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Bis(pentamethylene)urea complexes of the lanthanide nitrates: synthesis, characterization, properties

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Abstract

Lanthanide nitrate complexes of bis(pentamethylene)urea (BPMU) with general formula $Ln(NO_3)_3 3BPMU$, where Ln: La, Nd, Sm, Eu, Ho and Er have been prepared and characterized based on CHN elemental analyses, lanthanide titration with EDTA, molar conductivity, spectroscopic data and thermal studies. The infrared spectra show that ligands (BPMU) are bonded through the carbonyl oxygen, nitrate counter-ions are bidentate linked to the central ions.

The structure of the neodymium complex was determined. The crystal is monoclinic, $P2_{1/c}, Z = 4$, with the following parameters: $a = 10.148(1)$ Å, $b = 21.879(2)$, $c = 19.154(2)$ Å, $\beta = 104.11(1)^\circ$, $V = 4124.3(7)$ Å^3. The polyhedron is a distorted tricapped trigonal prism, coordination number nine.

Keywords: Lanthanide; Bis(pentamethylene)urea; Nitrates

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1. Introduction

The coordination chemistry of the lanthanides has become of great importance over the last few decades for its use in several applications. Lanthanide nitrate complexes have been described in literature [1–4]. The interest in nitrates comes from the fact that they may act as bidentate ligands. Compounds with bis(pentamethylene)urea with formula $Ln(TFMS)_3 \cdot 5BPMU \cdot 2H_2O$ ($TFMS = CF_3SO_3^-$, Ln = La, Ce, Nd, Sm, Eu, Gd, Ho and Yb) [5]; $Eu(HBpz_3)_2 \cdot BPMU$ ($HBpz_3$ = hydrotris (pyrazol-1-yl)borate [6] were synthesized and studied. BPMU is used as dietary complement to increase the digestibility of nutrients [7].

In this article the complexes formed by reactions of hydrated lanthanide nitrate and BPMU with composition $Ln(NO_3)_3 \cdot 3BPMU$ (Ln = La, Nd, Sm, Eu, Ho and Er) are described.

The addition compounds were characterized by CHN elemental analyses. Determination of Ln by complexometric titration with EDTA and absorption spectroscopy in the infrared region. X-ray single-crystal diffraction studies thermal study, conductance measurements, absorption spectroscopy in the visible region for the Nd compound and emission spectroscopy for the Eu compound were also performed.

2. Experimental

The complexes were prepared by the reaction of hydrated lanthanide nitrates with BPMU in absolute ethanol (molar ratio 1:3), and dried in vacuo over P_2O_5.

Carbon, hydrogen and nitrogen contents were determined using a CHN Perkin-Elmer model 240 instrument. EDTA titrations were performed using an acetate—acetic acid buffer (pH 5.8) with a pyridine drop and ortho-xylenol orange as indicator [8].

Conductance measurements of millimolar solutions in ethanol and acetronitrile were realized in a QUIMIS-450 instrument with a cell constant ($K_c = 0.101\,\mathrm{cm}^{-1}$).

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IR spectra were performed on a FTIR BOMEM spectrometer, using KBr pellets. Emission spectra of the europium compound was recorded on a Hitachi–Perkin Elmer MPF-4 spectrofluorimeter using 394 nm excitation radiation at room temperature and at 77 K.

The absorption spectrum of the neodymium compound was registered on a Zeiss DMR-10 spectrophotometer, using a silicon mull in a 0.5 mm cell.

Thermogravimetric curves were obtained on a SHIMADZU 50-H instrument at a heating rate 10°C min^{-1} in nitrogen (50 cm^3 min^{-1}flow).

DSC curves were determined on a SHIMADZU 50 thermobalance in nitrogen atmosphere (50 mm min^{-1}) with 10°C min^{-1} heating rate.

3. Crystal structure determination

Data were collected on a CAD-4 Mach 3 Enraf-Nonius diffractometer, in the $\omega/2\theta$ scan mode with scan width $\omega = 0.80 + 0.35\tan\theta$, using graphite monochromated Mo$K\alpha$ radiation. Data were corrected for Lorentz, polarization and absorption effects. The structure was solved by the standard Patterson heavy-atom method followed by normal difference Fourier techniques. H-atoms were located on stereochemical grounds, except those that could be localized of the water molecules, and refined with fixed geometry each riding on a carrier atom with an isotropic displacement parameter amounting to 1.2 times the value of the equivalent isotropic displacement parameter of the atoms to which they are attached. A summary of crystallographic parameters is presented in Table 3. Fig. 3 shows the coordination polyhedron and Fig. 4 a ZORTEP view of the complex. The programs used were SHELXS-86 [9], SHELXL-97 [10] and ZORTEP [11].

4. Results and discussion

The analytical results (Table 1) are in agreement with the composition $Ln(NO_3)_3 \cdot 3$BPMU (Ln = La, Nd, Sm, Eu, Ho and Er). BPMU = bis (pentamethylene)urea.

The strong carbonyl absorption peak of the ligand is located at 1643 cm^{-1}. Table 2 shows that it moves to the 1561–1597 cm^{-1} region in the complexes. This indicates that the ligand is coordinated to the lanthanide ions through the carbonyl oxygen atoms. The characteristic frequencies of the coordinated nitrates are shown in Table 2. The magnitude of $v_4 - v_1$ of the nitrate group is nearly 200 cm^{-1}, indicating that the nitrate groups are coordinated to the metal ions as a bidentate ligands [12]. The IR spectra of all these complexes are similar.

Conductance data in acetonitrile were compared with that presented by Geary [13] and indicate a non-electrolyte behavior (Tables 1–4).

Table 1
Summary of analytical results (%)

Ln	Titration		C		H		N	
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.
La	15.2	15.7	43.4	43.0	6.6	6.6	13.7	13.7
Nd	15.7	15.4	43.1	42.8	6.6	6.4	13.7	13.9
Sm	16.3	16.6	42.8	42.7	6.5	6.5	13.6	13.8
Eu	16.4	16.7	42.8	43.0	6.5	6.0	13.6	13.7
Ho	17.6	17.9	41.8	42.2	6.4	6.2	13.4	13.4
Er	17.6	17.9	42.1	42.2	6.4	6.4	13.4	13.4

Table 2
IR spectra (cm^{-1}) for the complexes

Ln	v_{CO}	v_1	v_2	v_3	v_4	v_6
La	1587	1288	1028	739	1508	816
Nd	1590	1297	1029	741	1509	818
Sm	1592	1299	1030	740	1507	816
Eu	1596	1299	1028	722	1509	816
Ho	1597	1304	1033	747	1507	814
Er	1591	1306	1030	747	1507	814

Table 3
Crystal data and structure refinement

Empirical formula	C39 H60 N3 Nd O12
Formula weight	907.14
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_{1/c}$
Unit cell dimensions	$a = 10.1475(10)$ Å $b = 21.879(2)$ Å $c = 19.154(2)$ Å $\beta = 104.105(10)$ o
Volume	4124.3(7) Å^3
Z, Calculated density	4.1.461 mg/m^3
Absorption coefficient	1.322 mm^{-1}
$F(000)$	1884
Crystal size	$0.40 \times 0.40 \times 0.15$ mm
?range for data collection	1.44 to 25.0 o
Limiting indices	$-11 \leqslant h \leqslant 12$, $-25 \leqslant k \leqslant 0$, $-22 \leqslant l \leqslant 0$
Reflections collected /unique	7459/7229 [R_{int}= 0.0269]
Refinement method	Full-matrix least-squares on $F2$
Data/restraints/parameters	7229/0/496
Goodness-of-fit on $F2$	0.964
Final R indices [$I > 2(I)$]	$R_1 = 0.0573$, w$R_2 = 0.1426$
R indices (all data)	$R_1 = 0.0992$, w$R_2 = 0.1733$
Largest diff. Peak and hole	0.743 and -0.840 e Å^{-3}

From the neodymium absorbtion spectrum the nephelauxetic parameter ($\beta = 0.991$) [14], covalency factor ($b_{1/2} = 0.063$) [15] and Sinha's ($\delta = 0.81$) [16] were calculated from the curve baricenter showing essentially elecstrostatic metal–ligand interactions (Fig. 1).

Table 4
Bond lengths (Å) and angles (deg.)

Nd–O(1)	2.384(6)
Nd–O(2)	2.390(5)
Nd–O(3)	2.393(6)
Nd–O(31)	2.529(6)
Nd–O(21)	2.539(7)
Nd–O(12)	2.543(5)
Nd–O(32)	2.551(7)
Nd–O(11)	2.568(6)
Nd–O(22)	2.574(7)
O(1)–Nd–O(2)	86.2(2)
O(1)–Nd–O(3)	87.2(2)
O(2)–Nd–O(3)	85.2(2)
O(1)–Nd–O(31)	120.0(2)
O(2)–Nd–O(31)	87.1(2)
O(3)–Nd–O(31)	151.2(2)
O(1)–Nd–O(21)	150.0(2)
O(2)–Nd–O(21)	121.3(2)
O(3)–Nd–O(21)	83.6(2)
O(31)–Nd–O(21)	76.8(2)
O(1)–Nd–O(12)	89.8(2)
O(2)–Nd–O(12)	151.1(2)
O(3)–Nd–O(12)	123.2(2)
O(31)–Nd–O(12)	70.3(2)
O(21)–Nd–O(12)	71.9(2)
O(1)–Nd–O(32)	70.1(2)
O(2)–Nd–O(32)	81.2(2)
O(3)–Nd–O(32)	154.1(2)
O(31)–Nd–O(32)	49.9(2)
O(21)–Nd–O(32)	122.2(2)
O(12)–Nd–O(32)	70.6(2)
O(1)–Nd–O(11)	79.5(2)
O(2)–Nd–O(11)	155.4(2)
O(3)–Nd–O(11)	74.4(2)
O(31)–Nd–O(11)	117.3(2)
O(21)–Nd–O(11)	70.6(2)
O(12)–Nd–O(11)	49.42(19)
O(32)–Nd–O(11)	111.8(2)
O(1)–Nd–O(22)	154.8(2)
O(2)–Nd–O(22)	71.6(3)
O(3)–Nd–O(22)	79.4(2)
O(31)–Nd–O(22)	71.8(2)
O(21)–Nd–O(22)	49.7(2)
O(12)–Nd–O(22)	115.4(2)
O(32)–Nd–O(22)	116.3(2)
O(11)–Nd–O(22)	116.6(2)

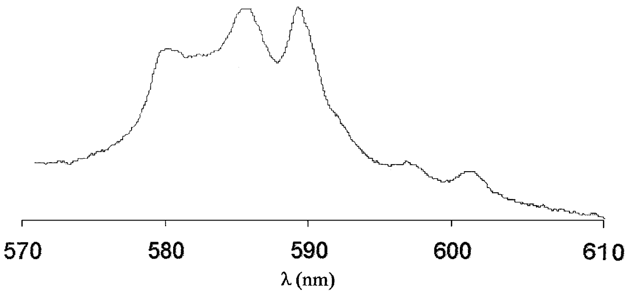

Fig. 1. Absorption spectrum of the neodymium compound.

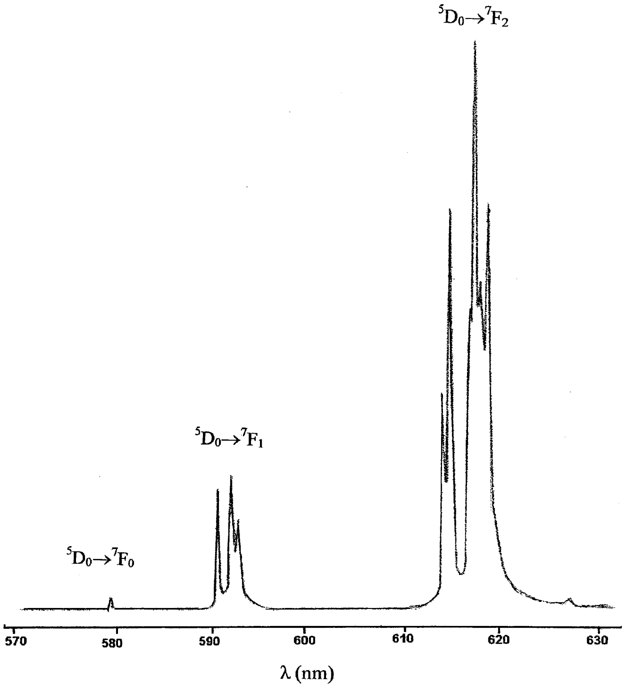

Fig. 2. Emission spectrum of the europium compound at 77 K.

The Eu^{3+} emission spectra at room temperature and at 77 K are similar; the low temperature one is well resolved and presents a very weak $^5D_0 \rightarrow {}^7F_0$ band, three peaks due to $^5D_0 \rightarrow {}^7F_1$ (two peaks very close due to E levels and one due to A_1 level). The $^5D_0 \rightarrow {}^7F_2$ transition also presents four peaks (one due to an A level and three due to E levels (Fig. 2). The spectrum was interpreted in terms of a distorted C_{3v} symmetry [17].

Thermogravimetric curves were recorded to evaluate the thermal stability of the compounds. The first step indicates decomposition of BPMU, occurring between ~220°C and 350°C. After this temperature decomposition of nitrates occurs, leaving oxides as residues. DSC curves, obtained under the same conditions as TG show clearly one endothermic peak between 188 and 221, indicative of melting. After such events, exothermic peaks were observed due to decomposition of BPMU.

The Nd achieves a coordination number of nine by the bonding or three nitrate ligands attached in a bidentate fashion and three oxygens of the BMPU groups, in a distorted trigonal prism fashion (point symmetry C_{3v}). One base of the prism is formed by three oxygens of the BPMU moieties while all the nitrate groups contribute with one oxygen to the other base and the other is in the capping position. The dihedral angle between the bases being of 3.3(3)°.

Several geometric parameters to quantify the deformation of the coordination polyhedron, introduced by Balic Zunic and Makovicky [18] and implemented in IVTON [19], are given. These parameters are calculated in relation to the 'centroid of the coordination polyhedron', which is the point in the coordination polyhedron for which the variance of squares of distances to ligands is minimum. These are: the central

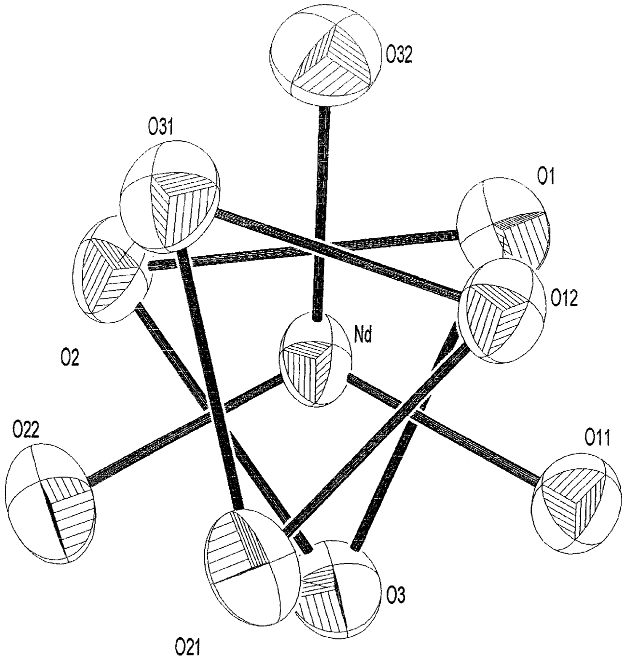

Fig. 3. Coordination polyhedron around the Nd^{3+} ion.

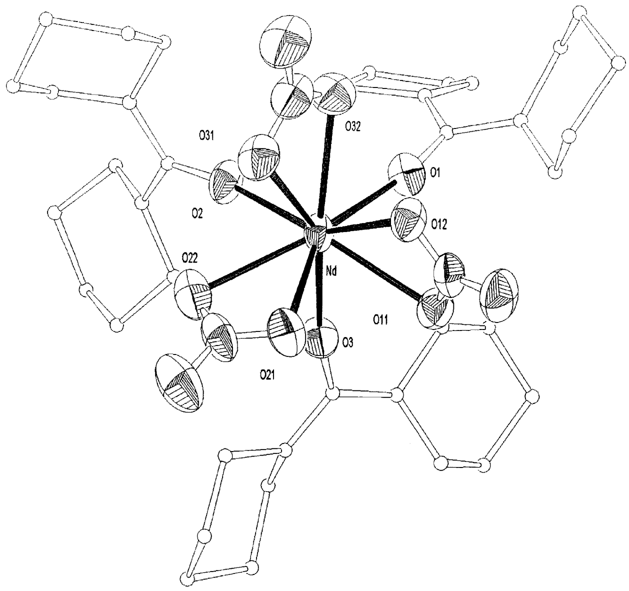

Fig. 4. ZORTEP view of $Nd(NO_3)_3 \cdot 3BPMU$. For a sake of clarity only the Nd and the oxygen and nitrogen atoms are shown as 50% probability ellipsoids, all other are at an arbitrary scale.

atom-centroid distance (Δ) is 0.120 Å, the average distance from the centroid to the ligands (r) is 2.49 Å, and the 'sphericity' ($1 - \sigma_r/r$) is 0.983 (σ_r is the standard deviation of the distances from the centroid to the ligands) (Figs. 3 and 4).

The complexes are linked through two C–H···O interactions:

$C26{-}H26\cdots O13^{i}$[$O\cdots H = 2.72$ Å, $C{-}H\cdots O = 127.4°$; $i = -x, -0.5 + y, 0.5 + z$] and $C212\text{-}H21B\cdots O33^{ii}$ [$O\cdots H = 2.67$ Å, $C{-}H\cdots O = 154.5°$; $ii = x, 0.5 - y, -0.5 + z$].

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