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Preparation and characterization of single crystals $[Ln(TBPO)_4(NO_3)_2]NTf_2$ (Ln = Eu, Gd)

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Two single crystals $[Ln(TBPO)_4(NO_3)_2]NTf_2$ (Ln = Eu, Gd) were prepared and characterized by element analysis, single crystal X-ray diffraction, PXRD, FT-IR, TGA and fluorescence spectroscopy. The two compounds have similar coordinate structures, in which the central metal ion is coordinated by four TBPO (Tri-*n*-butylphosphine oxide) molecules and two bidentate nitrates, while NTf_2^-(bis(trifluor-(bis(trifluoromethylsulfonyl)imide anion) acts as the counter anion. The packing modes of the two crystals are same. The two single crystals are the focus on 8-coordinate tetra-TRPO complexes (TRPO is Trialkyphosphine oxides).

1. Introduction

The coordination chemistry of complexes of lanthanide nitrates with phosphine oxides has attracted interest for a number of years. The isolation of the complexes $Ln(TRPO)_3(NO_3)_3$ and $Ln(TRPO)_2(NO_3)_3$ (R represents alkyl groups, *e.g.* methyl, ethyl, butyl, octyl, cyclohexyl, isobutyl and isopropyl) shows that the 9-coordinate or 8-coordinate structures and the 3:1 or 2:1 molar ratios of ligand to metal ion are common in these systems [1–5]. For the lighter lanthanide (Ce, Pr, Nd, Eu) ions, 9-coordinate complexes $Ln(TEtPO)_3(NO_3)_3$ were formed, while both 9-coordinate $Ln(TEtPO)_3(NO_3)_3$ and 8-coordinate $Ln(TEtPO)_2(NO_3)_3$ were formed for the heavier lanthanide (Tb and Ho) ions [6]. On an increase in the size of the ligand, 9-coordinate $Ln(TRPO)_3(NO_3)_3$ (R = cyclohexyl [2] and isobutyl [3]) were formed throughout the lanthanide series. When the ligand was bulky T^tBuPO (Tri-tertbutylphosphine oxide), 8-coordinate $Ln(T^tBuPO)_2(NO_3)_3$ instead of $Ln(T^tBuPO)_3(NO_3)_3$ were formed for all lanthanides [7]. Platt et al. [6,8] found that solid state structures and solution properties depend on a balance between steric and electronic effects of TRPO and the size of the lanthanide ions.

Recently, several reviews, concerning the extraction of lanthanides in the ionic liquid (IL) based systems, were published [9–12]. As known, TRPO are traditional extractants with high extraction efficiency on lanthanides. In traditional solvent extraction, extensive studies on lanthanide complexes revealed that $Ln(TRPO)_3(NO_3)_3$ and $Ln(TRPO)_2(NO_3)_3$ are often formed [1,5], but in the IL-based extraction systems, we have to take the influence of ILs on the extraction complexes into consideration. Now, the most widely used ILs are $C_n$mimNTf_2 (1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) are the most widely used ILs. The influence of IL anion NTf_2^- on the structure of complexes is the focus study of this work [13–15].

Our research group has synthesized and characterized two Eu-containing ILs, *i.e.* $[Eu(TBPO)_4(NO_3)_2]NTf_2$ (TBPO: Tri-*n*-butylphosphine oxide) and $[Eu(TOPO)_4(NO_3)_2]NTf_2$ (TOPO: tri-*n*-octylphosphine oxide), and a single crystal $[Eu(TPhPO)_4(NO_3)_2]NTf_2$ (TPhPO: triphenylphosphine oxide) [16]. However, the coordination structures of the above two Eu-containing ILs were just speculated from the single crystal structure of $[Eu(TPhPO)_4(NO_3)_2]NTf_2$ characterized by X-ray diffraction measurements. On the basis of the above work, we tried to prepare the colorless crystal of X-ray quality, $[Eu(TBPO)_4(NO_3)_2]NTf_2$, by cooling the ethanol solution and recrystallization of the IL $[Eu(TBPO)_4(NO_3)_2]NTf_2$. For comparison, we used the same method to get the single crystal $[Gd(TBPO)_4(NO_3)_2]NTf_2$. Although the complexes of lanthanide nitrates with tetra-TPhPO crystals have been studied [16,17], to the best of our knowledge, there have been no reports so

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far on the tetra-TRPO crystals formed by $Ln(NO_3)_3$ with TRPO molecules. The two single crystals, therefore, are the focus on such 8-coordinate tetra-TRPO complexes.

2. Experimental

2.1. Materials and methods

All chemicals were purchased commercially and used without further purification. The organic element analyses were performed on an elemental analyzer, vario EL (Elementar Analysensysteme GmbH, Germany). FT-IR spectra of the complexes were recorded on a NICOLET iN10 MX spectrometer. The thermogravimetric analyses (TGA) were measured on a Q600 SDT thermoanalyzer under N_2 atmosphere with the temperature ranging from room temperature to 700 °C at a heating rate of 10 °C min^{-1}. Powder X-ray diffraction (PXRD) data were measured on a DMAX-2400 diffractometer using Cu Kα radiation (λ = 1.5406 Å) and the simulated data were carried out by the crystal analytic software 'Mercury'. Solid-state fluorescence measurements were performed on an F-4500 (Hitachi) spectrophotometer. The crystallographic data for the single crystals were collected on an Agilent SuperNova Dual Atlas CCD diffractometer. Monochromated MoK_{α} (λ = 0.71073 Å) radiation was used. Using Olex2, the structure was solved with the XS structure solution program using direct methods.

2.2. Syntheses

$[Ln(TBPO)_4(NO_3)_2]NTf_2$ (Ln = Eu, Gd) were formed during the reaction between $Ln(NO_3)_3$ (Ln = Eu, Gd) and ethanol solution containing both TBPO and $LiNTf_2$ at 60 °C. The products were colorless fluid at 30 °C. Colorless crystals of X-ray quality were obtained upon recrystallisation from ethanol solution at 10 °C. Anal. calcd. (found) for $Eu(TBPO)_4(NO_3)_2NTf_2$ ($C_{50}H_{108}EuF_6N_3O_{14}P_4S_2$): C, 42.01% (42.09%); H, 7.62% (7.46%); N, 2.94% (2.62%). Anal. calcd. (found) for $Gd(TBPO)_4(NO_3)_2NTf_2$ ($C_{50}H_{108}GdF_6N_3O_{14}P_4S_2$): C, 41.86% (41.99%); H, 7.59% (7.76%); N, 2.93% (2.89%).

3. Results and discussion

The molecular structures of $[Ln(TBPO)_4(NO_3)_2]NTf_2$ (Ln = Eu, Gd) are presented in Fig. 1. The two compounds have similar coordinate structures, in which the central metal ion is coordinated by four TBPO molecules and two bidentate nitrates. Four oxygen atoms of TBPO molecules are almost in a same plane, while two bidentate nitrates coordinate with the central metal ion oppositely. From the selected bond lengths data, the average distances of Eu–O(P) (Eu–O(P) band represents that the metal ion is coordinated with the oxygen atom of TBPO molecule) and Eu–O(N) (Eu–O(N) band represents that the metal ion is linked with the oxygen atom of the bidentate nitrate) bonds are 2.3194 Å and 2.9392 Å, respectively, while those of Gd–O(P) and Gd–O(N) are 2.3071 Å and 2.9268 Å, separately. It is noted that NTf_2^- is not coordinated with the central metal ion, but functions as a counter anion. NTf_2^- can coordinate with lanthanides or alkaline earth metal ions through an oxygen atom of each sulfonyl group without the additional coordination of other molecules, and can also stabilize deficient transition metal or uranyl complexes *via* distinct modes [18]. A complex of Cs^+ with a calixcrown bis(2-propyloxy)calix[4]crown-6 (BPC6) and NTf_2^-, in which NTf_2^- coordinates with Cs^+ ion directly, has been synthesized and characterized in our previous work [19]. Our research group has been dedicating into the applications of ionic liquid on the extraction and separation of lanthanide ions. We have reported the effective extraction of Eu^{3+} by TRPO in $C_n$mimNTf_2 and the extraction species in the system was found to be $[Eu(TBPO)_4(NO_3)_2]NTf_2$ [16]. Lanthanide complexes $Ln(TRPO)_3(NO_3)_3$ are often formed in traditional solvent extraction systems [1,5]. In IL-extraction systems, however, the extraction species and extraction mechanism of TRPO are different from those of the normal organic solvent systems.

The crystal data and structure refinement of the two complexes are shown in Table 1. The two compounds are isostructural, with space group $P2_1/n$. In particular, the crystal cell parameters are basically same. In the crystal lattice (Fig. 2), the column like $[Eu(TBPO)_4(NO_3)_2]NTf_2$ molecules are arranged head-to-end along a direction, and further arrange in a nearly hexagonal closest packing extending along b and c directions. It is interesting to note that the crystal packing mode of $[Gd(TBPO)_4(NO_3)_2]NTf_2$ is

Table 1
Crystal data and structure refinement of $[Ln(TBPO)_4(NO_3)_2]NTf_2$ (Ln = Eu, Gd).

Chemical formula	$C_{50}H_{108}EuF_6N_3O_{14}P_4S_2$	$C_{50}H_{108}GdF_6N_3O_{14}P_4S_2$
Formula weight	1429.35	1434.64
Temperature/K	103.3	104.1
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	

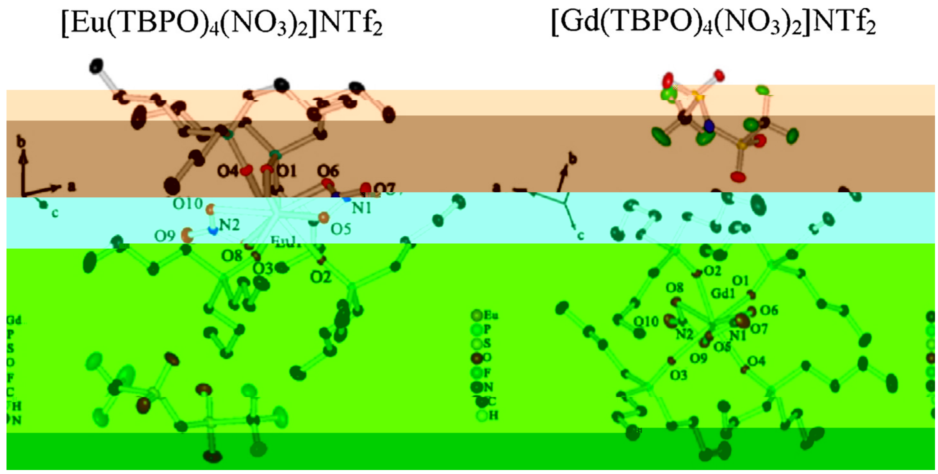


Fig. 1. Ellipsoid representation of the molecular structure of $[Ln(TBPO)_4(NO_3)_2]NTf_2$ (Ln = Eu, Gd). Selected bond lengths: Eu1–O1 2.3165(17); Eu1–O2 2.3516(17); Eu1–O3 2.3028(17); Eu1–O4 2.3065(17); Eu1–O5 2.5075(18); Eu1–O6 2.5075(18); Eu1–O8 2.5046(17); Eu1–O10 2.5557(17); Eu1–N1 2.925(2); Eu1–N2 2.953(2) Å. Gd1–O1 2.2973(19); Gd1–O2 2.302(2); Gd1–O3 2.3396(19); Gd1–O4 2.289(2); Gd1–O5 2.487(2); Gd1–O6 2.541(2); Gd1–O8 2.482(2); Gd1–O9 2.490(2); Gd1–N1 2.943(3); Gd1–N2 2.910(3) Å.

consistent with that of europium complex. The two crystals were also investigated by powder X-ray diffraction (Fig. 3). The PXRD patterns of the two crystals are same. The main peaks of $2\theta = 6.36°$, 7.08°, 8.06°, 9.22°, 10.14°, 11.60°, 13.04°, 18.64° and 20.62° in the PXRD patterns agree well with the simulated patterns.

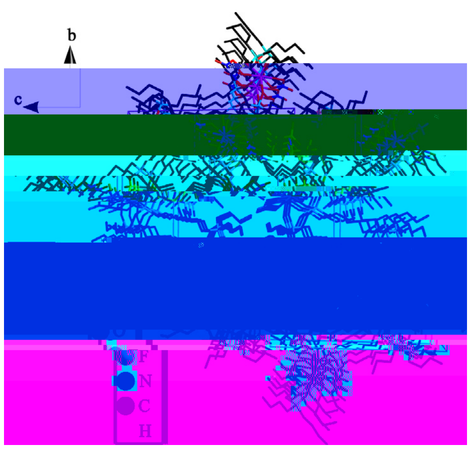
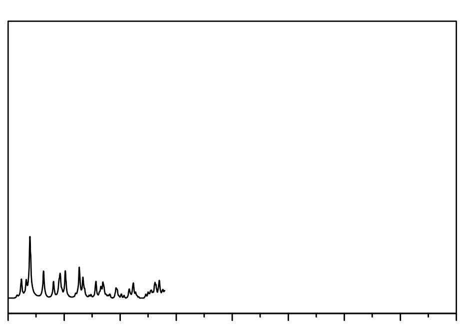


Fig. 2. Packing of $[Eu(TBPO)_4(NO_3)_2]NTf_2$ molecules in the crystal structure, viewed along *a* direction.



The infrared spectra (Fig. 4) of the two complexes contain some typical features of the phosphine oxide and nitrate. The two similar IR spectra results show the presence of bidentate nitrates (Scheme 1) in the complexes. The symmetric stretching mode (υ_1) of the $-NO_2$ group in the two complexes can be assigned at 1294 cm^{-1}. Peaks of N–O stretching mode (υ_2) appear at around 1030 cm^{-1}. The asymmetric stretching mode (υ_3) of the $-NO_2$ group for the ionic liquid $[Eu(TBPO)_4(NO_3)_2]NTf_2$ is split (1466 and 1495 cm^{-1}) [16], while the solid state $[Eu(TBPO)_4(NO_3)_2]NTf_2$ has no splitting at 1463 cm^{-1}. The P–O stretch is observed at 1113 cm^{-1} for $[Ln(TBPO)_4(NO_3)_2]NTf_2$ (Ln = Eu, Gd), which is at lower wavenumbers than the corresponding P–O stretch of the free ligand TBPO (1154 cm^{-1}). Other peaks wavenumbers like 1351 cm^{-1} and 1055 cm^{-1} are associated with the characteristics of NTf_2^- as compared with the IR spectra of $LiNTf_2$.

In order to assess the thermal stabilities and the phase behaviors of the two complexes, the decomposition temperatures were determined using TGA. The two complexes possess good thermal stability up to 250 °C due to the absence of phosphine oxides and nitrate ligands (Fig. 5). The TGA curves of $[Eu(TBPO)_4(NO_3)_2]NTf_2$ and $[Gd(TBPO)_4(NO_3)_2]NTf_2$ show similar one-step weight loss profiles. In the temperature range 250–500 °C, the two compounds rapidly decompose to their respective metal oxides. One-step weight loss is common in the TGA profiles of lanthanide compounds due to the continuous decomposition of constituents, such as $Ln(TPhPO)_2(phen)(NO_3)_3$ (phen = 1,10-phenanthroline, Ln = Ce, Gd, Tb, Ho, Eu), but no optimal result of

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