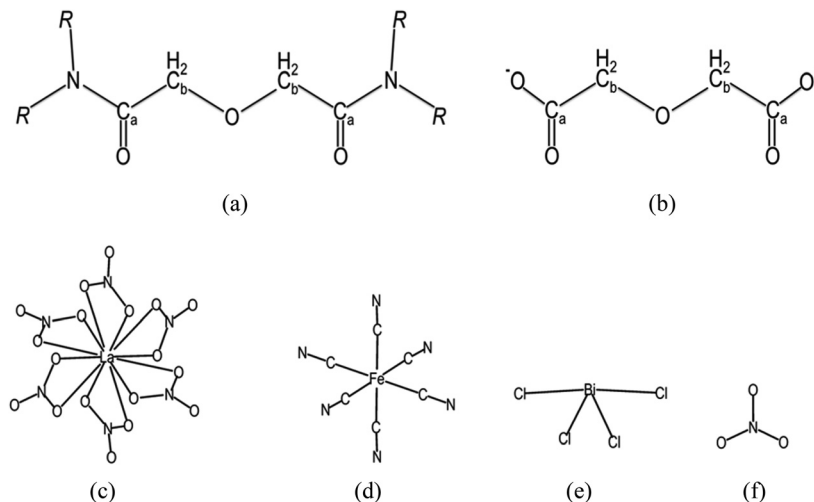


Fig. 1 (a) Core structures of neutral, symmetrical tetraalkyldiglycolamide extractants, including TODGA (for $R = n\text{-C}_8\text{H}_{17}$; N,N,N',N' -tetra- n -octyldiglycolamide), T2EHDGA (for $R = \text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9$; N,N,N',N' -tetra(2-ethylhexyl)diglycolamide), TiBuDGA (for $R = i\text{-C}_4\text{H}_9$; N,N,N',N' -tetra- i -butyldiglycolamide), and TiPrDGA (for $R = i\text{-C}_3\text{H}_7$; N,N,N',N' -tetra- i -propyldiglycolamide). The sp^2 -hybridized carbonyl C and the sp^3 -hybridized ether C atoms are labeled a and b, respectively. (b) The dianion of oxydiacetic acid (ODA) has the $\text{O}=\text{C}_a-\text{C}_b-\text{O}-\text{C}_b-\text{C}_a=\text{O}$ backbone of the diglycolamides. The homoleptic hexanitratolanthanum(III), $[\text{La}(\text{NO}_3)_6]^{3-}$ (c), and ferricyanide, $[\text{Fe}(\text{CN})_6]^{3-}$ (d), trianions as well as the nitrate, $[\text{NO}_3]^-$ (f), anion that have been used as counterions for X-ray crystallographic studies of tetraalkyldiglycolamide salts. (e) The homoleptic $[\text{BiCl}_4]^-$ anion employed here has a see-saw-like shape due to the stereochemically active lone pair of electrons on Bi^{3+} .

aqueous acidity significantly affecting the aggregation of TODGA in the organic phase.^{7–9} For TODGA in aliphatic diluents and aqueous nitric acid concentrations above 0.7 M, the high distribution ratios of tracer concentrations of Ln^{3+} (An^{3+}) have been attributed primarily to the formation of small reverse micelles of TODGA tetramers that provide “an environment predisposed to the complexation of trivalent lanthanide and actinide cations”.¹⁰ However, extraction of the same organic phase from 0.1–0.7 M HNO_3 and 3 M NaNO_3 at pH 4 seems to primarily involve two and three TODGA molecules, respectively.^{7,8,11} Solvent extraction and extraction chromatography data for the extraction of Ln^{3+} from acidic chloride and nitrate media at high metal loadings of the TODGA phase suggest complexation *via* three TODGA molecules.^{2,3,7,8,11} Although the solvent extraction of metal ions represents inner-sphere coordination chemistry at the most fundamental level,^{12–17} the metal environments of the three different stoichiometric molecular entities involving 1 : 2, 1 : 3, and 1 : 4 Ln (An):TODGA ratios is not known. Furthermore, outer-sphere and higher-order—supramolecular—effects like ion-pairing and micellization, respectively, stand to be exploited to facilitate the extraction of actinides and lanthanides.^{18,19}

The results of this X-ray absorption spectroscopy investigation of the $\text{Eu}(\text{TODGA})_3(\text{BiCl}_4)_3$ coordination complex complement the X-ray crystallography studies of short-chain tetraalkyldiglycolamide complexes of Ln^{3+} .^{20–22} In these, N,N,N',N' -tetra- i -propyldiglycolamide (TiPrDGA) and N,N,N',N' -tetra- i -butyldiglycolamide (TiBuDGA), see Fig. 1(a), have been exploited for the growth of single-crystals suitable for molecular and crystal structure determinations. Whereas TODGA is a better extractant than either TiPrDGA or TiBuDGA, no single-crystal structures of TODGA complexes with $\text{Ln}^{3+}/\text{An}^{3+}$ ions

have been reported. In the context of advanced nuclear fuel processing, the present results set the foundation for understanding the ALSEP solvent extraction process from the perspective of the complexation and structure of Eu^{3+} in a coordination complex with TODGA.

Experimental section

Materials

Europium chloride hexahydrate (99.9%) and anhydrous bismuth chloride (99.9%) were obtained from Strem Chemicals (Newburyport, MA). N,N,N',N' -Tetraoctyldiglycolamide (TODGA) was obtained from Eichrom Technologies, LLC (Darien, IL). Methanol (Reagent ACS/USP/BP grade) was obtained from Pharmco-AAPER (Brookfield, CT). Trace metal grade hydrochloric acid (37%), nitric acid (70%), silver nitrate (99+%), and hydrogen peroxide (30%) were obtained from Fisher Scientific (Waltham, MA). ASTM reagent grade II deionized water was produced using a Crossbow Water deionization system (Glenwood, IL).

Synthesis

The $\text{Eu}(\text{TODGA})_3(\text{BiCl}_4)_3$ complex was synthesized by dissolving 1.00 gram (3.2 mmol) of anhydrous bismuth chloride, 0.37 gram (1 mmol) of europium chloride hexahydrate, 1.0 mL of 37% hydrochloric acid and 1.86 grams (3.2 mmol) of TODGA in 100 mL of methanol. The solution was filtered using a 24 mm, 0.45 μm pore size polyethersulfone syringe filter (Macherey-Nagel, Duren, Germany) to remove any residual solids (likely BiOCl). While stirring using a magnetic stir plate and Teflon coated magnetic stir bar, deionized water

was added dropwise until a white precipitate was formed. Stirring was continued for one hour. The solid was isolated by vacuum filtration on a Whatman no. 42 ashless filter paper and washed with three portions of 5 mL 50% (v:v) methanol in deionized water. After air drying, the white precipitate was transferred to a 20 mL borosilicate glass vial and dried in an oven to constant weight (2.36 grams) at 70 °C over 24 hours.

Metal analyses

Europium and bismuth contents were determined by weighing 1.01 grams of the dried metal-TODGA complex into a zirconium crucible (MTI Metal Technology, Albany, OR). The sample was fired in a muffle oven at 800 °F for 8 hours to destroy the organic portion of the complex. The residual white solid (0.30 gram) was dissolved using 10 mL of 70% HNO₃ and 500 µL of 30% H₂O₂, transferred to a 250 mL glass volumetric flask and diluted to 250 mL with deionized water. The dissolved residue was analyzed for europium (381.967 nm) and bismuth (306.772 nm) using an Agilent Technologies 4100 microwave plasma atomic emission spectrometer (MP-AES). The analysis identified 0.048 g (0.32 mmol per g-complex) Eu and 0.22 g (1.05 mmol per g-complex) Bi.

Chlorine analysis

Chloride content was determined by dissolving 0.50 gram of the dried metal-TODGA complex in 40 mL of anhydrous methanol by heating in a water bath at 40 °C. While stirring the dissolved metal-TODGA complex with a magnetic stir bar, silver nitrate (0.60 g in 40 mL of methanol) was slowly added, forming a white precipitate (AgCl). Stirring was continued for 2 hours after the final addition of AgNO₃ to ensure complete exchange and precipitation of the Cl[−] as AgCl. The precipitate and supernate were transferred to two 50 mL polypropylene centrifuge tubes and centrifuged at 2000 rpm for 10 minutes. After decanting the supernate, the precipitate was washed with 2 × 10 mL of methanol and then 2 × 10 mL of 1 M HNO₃. The washed precipitate was transferred to a tared zirconium crucible and dried at 130 °C until a constant weight was achieved (0.30 gram, 4.2 mmol per g-complex). The AgCl precipitate was dissolved in NH₄OH–(NH₄)₂NO₃, followed by 70% HNO₃ for a small amount of material that did not dissolve in the ammoniacal solution. Analysis of the dissolved precipitate by MP-AES identified >98% of mass Ag, and <2% Bi and Eu contents below the limit of detection (<0.01%).

Stoichiometry

Combining the chemical analysis results for Eu, Bi, and Cl[−] and assigning the remaining mass of the compound (0.59 g, 1.0 mmol per g-complex) to the TODGA extractant led to a stoichiometry of Eu(TODGA)_{3.1}Bi_{3.2}Cl₁₃. This is within the analytical error of the Eu(TODGA)₃Bi₃Cl₁₂ stoichiometry expected for Eu(TODGA)₃(BiCl₄)₃ suggested by solvent extraction data.^{2,3} The additional Cl[−] found in the chemical analysis may be due to an HCl adduct, which was found in similar complexes in solvent extraction studies.^{2,3}

X-ray absorption fine structure

Europium L₃-edge X-ray absorption spectra were acquired for a pressed pellet of Eu(TODGA)₃(BiCl₄)₃ at room temperature using a multi-element fluorescence detector at beamline 12-BM-B of the Advanced Photon Source at the Argonne National Laboratory.²³ All analyses were performed with EXAFS-PAK. As described beforehand,²⁴ curve fitting of the $k^3\chi(k)$ EXAFS was performed with phase and amplitude functions from FEFF8.0²⁵ and a fixed scale factor (0.9) using models of Eu³⁺ coordination with O and C atom neighbors. Even for the most detailed fitting model with O nearest neighbors and C next-nearest neighbors of Eu, the number of refined parameters (6) was less than the maximum number of independent parameters (9) available in the primary data with $k_{\text{max}} = 12.2 \text{ \AA}^{-1}$ and an expected interatomic distance resolution of 0.15 Å.

Results and discussion

EXAFS

The experimental $k^3\chi(k)$ EXAFS data, which are shown as the solid line in Fig. 2(a), were Fourier transformed without phase shift correction to provide the response shown as the solid line in Fig. 2(b). The principal feature at 1.96 Å is typical of oxygen coordination to Eu³⁺.^{26,27} Quantitative metrical information, in terms of the O coordination number and the average Eu–O interatomic distance, was obtained from a single-shell fit of the $k^3\chi(k)$ EXAFS. The results reveal that there are 9 ± 1 O atoms around Eu at an average distance of 2.40(1) Å. In combination with the stoichiometric information about the Eu : TODGA ratio (1 : 3), we interpret this EXAFS result to suggest that the two carbonyl O atoms and the single ether O atom of each of three TODGA ligands (for a total of 9 O) coordinate to Eu in the fashion depicted in Fig. 3. In this proposed manner of coordination as a cationic tris(TODGA)Eu complex, [Eu(TODGA)₃]³⁺, we would expect that backscattering from the 6 sp²-hybridized C atoms (associated with the carbonyl moieties labeled C_a) as well as the 6 sp³ hybridized C atoms (associated with the ether moiety labeled C_b) would contribute to the Eu EXAFS response. In fact, the Fourier transform data of Fig. 2(b) reveal two weak, distant peaks at 2.73 and 3.11 Å, which are labeled C_a and C_b, respectively. Beyond these there are no features of structural significance, which may be attributable to the N atoms of TODGA or to distant interactions with either Cl and/or Bi atoms of the [BiCl₄][−] counter anions, Fig. 1(e).

As a test of the validity of the Eu coordination depicted in Fig. 3, a three-shell fit was performed with Eu–O, Eu–C_a, and Eu–C_b interactions and fixed coordination numbers of 9 O, 6 C_a, and 6 C_b. The fit and the Fourier transform of the fit, which are shown as dashed black lines in Fig. 2(a) and (b), respectively, reveal a direct and excellent correspondence with the experimental data, thereby confirming that the model of Fig. 3 adequately describes the local coordination environment of Eu. The refined, average Eu–C_a, and Eu–C_b interatomic distances are 3.34(3) and 3.55(2) Å, respectively. Whereas the

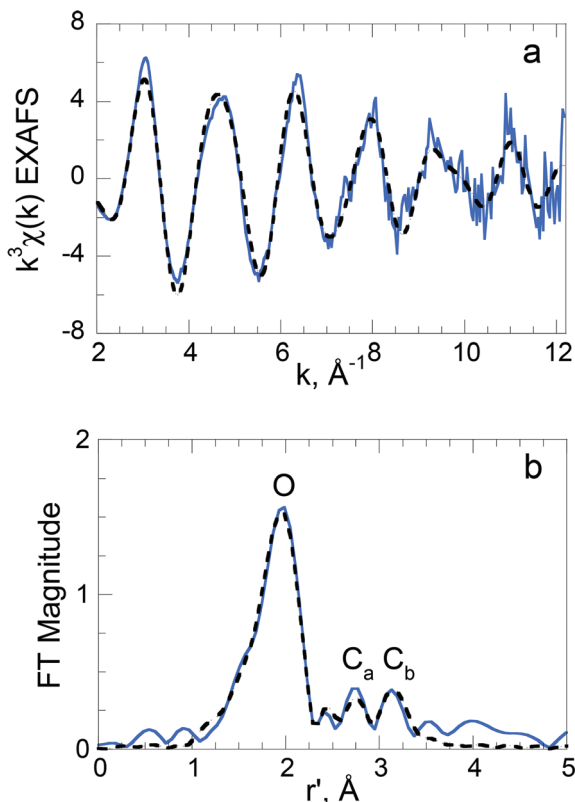


Fig. 2 (a) The primary $k^3\chi(k)$ Eu EXAFS data and (b) the Fourier transform data of the $k^3\chi(k)$ EXAFS of the solid salt $\text{Eu}(\text{TODGA})_3(\text{BiCl}_4)_3$. In both panels, the experimental data are shown as solid blue lines, and the fit to the $k^3\chi(k)$ EXAFS as well as the Fourier transform of the fit are shown as dashed black lines. The best fit Eu–O, –C_a, and –C_b distances are 2.40(1), 3.34(3) and 3.55(2) Å, respectively. The best fit O and C_{a,b} Debye–Waller factors (σ^2) are 0.008(1) and 0.005(2) Å², respectively, and the refined energy shift (ΔE_0) is 0.7 eV. The O, C_a, and C_b coordination numbers were fixed at 9, 6, and 6, respectively.

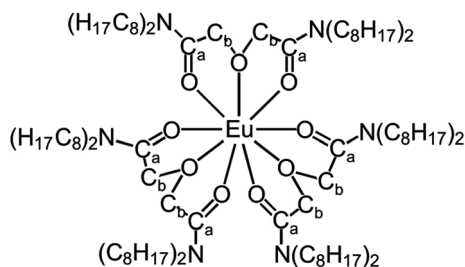


Fig. 3 Structure of the homoleptic, cationic tris(TODGA)europium(III) coordination complex proposed from the metrical results obtained from the Eu EXAFS of the solid salt with the anionic bismuth tetrachloride counterion. Each TODGA ligand coordinates to Eu in a tridentate fashion via two carbonyl O atoms and one ether O atom, resulting in a 9-O coordinate Eu³⁺ with 12 distant C neighbors—6 nearest ones from the carbonyl C atoms (C_a) and 6 slightly more distant ones from the ether C atoms (C_b). The result is the formation of six 5-membered chelate rings that add stability to the molecular architecture. The hydrogen atoms on the sp³-hybridized C_b atoms are omitted for clarity of presentation.

EXAFS reveal a 0.21 Å difference between the Eu–C interactions, the distances alone are insufficient to assign the short C_a interaction to the sp²-hybridized C atoms and the long C_b interaction to the sp³-hybridized C atoms (or *vice versa*). In this regard, the relevant structure precedents for Ln³⁺ complexes of TiPrDGA, TiBuDGA, and the oxydiacetate (ODA) dianion, see Fig. 1(b) are summarized below.

Structure precedent

There are six independent X-ray crystallographic investigations of relevance to the $[\text{Eu}(\text{TODGA})_3]^{3+}$ system: two with the TiPrDGA extractant, one with the TiBuDGA extractant, and three with the ODA dianion. In each of these, the Ln³⁺ ions are 9 coordinate with O atoms from three tetraalkyldiglycolamide extractants and three ODA dianions acting as tridentate ligands. The structures are shown in Fig. 4. The molecular complexes of $[\text{La}(\text{TiBuDGA})_3][\text{La}(\text{NO}_3)_6]^{21}$, $[\text{Tb}(\text{TiPrDGA})_3][\text{Fe}(\text{CN})_6]^{20}$ and $[\text{Yb}(\text{TiPrDGA})_3][\text{NO}_3]^{22}$ consist of homoleptic cationic lanthanide complexes, $[\text{La}(\text{TiBuDGA})_3]^{3+}$ and $[\text{Ln}(\text{TiPrDGA})_3]^{3+}$, in which each tetraalkyldiglycolamide acts as a tridentate oxygen donor providing a 9 O inner-sphere coordination environment of Ln³⁺. Charge balance is maintained with 1 : 1 stoichiometric quantities of the homoleptic anionic coordination complexes, $[\text{La}(\text{NO}_3)_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$, illustrated in Fig. 1(c) and (d), respectively, and a 1 : 3 stoichiometry with the ordinary anionic nitrate counterion (Fig. 1(f)). The tetraalkyldiglycolamide structures of Fig. 4 support the model of Fig. 3 deduced from the EXAFS data for the $[\text{Eu}(\text{TODGA})_3]^{3+}$ cation. Furthermore, the tris(TiPrDGA)Ln and tris(TiBuDGA)La complexes have average Ln–O bond lengths that decrease from 2.53(5) Å for La³⁺ (*Z* = 57) to *ca.* 2.4 Å for Tb³⁺ (*Z* = 65) to 2.35(6) Å for Yb³⁺ (*Z* = 70) consistent with the lanthanide contraction of ionic radii from, in order, 1.216 to 1.095 to 1.042 Å (for CN = IX).²⁸ The 0.18 Å average Ln–O₉ distance difference between the La and Yb cationic complexes is mirrored by the 0.174 Å difference between the ionic radii. Most importantly, the EXAFS-determined average Eu–O bond length of 2.40(1) Å for $[\text{Eu}(\text{TODGA})_3]^{3+}$ is in line with the distance predicted for Eu³⁺ (*Z* = 63) for CN = IX based upon its position in the lanthanide period. Furthermore, the average distance difference between the Ln–C_b and Ln–C_a interactions increases from 0.17 Å (La; 3.583(18) and 3.412(1) Å, respectively) to 0.2 Å (Tb; 3.482(12) and 3.283(8) Å, respectively) to 0.22 Å (Yb; 3.437(15) and 3.222(21) Å, respectively).^{20–22} The EXAFS-determined value of 0.21 Å is consistent with the Eu position in the series of cationic coordination complexes with the basic structure illustrated in Fig. 4(a).

In addition to the tris(tetraalkyldiglycolamide)Ln³⁺ complexes of Fig. 4(a), there are four structures of bis(aryldiglycolamide)Ln³⁺ complexes with *N,N'*-diethyl-*N,N'*-diphenyldiglycolamide (for La),²⁹ *N,N'*-bis(*p*-methoxyphenyl)diglycolamide (for Pr and Nd),³⁰ *N,N'*-dimethyl-*N,N'*-diphenyldiglycolamide (for Er).³¹ Although these are ancillary and indirectly relevant to the subject system because their 1 : 2 Ln³⁺ : diglycolamide stoichiometries do not correspond to the 1 : 3 Eu³⁺ : TODGA complex of this article, it is relevant to note that

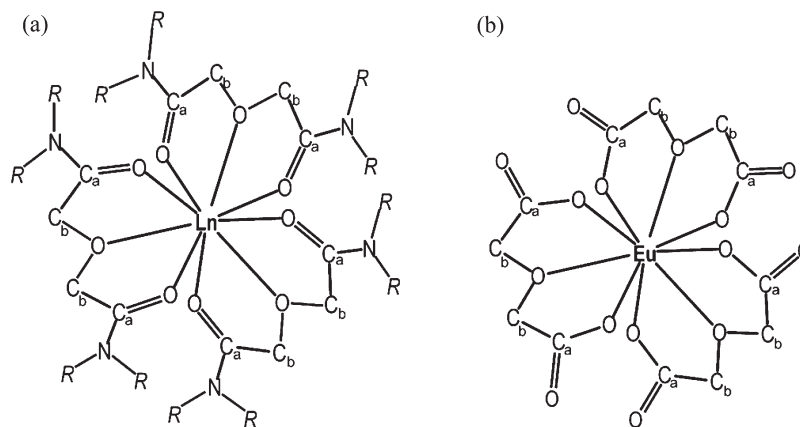


Fig. 4 (a) Molecular structure showing the coordination of one Ln^{3+} to three neutral tetraalkyldiglycolamide extractants with $R = i\text{-Bu}$ for La^{21} and $R = i\text{-Pr}$ for Tb^{3+} and Yb^{3+} ,^{20,22} the tris(tetraalkyldiglycolamide) Ln^{3+} complexes are cationic (3+). Charge balance in the crystalline salts is achieved with $[\text{La}(\text{NO}_3)_6]^{3-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, and $3[\text{NO}_3]^-$ counteranions, respectively. (b) Molecular structure showing the coordination of one Eu^{3+} to three oxydiacetate(2-) ligands,^{32–34} the tris(ODA) Eu^{3+} complex is anionic (3-). Solid salts were crystallized with sodium counteranions. All hydrogen atoms on the sp^3 -hybridized C_b atoms are omitted for clarity of presentation.

the aforementioned aryldiglycolamides act as tridentate ligands in the same manner as TODGA. The La^{3+} , Pr^{3+} , and Nd^{3+} ions are coordinated to 10 O atoms, including 6 from the two tridentate diglycolamides and 4 from various combinations of picrate O, nitrate O, and water coordination, leading to the formation of heteroleptic neutral²⁹ and dicationic³⁰ coordination complexes. The heteroleptic Er complex is a trication; it has three inner-sphere water molecules for a total O CN of 9.³¹ The stoichiometric and charge differences in combination with the coordination of two (or three) different ligands to Ln^{3+} impact the metrical details, which do not fall in line with those for the homoleptic series of tris(tetraalkyldiglycolamide) Ln complexes, including $[\text{Eu}(\text{TODGA})_3][(\text{BiCl}_4)_3]$.

The X-ray crystallographic investigations of trisodium salts of tris(oxydiacetato)europium(III) reveal homoleptic anionic $[\text{Eu}(\text{ODA})_3]^{3-}$ complexes in which each ODA acts as a tridentate oxygen donor providing a 9 O inner-sphere coordination environment of Eu^{3+} as shown in Fig. 4(b). The average $\text{Eu}-\text{O}_9$ distance of 2.43(6) Å is within the statistical error of that for the corresponding EXAFS distance of 2.40(1) Å for $[\text{Eu}(\text{TODGA})_3]^{3+}$. Charge balance is maintained with three outer sphere Na ions.^{32–34} The most relevant metrical comparison with the structure of $[\text{Eu}(\text{TODGA})_3]^{3+}$ (Fig. 3) concerns the magnitude of Eu interactions with the six sp^2 -hybridized C atoms (C_a) and the six sp^3 -hybridized ones (C_b). The $\text{Eu}-\text{C}_a$ distances are 0.13–0.17 Å shorter than the $\text{Eu}-\text{C}_b$ distances.^{32–34} The absolute average distances amount to 3.30–3.32 and 3.45–3.47 Å, respectively, which are consistent with the EXAFS results for $[\text{Eu}(\text{TODGA})_3]^{3+}$. This comparison provides further evidence that the complex depicted in the structure model of Fig. 3 for the tris(TODGA)europium(III) complex cation is similar, albeit distinctive, from the related Eu-tris(oxydiacetato)europium(III) complex anion of Fig. 4(b). With this final crystallographic information comparison, we conclude that the peaks labeled C_a and C_b in the Fourier transform data of Fig. 2(b) arise from the sp^2 -hybridized

C atoms of the carbonyl moieties and the sp^3 -hybridized C atoms adjacent to the ether O atoms, respectively.

Conclusions

The twelve *n*-octyl groups in the cationic $[\text{Eu}(\text{TODGA})_3]^{3+}$ complex contribute 96 atoms to the carbon balance of the system, wherein the hydrophilic $\text{Eu}-\text{O}_9$ inner sphere coordination determined by EXAFS is essentially encrypted by an oleophilic shell (see Fig. 3), much like a molecular version of a reverse micelle. Because the nine-O coordination environment is independent of the nature of the tetraalkyl substituents (*e.g.*, *n*-octyl, *i*-propyl, *i*-butyl) of various diglycolamides in solid salts with other Ln^{3+} ions (whose crystallographic structures reveal tridentate O-coordination and 1 : 3 metal : ligand stoichiometries), previously observed variations in solvent extraction performance attributed to Ln^{3+} coordination chemistry are unlikely. Instead, differences in complex oleophilicities in combination with outer-sphere effects of different charge balancing anions are more likely to impact solution behavior.³⁵ In this instance, the anionic bismuth tetrachloride, BiCl_4^- (Fig. 1(e)), counterion is particularly effective at improving the solvent extraction of Ln^{3+} and An^{3+} ions from HCl media into a bulk organic phase, such as *o*-xylene,³ containing TODGA or with TODGA supported on an inert extraction chromatographic resin.² The bonding motif of the homoleptic $[\text{Eu}(\text{TODGA})_3]^{3+}$ trication is rigid enough to resolve the six closest $\text{Eu}-\text{C}_a$ interactions to the carbonyl carbons (C_a) from the six next-nearest $\text{Eu}-\text{C}_b$ interactions to the ether carbons (C_b). No evidence for interactions between Eu^{3+} and the BiCl_4^- anions was obtained from the EXAFS data, presumably because the Cl^- and Bi^{3+} are in a too distant location to be observed by Eu X-ray absorption spectroscopy at room temperature.

The $\text{Ln}^{3+}:\text{TODGA}$ and $\text{An}^{3+}:\text{TODGA}$ ratios determined in solution by solvent extraction experiments vary from 1 : 2 to

1:4,^{2,3,7,8,10,11} with 1:3 being a typical value.^{5,6} In the solid state, the consensus of structural data for 1:2 and 1:3 stoichiometric complexes reveals tridentate O coordination by both alkyl- and aryl diglycolamides.^{20–22,29–31} In the absence of solid-state structural data for 1:4 complexes, if we were to assume that they exhibit the tridentate coordination motif of the 1:2 and 1:3 systems, then the O coordination number would be 12 in $[\text{Ln}(\text{TODGA})_4]^{3+}$. This seems sterically unviable,¹⁰ especially with the prospect of conformational entanglement by sixteen *n*-octyl chains, and suggests a different coordination motif wherein one (or more) TODGA may be monodentate or bidentate with Ln^{3+} . This can be envisioned to occur with conformers of TODGA that differ from those depicted in Fig. 1(a) by rotations along the $\text{C}_a\text{--C}_b$ and $\text{C}_b\text{--O}$ bonds. The fact that the observed 1:3 Eu : TODGA stoichiometry in the solid salt, $\text{Eu}(\text{TODGA})_3(\text{BiCl}_4)_3$, synthesized and characterized here is different from the 1:4 Ln : TODGA ratio reported for solutions of aliphatic organic solvents indicates a change in speciation. Whereas the solid salt is a classical coordination complex, the effects of organic solvent polarities and aqueous acidities on the interactions between Ln^{3+} ions and TODGA are pivotal in determining the stoichiometry of the stable speciation in solution. These effects are generally attributable to TODGA aggregation and micellization, which would not be favored in polar diluents, *e.g.*, alcohols, such as methanol used in our single-phase preparative procedure, and favored in apolar ones, *e.g.*, octane or dodecane. The EXAFS results provide a view into the molecular complexation and structure of Eu^{3+} in a coordination complex with TODGA that is relevant to contemporary advances in the hydrometallurgy of 4f/5f elements, such as ALSEP.

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