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Preparation and characterization of single crystals [Ln(TBPO)₄(NO₃)₂]NTf₂ (Ln = Eu, Gd)

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ABSTRACT

Two single crystals [Ln(TBPO)₄(NO₃)₂]NTf₂ (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 NTf₂⁻ (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 Trialkylphosphine oxides).

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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(NO₃)₃ and Ln(TRPO)₂(NO₃)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(NO₃)₃ were formed, while both 9-coordinate Ln(TEtPO)₃(NO₃)₃ and 8-coordinate Ln(TEtPO)₂(NO₃)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(NO₃)₃ (R = cyclohexyl [2] and isobutyl [3]) were formed throughout the lanthanide series. When the ligand was bulky T^tBuPO (Tri-*t*-butylphosphine oxide), 8-coordinate Ln(T^tBuPO)₂(NO₃)₃ instead of Ln(T^tBuPO)₃(NO₃)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(NO₃)₃ and Ln(TRPO)₂(NO₃)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_nmimNTf₂ (1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) are the most widely used ILs. The influence of IL anion NTf₂⁻ 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(NO₃)₂]NTf₂ (TBPO: Tri-*n*-butylphosphine oxide) and [Eu(TOPO)₄(NO₃)₂]NTf₂ (TOPO: tri-*n*-octylphosphine oxide), and a single crystal [Eu(TPhPO)₄(NO₃)₂]NTf₂ (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(NO₃)₂]NTf₂ 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(NO₃)₂]NTf₂, by cooling the ethanol solution and recrystallization of the IL [Eu(TBPO)₄(NO₃)₂]NTf₂. For comparison, we used the same method to get the single crystal [Gd(TBPO)₄(NO₃)₂]NTf₂. 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 $\text{Ln}(\text{NO}_3)_3$ 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 $700\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. Powder X-ray diffraction (PXRD) data were measured on a DMAX-2400 diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406\text{ \AA}$) 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 $\text{MoK}\alpha$ ($\lambda = 0.71073\text{ \AA}$) radiation was used. Using Olex2, the structure was solved with the XS structure solution program using direct methods.

2.2. Syntheses

$[\text{Ln}(\text{TBPO})_4(\text{NO}_3)_2]\text{NTf}_2$ ($\text{Ln} = \text{Eu}, \text{Gd}$) were formed during the reaction between $\text{Ln}(\text{NO}_3)_3$ ($\text{Ln} = \text{Eu}, \text{Gd}$) and ethanol solution containing both TBPO and LiNTf_2 at $60\text{ }^\circ\text{C}$. The products were colorless fluid at $30\text{ }^\circ\text{C}$. Colorless crystals of X-ray quality were obtained upon recrystallisation from ethanol solution at $10\text{ }^\circ\text{C}$. Anal. calcd. (found) for $\text{Eu}(\text{TBPO})_4(\text{NO}_3)_2\text{NTf}_2$ ($\text{C}_{50}\text{H}_{108}\text{EuF}_6\text{N}_3\text{O}_{14}\text{P}_4\text{S}_2$): C, 42.01% (42.09%); H, 7.62% (7.46%); N, 2.94% (2.62%). Anal. calcd. (found) for $\text{Gd}(\text{TBPO})_4(\text{NO}_3)_2\text{NTf}_2$ ($\text{C}_{50}\text{H}_{108}\text{GdF}_6\text{N}_3\text{O}_{14}\text{P}_4\text{S}_2$): C, 41.86% (41.99%); H, 7.59% (7.76%); N, 2.93% (2.89%).

3. Results and discussion

The molecular structures of $[\text{Ln}(\text{TBPO})_4(\text{NO}_3)_2]\text{NTf}_2$ ($\text{Ln} = \text{Eu}, \text{Gd}$) 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 $\text{Eu}-\text{O}(\text{P})$ ($\text{Eu}-\text{O}(\text{P})$ band represents that the metal ion is coordinated with the oxygen atom of TBPO molecule) and $\text{Eu}-\text{O}(\text{N})$ ($\text{Eu}-\text{O}(\text{N})$ band represents that the metal ion is linked with the oxygen atom of the bidentate nitrate) bonds are 2.3194 \AA and 2.9392 \AA , respectively, while those of $\text{Gd}-\text{O}(\text{P})$ and $\text{Gd}-\text{O}(\text{N})$ are 2.3071 \AA and 2.9268 \AA , 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 $\text{C}_n\text{mimNTf}_2$ and the extraction species in the system was found to be $[\text{Eu}(\text{TBPO})_4(\text{NO}_3)_2]\text{NTf}_2$ [16]. Lanthanide complexes $\text{Ln}(\text{TRPO})_3(\text{NO}_3)_3$ 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 $\text{P2}_1/\text{n}$. In particular, the crystal cell parameters are basically same. In the crystal lattice (Fig. 2), the column like $[\text{Eu}(\text{TBPO})_4(\text{NO}_3)_2]\text{NTf}_2$ 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 $[\text{Gd}(\text{TBPO})_4(\text{NO}_3)_2]\text{NTf}_2$ is

Table 1
Crystal data and structure refinement of $[\text{Ln}(\text{TBPO})_4(\text{NO}_3)_2]\text{NTf}_2$ ($\text{Ln} = \text{Eu}, \text{Gd}$).

Chemical formula	$\text{C}_{50}\text{H}_{108}\text{EuF}_6\text{N}_3\text{O}_{14}\text{P}_4\text{S}_2$	$\text{C}_{50}\text{H}_{108}\text{GdF}_6\text{N}_3\text{O}_{14}\text{P}_4\text{S}_2$
Formula weight	1429.35	1434.64
Temperature/K	103.3	104.1
Crystal system	Monoclinic	Monoclinic
Space group	$\text{P2}_1/\text{n}$	$\text{P2}_1/\text{n}$
$a/\text{\AA}, b/\text{\AA}, c/\text{\AA}$	15.1679(2), 25.9557(3), 19.4246(4)	15.1442(3), 25.9182(4), 19.3984(4)
$\alpha/^\circ, \beta/^\circ, \gamma/^\circ$	90.00, 111.961(2), 90.00	90.00, 111.961(2), 90.00
Volume/ \AA^3	7092.5(2)	7061.6(2)
Z	4	4
$\rho_{\text{calc}}/\text{mg mm}^{-3}$	1.339	1.349
μ/mm^{-1}	1.104	1.159
$F(000)$	3000	3004
Crystal size/ mm^3	$0.35 \times 0.30 \times 0.30$	$0.30 \times 0.25 \times 0.25$
2θ range for data collection	6.08 to 52°	6.02 to 52°
Index ranges	$-18 \leq h \leq 18, -32 \leq k \leq 32, -13 \leq l \leq 23$	$-18 \leq h \leq 18, -31 \leq k \leq 31, -23 \leq l \leq 23$
Reflections collected	39102	69537
Independent reflections	13904 [$R(\text{int}) = 0.0284$ (inf-0.9 \AA)]	13839 [$R(\text{int}) = 0.0426$ (inf-0.9 \AA)]
Data/restraints/parameters	13904/0/733	13839/0/733
Goodness-of-fit on F^2	1.075	1.160
Final R indexes [$I > 2\sigma(I)$ i.e. $F_0 > 4\sigma(F_0)$]	$R_1 = 0.0309, wR_2 = 0.0567$	$R_1 = 0.0370, wR_2 = 0.0654$
Final R indexes [all data]	$R_1 = 0.0417, wR_2 = 0.0610$	$R_1 = 0.0470, wR_2 = 0.0694$
Largest diff. peak/hole/ $e\text{ \AA}^{-3}$	0.895/-0.513	0.949/-1.016
Flack parameters	N	N
Completeness	0.998	0.998

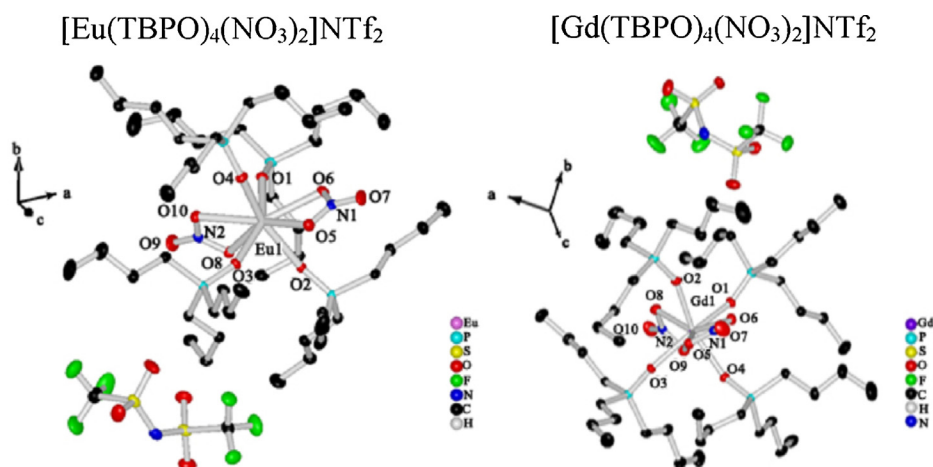


Fig. 1. Ellipsoid representation of the molecular structure of $[\text{Ln}(\text{TBPO})_4(\text{NO}_3)_2]\text{NTf}_2$ ($\text{Ln} = \text{Eu}, \text{Gd}$). Selected bond lengths: Eu1–O1 2.3165(17); Eu1–O2 2.3516(17); Eu1–O3 2.3028(17); Eu1–O4 2.3065(17); Eu1–O5 2.5075(18); Eu1–O6 2.5075(18); Eu1–O8 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 $2\theta = 6.36^\circ, 7.08^\circ, 8.06^\circ, 9.22^\circ, 10.14^\circ, 11.60^\circ, 13.04^\circ, 18.64^\circ$ and 20.62° in the PXRD patterns agree well with the simulated patterns.

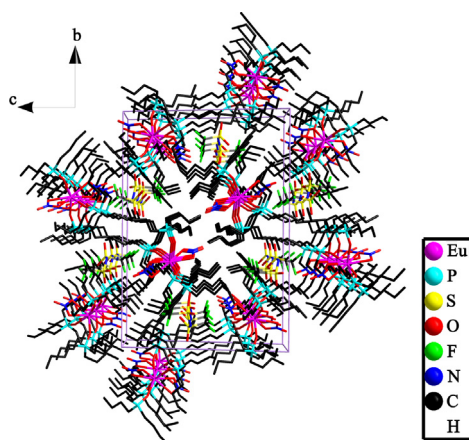


Fig. 2. Packing of $[\text{Eu}(\text{TBPO})_4(\text{NO}_3)_2]\text{NTf}_2$ molecules in the crystal structure, viewed along a direction.

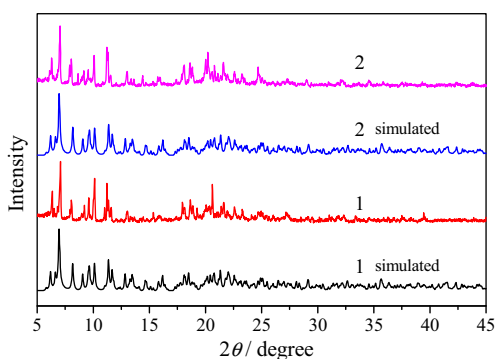


Fig. 3. Experimental PXRD of single crystals $[\text{Eu}(\text{TBPO})_4(\text{NO}_3)_2]\text{NTf}_2$ (1) and $[\text{Gd}(\text{TBPO})_4(\text{NO}_3)_2]\text{NTf}_2$ (2), compared with the simulated results.

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 (ν_1) of the $-\text{NO}_2$ group in the two complexes can be assigned at 1294 cm^{-1} . Peaks of N–O stretching mode (ν_2) appear at around 1030 cm^{-1} . The asymmetric stretching mode (ν_3) of the $-\text{NO}_2$ group for the ionic liquid $[\text{Eu}(\text{TBPO})_4(\text{NO}_3)_2]\text{NTf}_2$ is split (1466 and 1495 cm^{-1}) [16], while the solid state $[\text{Eu}(\text{TBPO})_4(\text{NO}_3)_2]\text{NTf}_2$ has no splitting at 1463 cm^{-1} . The P–O stretch is observed at 1113 cm^{-1} for $[\text{Ln}(\text{TBPO})_4(\text{NO}_3)_2]\text{NTf}_2$ ($\text{Ln} = \text{Eu}, \text{Gd}$), 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 $[\text{Eu}(\text{TBPO})_4(\text{NO}_3)_2]\text{NTf}_2$ and $[\text{Gd}(\text{TBPO})_4(\text{NO}_3)_2]\text{NTf}_2$ show similar one-step weight loss profiles. In the temperature range $250\text{--}500^\circ\text{C}$, 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 $\text{Ln}(\text{TPhPO})_2(\text{phen})(\text{NO}_3)_3$ ($\text{phen} = 1,10\text{-phenanthroline}$,

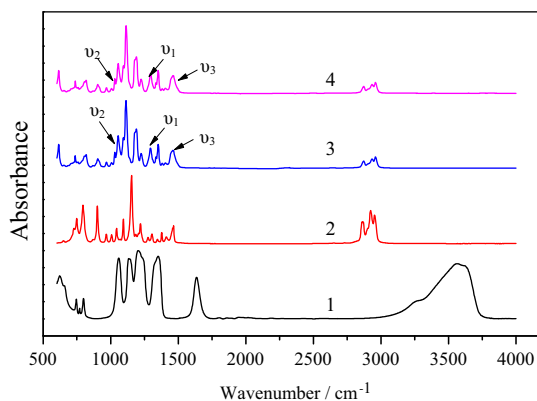
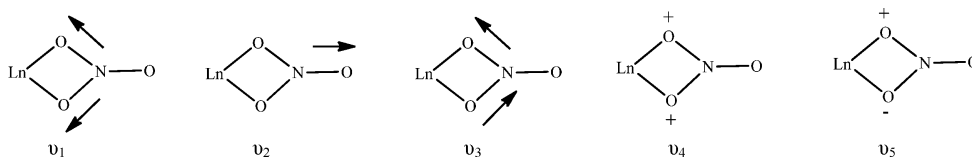


Fig. 4. IR spectra of LiNTf_2 (1), TBPO (2), $[\text{Eu}(\text{TBPO})_4(\text{NO}_3)_2]\text{NTf}_2$ (3), $[\text{Gd}(\text{TBPO})_4(\text{NO}_3)_2]\text{NTf}_2$ (4).



Scheme 1. Stretching modes of NO_3^- in complexes. ν_1 , symmetric stretching mode of the $-\text{NO}_2$ group; ν_2 , N–O stretching mode; ν_3 , asymmetric stretching mode of the $-\text{NO}_2$ group; ν_4 and ν_5 , non planar rocking frequency modes.

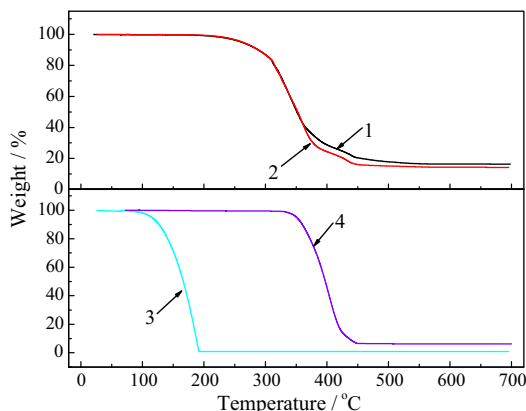


Fig. 5. TGA curves of $[\text{Eu}(\text{TBPO})_4(\text{NO}_3)_2]\text{NTf}_2$ (1), $[\text{Gd}(\text{TBPO})_4(\text{NO}_3)_2]\text{NTf}_2$ (2), TBPO (3), and LiNTf_2 (4) (the curve of LiNTf_2 cited from the Ref. [20]).

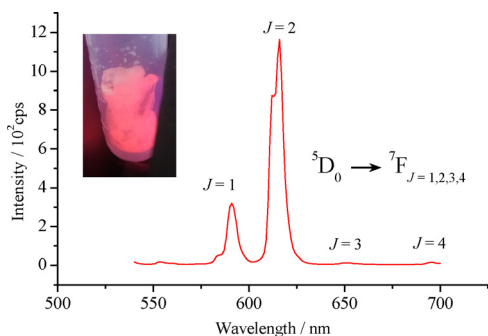


Fig. 6. Emission spectrum of the crystal $[\text{Eu}(\text{TBPO})_4(\text{NO}_3)_2]\text{NTf}_2$ at room temperature ($\lambda_{\text{ex}} = 395 \text{ nm}$). Inset: the picture of the compound under UV radiation.

$\text{Ln} = \text{Ce}, \text{Gd}, \text{Tb}, \text{Ho}, \text{Eu}$), but no optimal result of $\text{Eu}(\text{TPhPO})_2(\text{phen})(\text{NO}_3)_3$ could be obtained [20].

In addition, the crystal $[\text{Eu}(\text{TBPO})_4(\text{NO}_3)_2]\text{NTf}_2$ exhibits excellent luminescent property as illustrated in Fig. 6. The strongest emission which splits into two peaks centered at 613 nm and 617 nm can be attributed to the forced electric dipole $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu^{3+} ions [21]. This is different from the sharp and narrow emission band at 616 nm of the emission spectrum of 1 mmol dm^{-3} $[\text{Eu}(\text{TBPO})_4(\text{NO}_3)_2]\text{NTf}_2$ in acetonitrile [16]. The other three bands at 590, 651 and 696 nm correspond to the characteristic transitions for Eu^{3+} ion ($^5\text{D}_0 \rightarrow ^7\text{F}_j$, $J = 1, 3, 4$) [22]. The emission spectrum of the crystal $[\text{Gd}(\text{TBPO})_4(\text{NO}_3)_2]\text{NTf}_2$ on excitation at 243 nm shows one main band at 488 nm, corresponding to the $^6\text{F}_{3/2} \rightarrow ^6\text{P}_{1/2}$ transition of Gd^{3+} ion (figure not shown). This emission spectrum is similar to the result reported in the literature [23].

4. Conclusions

Two single crystals $[\text{Ln}(\text{TBPO})_4(\text{NO}_3)_2]\text{NTf}_2$ ($\text{Ln} = \text{Eu}, \text{Gd}$) were synthesized and characterized. The infrared spectra of the compounds exhibited some typical features of the phosphine oxides and

two bidentate nitrates. The TGA curves of two complexes showed similar one-step weight loss profiles. The two complexes exhibited good thermal stability up to 250°C , and then rapidly decomposed to their respective metal oxides in the temperature range $250\text{--}500^\circ\text{C}$. The crystal $[\text{Eu}(\text{TBPO})_4(\text{NO}_3)_2]\text{NTf}_2$ showed excellent luminescent property and the strongest emission splitted into two peaks centered at 613 nm and 617 nm, attributing to the forced electric dipole $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu^{3+} ions. The two compounds have similar coordinate structures, in which the central metal ion is coordinated by four TBPO molecules and two bidentate nitrates, while NTf_2^- acts as the counter anion. The structural difference between $[\text{Ln}(\text{TBPO})_4(\text{NO}_3)_2]\text{NTf}_2$ and $\text{Ln}(\text{TBPO})_3(\text{NO}_3)_3$ can help understand the new extraction mechanisms in the IL based systems as compared with the normal organic solvent systems.

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References

- [1] A.M.G. Massabni, M.L.R. Gibran, O.A. Serra, Phosphine oxides complexes of neodymium(III) nitrate, *Inorg. Nucl. Chem. Lett.* 14 (1978) 419–427.
- [2] A.P. Hunter, A.M.J. Lees, A.W.G. Platt, Synthesis, structures and mass spectrometry of lanthanide nitrate complexes with tricyclohexylphosphine oxide, *Polyhedron* 26 (2007) 4865–4876.
- [3] A. Bowden, P.N. Horton, A.W.G. Platt, Lanthanide nitrate complexes of tri-isobutylphosphine oxide: solid state and CD_2Cl_2 solution structures, *Inorg. Chem.* 50 (2011) 2553–2561.
- [4] A. Bowden, S.J. Coles, M.B. Pitak, A.W.G. Platt, Complexes of lanthanide nitrates with tri-isopropylphosphine oxide, *Polyhedron* 68 (2014) 258–264.
- [5] V.K. Manchanda, K. Chander, N.P. Singh, G.M. Nair, Complexes of lanthanides with triocetylphosphine oxide and tributylphosphine oxide, *J. Inorg. Nucl. Chem.* 39 (1977) 1039–1041.
- [6] A. Bowden, K. Singh, A.W.G. Platt, Lanthanide nitrate complexes with triethylphosphine oxide. Solid state and solution properties, *Polyhedron* 42 (2012) 30–35.
- [7] A. Bowden, S.J. Coles, M.B. Pitak, A.W.G. Platt, Complexes of lanthanide nitrates with tri tert butylphosphine oxide, *Inorg. Chem.* 51 (2012) 4379–4389.
- [8] A.W.G. Platt, K. Singh, The interactions between the sterically demanding trimesitylphosphine oxide and trimesitylphosphine with scandium and selected lanthanide ions, *J. Mol. Struct.* 1111 (2016) 180–184.
- [9] Y. Baba, F. Kubota, N. Kamiya, M. Goto, Recent advances in extraction and separation of rare-earth metals using ionic liquids, *J. Chem. Eng. Jpn.* 44 (2011) 679–685.
- [10] X.Q. Sun, H.M. Luo, S. Dai, Ionic liquids-based extraction: a promising strategy for the advanced nuclear fuel cycle, *Chem. Rev.* 112 (2012) 2100–2128.
- [11] M.L. Dietz, Ionic liquids as extraction solvents: where do we stand? *Sep. Sci. Technol.* 41 (2006) 2047–2063.
- [12] H.W. Liu, T. Yang, Q.D. Chen, X.H. Shen, Extraction behaviors of ionic liquid systems and application perspectives in reprocessing of spent nuclear fuel, *J. Nucl. Radiochem.* 37 (2015) 286–309.
- [13] M. Matsumiya, Y. Kikuchi, T. Yamada, S. Kawakami, Extraction of rare earth ions by tri-*n*-butylphosphate/phosphonium ionic liquids and the feasibility of recovery by direct electrodeposition, *Sep. Purif. Technol.* 130 (2014) 91–101.
- [14] G.L. Ma, W.J. Yuan, Z. Dong, et al., Extraction of lanthanides from nitric acid solution using isobutyl-BTP/ionic liquid system, *Nucl. Sci. Technol.* 26 (2015) S10305.
- [15] R. Turgis, G. Arrachart, V. Dubois, et al., Performances and mechanistic investigations of a triphosphine trioxide/ionic liquid system for rare earth extraction, *Dalton Trans.* 45 (2016) 1259–1268.
- [16] H.W. Liu, Extraction Study of U and Eu in Ionic Liquid Systems and the Synthesis of Europium-Containing Ionic Liquid Complexes, Master Thesis, Peking University, Beijing, 2015.

- [17] W. Levason, E.H. Newman, M. Webster, Tetrakis (triphenylphosphine oxide) complexes of the lanthanide nitrates; synthesis, characterisation and crystal structures of $[\text{La}(\text{Ph}_3\text{PO})_4(\text{NO}_3)_3] \text{Me}_2\text{CO}$ and $[\text{Lu}(\text{Ph}_3\text{PO})_4(\text{NO}_3)_2] \text{NO}_3$, *Polyhedron* 19 (2000) 2697–2705.
- [18] T.X. Sun, Application of Ionic Liquids in the Extraction of Sr, Cs, U and Tc, Ph.D. Thesis, Peking University, Beijing, 2013.
- [19] T.X. Sun, Z.M. Wang, X.H. Shen, Crystallization of cesium complex containing bis(2-propyloxy)calix [4] crown-6 and bis [(trifluoromethyl)sulfonyl] imide, *Inorg. Chim. Acta* 390 (2012) 8–11.
- [20] H.F. Li, B. Zheng, K.W. Huang, A new class of PN^3 -pincer ligands for metal-ligand cooperative catalysis, *Coord. Chem. Rev.* 293–294 (2015) 116–138.
- [21] F.S. Chen, G. Chen, T. Liu, et al., Controllable fabrication and optical properties of uniform gadolinium oxysulfate hollow spheres, *Sci. Rep.* 5 (2015) 17934.
- [22] J.H. Xue, X.H. Hua, L.M. Yang, et al., Synthesis, crystal structures and luminescence properties of europium and terbium picolinamide complexes, *Chin. Chem. Lett.* 25 (2014) 887–891.
- [23] W.J. Sun, Y.X. Wu, H.G. Zhang, L. Zhu, S.L. Gao, Spectra of rare earth complexes with salicylate, *Acta Photonica Sin.* 35 (2006) 1593–1596.