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SYNTHESIS AND CHARACTERIZATION OF COMPLEXES OF LANTHANIDE NITRATES WITH *N,N'*-DINAPHTHYL-*N,N'*-DIPHENYL-3,6-DIOXAOCTANEDIAMIDE

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Abstract—Solid complexes of lighter lanthanide nitrates with *N,N'*-dinaphthyl-*N,N'*-diphenyl-3,6-dioxaoctanediamide (DDD), $Ln(NO_3)_3(DDD)$ (Ln = La–Nd, Sm) have been prepared in non-aqueous media. These complexes have been characterized by elemental analysis, conductivity measurements, IR spectra, electronic spectra and TG–DTA techniques. In all the complexes, DDD and NO_3^- are coordinated to the lanthanide ions as tetradentate and bidentate ligands, respectively. The differences in the IR and electronic spectra between these complexes and lanthanide nitrate complexes with *N,N,N',N'*-tetraphenyl-3,6-dioxaoctanediamide (TDD) are discussed.

Non-cyclic polyethers offer many advantages over the use of crown ethers in the extraction and analysis of lanthanide ions.[1–4] Ding *et al.*[1] have reported the extraction of lighter lanthanide ions in picric acid solution with five derivatives of glycol-*O,O'*-diacetamide, among which *N,N,N',N'*-tetraphenyl-3,6-dioxaoctanediamide (TDD) has the largest separation factor, and both the factor and distribution ratio of lighter lanthanide ions for TDD are larger than those for dicyclohexyl-18-crown-6-ether.[2] In order to further research the mechanism of the extraction and to investigate the relation between structure and properties, we report the synthesis and characterization of *N,N'*-dinaphthyl-*N,N'*-diphenyl-3,6-dioxaoctanediamide (DDD) and its complexes of lighter lanthanide nitrates.

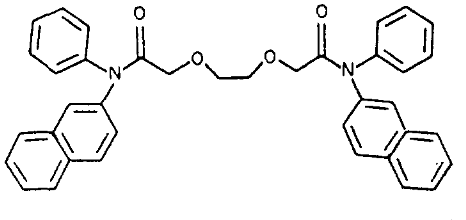
EXPERIMENTAL

Reagents

All solvents used were purified by standard methods. The hydrated lanthanide nitrates were obtained by dissolving the corresponding oxides (99.95%) in 30% nitric acid. 3,6-Dioxaoctanedioic acid and 3,6-dioxaoctanedionyl chloride were prepared according to the literature method.[5]

Chemical and physical measurements

The metal ion was determined by EDTA titration using Xylenol Orange as an indicator. Carbon, nitrogen and hydrogen were determined using a



N,N'–dinaphthyl–*N,N'*–diphenyl–3,6–dioxaoctanediamide (DDD)

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Carlo Erba 1106 elemental analyser. The IR spectra were recorded on a Nicolet 170 SX FT-IR instrument using KBr discs in the 220–4000 cm^{-1} region. Thermal analyses (TG and DTA) were performed on a Beijing PCD-2 thermobalance using about 10 mg powder sample and working at a heating rate of 5°C min^{-1} in static air. Conductivity measurements were carried out with a DDS-11A type conductivity bridge using 10^{-3}mol dm^{-3} solutions in methanol at 25°C. ^1H NMR spectra were measured on an FT-80A spectrometer in $CDCl_3$ solution, with TMS as internal standard. Electronic spectra were recorded with a Model UV-240 spectrophotometer in methanol solutions.

Preparation of DDD

A solution of 30 mmol 3,6-dioxaoctanedionyl chloride in 30 cm^3 of anhydrous benzene was added dropwise to a solution of 60 mmol phenyl-β-naphthylamine and 60 mmol pyridine in 70 cm^3 anhydrous benzene. The mixture was stirred at room temperature for 3 h. The precipitated solid was refluxed in distilled water for 1 h, then filtered, washed with benzene and dried *in vacuo* over P_4O_{10} for 48 h. The yield was 80%. The purity of the product was confirmed by elemental analysis and its ^1H NMR spectrum, and the compound is soluble in chloroform, acetone, acetonitrile, etc. Found: C, 78.2; H, 5.6; N, 4.9. Calc. for $C_{38}H_{32}N_2O_4$: C, 78.6; H, 5.6; N, 4.8%. ^1H NMR ($CDCl_3$, 25°C, ppm): δ 7.3 (m, naphthyl), 7.8 (m, —C_6H_5), 4.1 (s, —$COCH_2$—), 3.7 (s, —C_2H_4).

Preparation of the complexes

A solution of 0.203 mmol lanthanide nitrate in 10 cm^3 anhydrous ethanol was added dropwise to a solution of 0.200 mmol DDD in 10 cm^3 anhydrous ethanol. The mixture was stirred at room temperature for 4 h and then the solvent was partially evaporated. The products were isolated by filtration, washed with 2:1 (v/v) anhydrous ethanol–ether and dried *in vacuo* over P_4O_{10} for 48 h. All the complexes are powders and stable in air.

RESULTS AND DISCUSSION

Analytical data for the complexes, presented in Table 1, conform to $Ln(NO_3)_3(DDD)$ (where Ln = La–Nd, Sm). In their preparations, yields decrease with increasing atomic number similar to that for TDD, which has been successfully applied to the extraction of lanthanide ions.[6]

All complexes are soluble in chloroform, ethanol and methanol, slightly soluble in acetonitrile and acetone, and sparingly soluble in benzene, ether and cyclohexane. The molar conductance values of the complexes in methanol (Table 1) indicate that all complexes act as non-electrolytes,[7] implying that all the nitrate groups are in a coordination sphere.

IR spectra

The IR spectra of the complexes are very similar. Table 2 gives the characteristic bands of DDD and its lanthanum complex. The IR spectrum of the free DDD shows bands at 1683 and 1133 cm^{-1} which may be assigned to $\nu(C{=}O)$ and $\nu_{as}(C{-}O{-}C)$, respectively. In the complexes, these bands are shifted by 61–64 and 46–49 cm^{-1}, respectively, toward lower wavenumbers, thus indicating that all the ether oxygen atoms and the C=O groups take part in coordination to the metal ions. DDD therefore acts as a quadridentate ligand, forming a ring-like structure similar to that in (triethyleneglycol)trinitrolanthanide.[8,9] The larger shift for $\nu(C{=}O)$ in the spectra of the complexes suggests that the Ln—O(carbonyl) bond is stronger than the Ln—O(ether) one. Compared with TDD complexes of lanthanide nitrates, the DDD complexes show larger shifts for $\nu(C{=}O)$ and $\nu(C{-}O{-}C)$.[6] This indicates that the metal–ligand bond for DDD is stronger than that for TDD.

The absorption bands assigned to the coordinated nitrates were observed at about 1492, 1300 and 697 cm^{-1} for the complexes. There was no absorption band assigned to free nitrates at *ca* 1380 cm^{-1} in the spectra of the complexes. The IR spectral evidence above suggests that the three nitrate groups are all coordinated to the metal ions. In addition, the separation of the two highest-frequency bands is *ca* 200 cm^{-1}; thus, the NO_3^- ions in the complexes are bidentate ligands.[10]

Thermal analyses

The TG and DTA curves for DDD show that the compound has no melting point and decomposes from 360 to 670°C, producing two exothermic peaks at 374 and 615°C. All these complexes show similar patterns of decomposition, as shown in Table 3. They are stable up to *ca* 225°C and then decompose in the temperature range 225–870°C, producing three exothermic peaks. The residual weights were approximately consistent with the values required for the metal oxides.

Electronic spectra

Table 4 shows UV spectral data for DDD and complexes. The spectrum of DDD exhibits three

Table 1. Yield, elemental analysis and molar conductance data

Complex	Yield (%)	C (%) Found	C (%) (Calc.)	H (%) Found	H (%) (Calc.)	N (%) Found	N (%) (Calc.)	Ln (%) Found	Ln (%) (Calc.)	Λ_m (S cm^2 mol^{-1})
$La(NO_3)_3(DDD)$	88	50.9	(50.4)	3.7	(3.6)	7.4	(7.7)	15.2	(15.3)	65.6
$Ce(NO_3)_3(DDD)$	83	50.3	(50.3)	3.4	(3.6)	7.6	(7.7)	15.4	(15.4)	66.4
$Pr(NO_3)_3(DDD)$	82	50.7	(50.3)	3.6	(3.6)	7.3	(7.7)	15.6	(15.5)	59.3
$Nd(NO_3)_3(DDD)$	80	50.1	(50.1)	3.4	(3.5)	7.2	(7.7)	15.6	(15.8)	77.1
$Sm(NO_3)_3(DDD)$	74	49.8	(49.8)	3.5	(3.5)	7.3	(7.6)	16.3	(16.4)	52.3

Table 2. The relevant characteristic IR bands (cm^{-1})

Compound	ν(C═O)	ν(C—O—C)	$\nu_1(NO_3^-)$	$\nu_4(NO_3^-)$	$\nu_5(NO_3^-)$	$\nu_1-\nu_4$
DDD	1683s	1133m				
$La(NO_3)_3(DDD)$	1622s	1087m	1492s	1310w	696w	182

Table 3. Thermal analytical data

Complex	Exothermic process				
	DTA peak (°C)			Residue (%) Found	Residue (%) Calc.[a]
$La(NO_3)_3(DDD)$	326		440	18.6	18.0
$Ce(NO_3)_3(DDD)$	225	255	416	19.1	19.0
$Pr(NO_3)_3(DDD)$	294	460	533	19.2	18.8
$Nd(NO_3)_3(DDD)$	296	454	535	18.8	18.5
$Sm(NO_3)_3(DDD)$	294	459	539	19.4	19.0

[a] Calculated value for the residue of Ln_2O_3 (Pr_6O_{11} for the praseodymium complex; CeO_2 for the cerium complex).

Table 4. UV spectral data

Compound	^1B absorption band		K absorption band		B absorption band	
	λ (nm)	$\varepsilon_{max} \times 10^{-4}$	λ (nm)	$\varepsilon_{max} \times 10^{-4}$	λ (nm)	$\varepsilon_{max} \times 10^{-4}$
DDD	224.9	7.89	242.5	5.65	280.7	1.29
$La(NO_3)_3(DDD)$	222.4	9.01	239.6	5.73	277.0	1.35
$Ce(NO_3)_3(DDD)$	222.0	9.60	240.3	6.09	279.1	1.53
$Pr(NO_3)_3(DDD)$	221.0	8.13	240.3	4.09	279.2	1.08
$Nd(NO_3)_3(DDD)$	222.0	10.63	239.8	7.02	277.8	1.55
$Sm(NO_3)_3(DDD)$	220.0	7.97	239.6	4.80	277.2	1.17

absorption bands at 224.9, 242.5 and 280.7 nm, assigned to ^1B, K and B absorption bands of the naphthalene ring, respectively.[11] Upon coordination, all absorption bands move to lower wavenumbers, suggesting that the coordination of oxygen atoms of DDD to metal ions causes the conjugated system formed by the naphthalene ring, carbonyl and lone electron pair on the nitrogen

Table 5. Electronic spectral data and covalent parameters

Complex	Frequency (cm^{-1})	Assignment	Covalent parameter
$Pr(NO_3)_3(DDD)$	16,835	$^3H_4$–$^1D_2$	$\beta = 0.9951$
	20,712	–$^3P_1$	$\delta = 0.492$
	21,186	–$^1I_6$	$b^{1/2} = 0.0492$
	22,522	–$^3P_2$	
$Nd(NO_3)_3(DDD)$	17,182	$^4I_{9/2}$–$^4G_{5/2}$, $^2G_{7/2}$	$\beta = 0.9887$
	19,084	–$^4G_{9/2}$	$\delta = 1.143$
	19,562	–$^2G_{9/2}$	$b^{1/2} = 0.0752$
	22,482	–$^4G_{11/2}$	

atom to be weakened. The characteristic absorption bands of the benzene ring were concealed by those of the naphthalene ring.

The electronic spectra in the visible region of the Pr^{III} and Nd^{III} complexes exhibit alternations in intensity and shifts in position of the absorption bands relative to the corresponding Ln^{III} aquo ions. The shift has been attributed by Jørgensen to the effect of crystal fields upon inter-electronic repulsion between the 4*f* electrons and is related to covalence in the metal–ligand bond, assessed by Sinha's parameter (δ), the nephelauxetic ratio (β) and the bonding parameter ($b^{1/2}$).[12–14] The relative energy and *J* level assignments are given in Table 5; the values of covalent parameters are also presented.

The values of β, which are less than unity, and positive values of δ and $b^{1/2}$ support the existence of partial covalent bonding between metal and ligand.[15] The comparatively small magnitude of $b^{1/2}$ values also shows the involvement of the 4*f* orbital metal–ligand bond to be very small.[16] Moreover, the magnitudes of the covalency and bonding parameters increase from Pr^{III} to Nd^{III}, indicating that the extent of covalent character of the metal–ligand bond increases with increase in atomic number (in agreement with the lanthanide contraction).

In comparison with the corresponding TDD complexes,[6] β is smaller and $b^{1/2}$ is larger in the title complexes, suggesting that the covalency in the metal–ligand bond for DDD is stronger than that for TDD.

In conclusion, the open-chain analogue of crown ethers, DDD, can react with lanthanide nitrates in non-aqueous medium to form stable solid complexes, which may be formulated as $Ln(NO_3)_3(DDD)$ (Ln = La–Nd, Sm). DDD acts as a tetradentate ligand, forming a ring-like structure. In addition, some of the necessary complexation features are present in our studies: DDD has larger steric hindrance than TDD, so it may show higher complexation selectivity;[17,18] the differences in the IR and electronic spectra between these complexes and lanthanide nitrate complexes with TDD indicate that the metal–ligand bond and covalency for DDD is stronger than that for TDD; DDD is soluble in many organic solvents, similar to TDD, with excellent extraction properties. Thus, DDD may be a more promising reagent for the extraction and analysis (ion-selective electrodes) of the rare earths than TDD.

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