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SYNTHESIS, PROPERTIES AND STRUCTURE OF SOME LANTHANIDE NITRATE BINUCLEAR COMPLEX WITH N,N,N′,N′-TETRABUTYLADIPAMIDE $[Ln_2\mu\text{-}\{Bu_2NCO(CH_2)_4CONBu_2\}\{Bu_2NCO(CH_2)_4CONBu_2\}_2(NO_3)_6]$

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Abstract—Some lanthanide nitrate complexes with N,N,N′,N′-tetrabutyladipamide (TBAA) have been prepared. These complexes with the general formula $[Ln_2\mu$-(TBAA)(TBAA)$_2(NO_3)_6]$ have been characterized by means of elemental analysis, IR spectra and conductance measurement. The crystal and molecular structure of $[Gd_2\mu$-(TBAA)(TBAA)$_2(NO_3)_6]$ has been determined by single-crystal X-ray diffraction. This complex contains a binuclear molecule with three organic ligands. Two carbonyls of one organic ligand join two Gd(III) and each Gd(III) is coordinated through two carbonyls of one organic ligand. The six nitrates are all bidentate. Each Gd(III) is coordinated by nine oxygen atoms which form a distorted tricapped trigonal prism.

It has been reported that N,N′-dialkylamides are effective agents for the extraction and separation of lanthanides.[1] We have recently found that TBAA ligands are even more effective for this purpose. The crystal structure of the uranyl nitrate complex with TBAA has also been reported, but the crystal structures of lanthanide complexes have seldom been reported in which the binuclear molecules are coordinated with bidentate organic ligands. The synthesis, characterization and structure of the title complexes are important in investigating the extraction mechanism of the corresponding extractant and also the structure chemistry of the lanthanides.

EXPERIMENTAL

Reagents

Hydrated lanthanide nitrates were prepared by dissolving Ln_2O_3(AnalaR) in 1 : 1 nitric acid. TBAA was prepared by the method of ref. 3. All other chemicals were analytical reagent grade.

Chemical and physical measurements

Carbon, nitrogen and hydrogen contents were determined using an MOD-1106 element analyser. The IR spectra were recorded in the 4000–400 cm^{-1} region using KBr pellets and a Nicolet Co. Magna-IR 550 spetrometer. The crystal data were collected on a R3M/E diffractometer.

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Preparation of the complexes

To a 25 cm^3 round-bottomed flask, 2 mmol Ln $(NO_3)_3 \cdot 6H_2O$, 3 cm^3 ethyl-orthoformate and 1 cm^3 absolute alcohol were charged. The mixture was refluxed at 78°C for about 4 h, then 0.56 g organic ligand TBAA was added and refluxed for about 1 h. The solution was distilled *in vacuo* until it became sticky and then toluene was added, the mixture was filtered, cooled and recrystallized and particulate solids, with the characteristic colour of the corresponding lanthanide nitrates, were obtained.

All the complexes are sparingly soluble in petroleum benzene, slightly soluble in toluene and dichloromethane and soluble in ethanol and acetone. Single crystals of the gadolinium complex were obtained by dissolving the solid complex in toluene and maintaining the solution in the air at room temperature. After a week the colourless crystals of the complex were deposited.

Crystal structure analysis

X-Ray diffraction intensities were collected on an R3M/E diffractometer with graphite-monochromated Mo K_α radiation, using the $\theta/2\theta$ scan technique. The intensities were corrected for Lorentz polarization effects but not for absorption.

The atomic coordinates of metal atoms were first obtained by analysing the Patterson function, all the other non-hydrogen atom coordinates were gradually obtained by Fourier synthesis. Finally, the coordinates and the anisotropic thermal parameters for non-hydrogen atoms were refined by block diagonal matrix least-squares methods.

All calculations were performed using the SHELXTL system of computer programs. Crystal data for Gd(III) complex are given in Table 1.

Table 1. Crystal data

Formula	$C_{86}H_{132}N_{12}O_{24}Gd_2$
Molecular weight	1792.33
Crystal dimensions (mm)	0.40 × 0.40 × 0.40
System	Triclinic
Space group	$P\bar{1}$
Temperature (°C)	16 ± 1.5
Lattice parameters	
a (Å)	10.137(2)
b (Å)	11.226(2)
c (Å)	19.588(4)
α (°)	90.81(2)
β (°)	91.01(2)
γ (°)	92.48(2)
Cell volume (Å^3)	2226.3(8)
Molecules/unit cell	1
D_c (g cm^{-3})	1.34
μ (cm^{-1})	15.89
Radiation graphite monochromator	Mo K_α (λ 0.71073 Å)
$F(000)$	932
Scan type and rate (deg min^{-1})	$\theta/2\theta$,8
Collection range	$2° \leqslant 2\theta \leqslant 46°$
Unique data measured	6660
Observable data with $I \geqslant 3\sigma(I)$	5655
No. of variables	469
G_{oof} (or s)	1.265
R_w	0.0359
R	0.0385

RESULTS AND DISCUSSION

The composition of the complexes

The data of elemental analysis and molar conductance of the complexes, listed in Table 2, indicate that all the complexes conform to a 2:3 metal ion-to-organic ligand stoichiometry and are practically non-electrolytes in nitrobenzene according to Geary.[4]

IR spectra

The strong carbonyl absorption peak of the ligand is located at 1641 cm^{-1}; after forming the complexes, it moves into the 1583–1594 cm^{-1} region, with a shoulder in the 1597–1621 cm^{-1} region. This indicates that the ligand is coordinated to the lanthanide(III) ion through the oxygen atoms of carbonyls.

The characteristic frequencies of coordinating nitrate groups appear in the 1489–1502 (ν_1), 1289–1304 (ν_4), 1020–1033 (ν_2), 815–819 (ν_6), 738–747 (ν_3), 710–716 (ν_5) cm^{-1} regions in the IR spectra of the complexes, the difference between the two strongest absorptions (ν_1 and ν_4) of nitrate groups is *ca* 200 cm^{-1}, indicating that the nitrate groups in the complexes coordinate to the metal ions as a bidentate ligand.[5] The absence of the absorptions around 1360 cm^{-1} indicates that all the nitrate groups in the complexes coordinate to the lanthanide ions.

Crystal and molecule structure of Gd(III) complex

Figure 1 shows the molecular structure of complex, and Fig. 2 illustrates the molecular packing arrangement in the unit cell.

The X-ray structure analysis shows that the complex consists of binuclear molecules with three organic ligand molecules, in which two carbonyls of one organic ligand join two Gd(III), in addition

Table 2. The data of element analysis and molar conductance of complexes

Complex $Ln_2(TBAA)_3(NO_3)_6$	Element analysis % C Found (Calc.)	H Found (Calc.)	N Found (Calc.)	Molar conductance S cm^2 mol^{-1} (nitrobenzene)
La	45.2 (45.2)	7.8 (7.5)	9.7 (9.6)	3.52
Nd	44.9 (44.9)	7.3 (7.5)	9.9 (9.5)	5.19
Sm	44.4 (44.6)	7.2 (7.4)	9.4 (9.5)	6.67
Eu	44.0 (44.5)	7.5 (7.5)	9.6 (9.4)	4.44
Gd	44.2 (44.2)	7.7 (7.4)	9.4 (9.4)	8.04
Tb	44.4 (44.1)	7.2 (7.4)	9.6 (9.4)	9.62
Dy	44.2 (4.0)	7.4 (7.3)	9.4 (9.3)	10.19
Tm	43.8 (43.7)	7.4 (7.3)	9.2 (9.3)	9.38
Lu	43.3 (43.4)	7.2 (7.2)	9.1 (9.2)	9.29

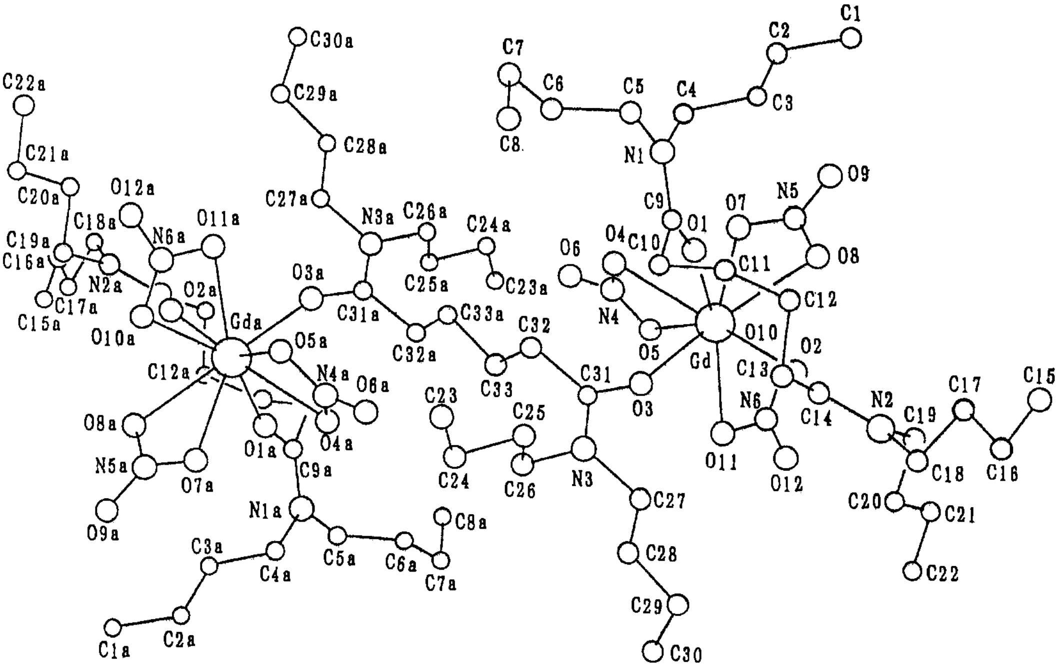

Fig. 1. Molecular structure of complex.

each Gd(III) is coordinated through two carbonyls of one organic ligand. The six nitrates are all bidentate ligands. The coordination number of each Gd(III) is nine.

This complex molecule has a centre of symmetry. The coordination around the Gd is equivalent to that around Gd(a). The coordination geometry around each Gd can be best described as a distorted tricapped trigonal prism (Fig. 3).

Figure 3 shows that the three oxygen atoms

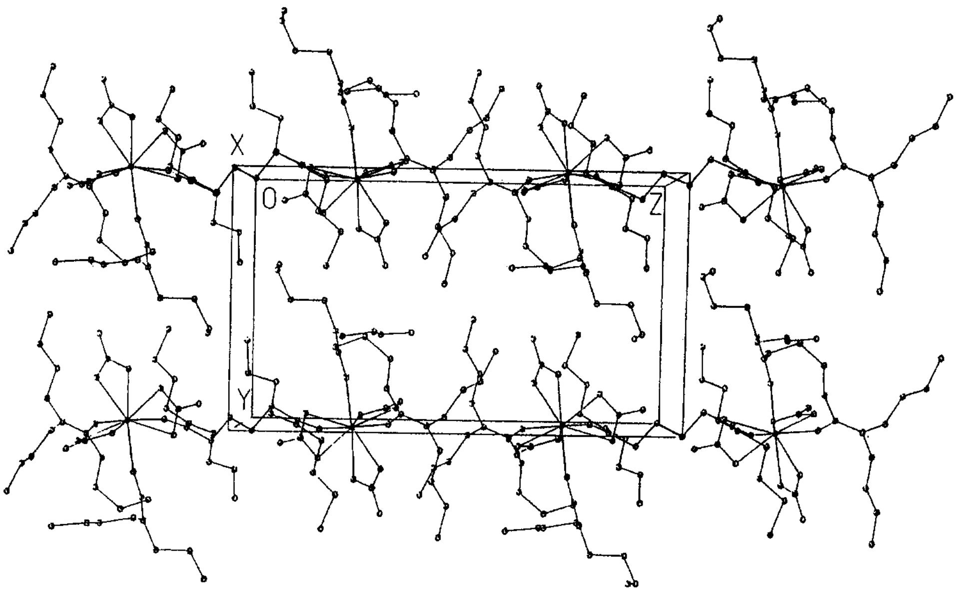

Fig. 2. Molecular packing arrangement in the unit cell.

[O(5), O(7), O(10)] of the nitrate ligands form one triangular face while the organic ligand oxygen atoms [O(1), O(2), O(3)] form another triangular face. The latter triangle is a little larger than the former and both are nearly parallel. In addition the capping atoms [O(4), O(8), O(11)] are nitrate oxygen atoms. The distances from the tops of the caps to the corners of the trigonal prism are not equivalent. For example, the interatomic distances O(4)—O(1), O(4)—O(3), O(4)—O(5) and O(4)—O(7) are 2.8856, 3.1129, 2.1470 and 2.8294 Å respectively. This indicates that the coordinating polyhedron of the tricapped trigonal prism is significantly distorted. Table 3 shows the dimensions of the polyhedron around the Gd atom.

The distances between the Gd(III) ions and the oxygen atoms lie in the ranges: Gd—O (carbonyl), 2.305(3)–2.329 (3) Å (av. 2.321); Gd—O(nitrate), 2.447(4)–2.530(4) Å (av. 2.487 Å). Similar differences in the coordinating distances were also found in La(DMSO)$_4$(NO$_3$)$_3$.[6]

The nitrate ion is nearer. After coordination the O—N—O angle for the O atoms bonded to the Gd atom is reduced from 120° to 112–117°, and these N—O bonds are elongated relative to the N—O bond to each terminal O atom. These facts are also found in other complexes containing bidentate nitrate groups.[7]

Figure 4 shows the structure around Gd, in which the three nitrates are all on one side of Gd and the oxygen atoms of organic ligands on the other side. Furthermore, the three nitrates are far away as possible because of charge repulsion between them.

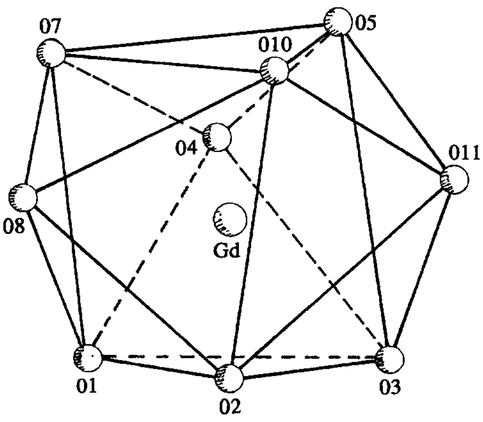

Fig. 3. Coordination polyhedron around Gd.

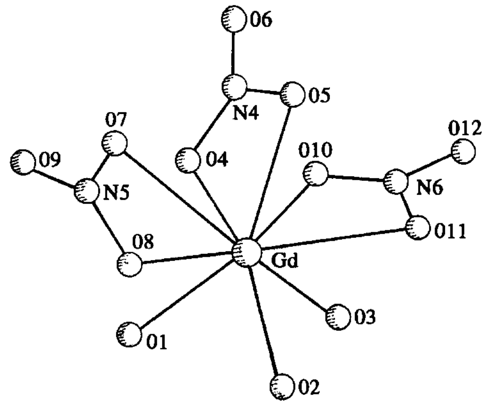

Fig. 4. The structure around Gd.

Table 3. Polyhedron around the Gd

Edges (Å)

O(5)—O(7)	2.9959	O(1)—O(2)	3.1698
O(7)—O(10)	3.0932	O(2)—O(3)	3.1254
O(10)—O(5)	2.9847	O(3)—O(1)	3.0506
O(4)—O(8)	4.2248	O(1)—O(7)	3.2345
O(8)—O(11)	4.2911	O(2)—O(10)	3.1604
O(4)—O(11)	4.2541	O(3)—O(5)	3.3705
O(8)—O(7)	2.1374	O(11)—O(3)	2.9117
O(8)—O(1)	3.0267	O(11)—O(5)	2.8841
O(8)—O(10)	2.9342	O(11)—O(2)	3.0174
O(8)—O(2)	2.8329	O(11)—O(10)	2.1268

Angles (°)

O(10)—O(5)—O(7)	62.29	O(1)—O(2)—O(3)	57.96
O(7)—O(10)—O(5)	59.03	O(3)—O(1)—O(2)	60.29
O(5)—O(7)—O(10)	58.68	O(2)—O(3)—O(1)	61.75
O(8)—O(4)—O(11)	60.81		
O(11)—O(8)—O(4)	59.93		
O(4)—O(11)—O(8)	59.26		

Table 4. Selected bond lengths (Å) and angles (°)

Gd—O(1)	2.329(3)	Gd—O(2)	2.305(3)	Gd—O(3)	2.329(3)
Gd—O(4)	2.530(4)	Gd—O(5)	2.472(4)	Gd—O(7)	2.471(3)
Gd—O(8)	2.499(4)	Gd—O(10)	2.447(4)	Gd—O(11)	2.503(4)
O(1)—C(9)	1.250(6)	O(2)—C(14)	1.258(6)	O(3)—C(31)	1.250(6)
N(4)—O(4)	1.254(8)	N(4)—O(5)	1.259(7)	N(5)—O(7)	1.256(6)
N(5)—O(8)	1.266(6)	N(6)—O(10)	1.250(7)	N(6)—O(11)	1.257(7)

N(4)—Gd—N(5)	94.5(1)	N(4)—Gd—N(6)	96.3(2)
N(5)—Gd—N(6)	98.0(1)	N(4)—Gd—O(1)	98.1(2)
N(5)—Gd—O(1)	81.2(1)	N(6)—Gd—O(1)	165.6(1)
N(4)—Gd—O(2)	167.6(1)	N(5)—Gd—O(2)	97.7(1)
N(6)—Gd—O(2)	79.5(1)	N(4)—Gd—O(3)	84.3(1)
N(5)—Gd—O(3)	162.7(1)	N(6)—Gd—O(3)	99.3(1)
O(1)—Gd—O(2)	86.3(1)	O(1)—Gd—O(3)	81.8(1)
O(2)—Gd—O(3)	84.8(1)	O(1)—Gd—O(4)	72.7(1)
O(2)—Gd—O(4)	155.3(1)	O(3)—Gd—O(4)	79.6(1)
O(1)—Gd—O(5)	123.5(1)	O(2)—Gd—O(5)	148.4(1)
O(3)—Gd—O(5)	89.1(1)	O(4)—Gd—O(5)	50.8(2)
O(1)—Gd—O(7)	84.7(1)	O(2)—Gd—O(7)	123.0(1)
O(3)—Gd—O(7)	148.1(1)	O(4)—Gd—O(7)	68.9(1)
O(5)—Gd—O(7)	74.6(1)	O(1)—Gd—O(8)	77.6(1)
O(2)—Gd—O(8)	72.1(1)	O(3)—Gd—O(8)	149.8(1)
O(4)—Gd—O(8)	114.3(1)	O(5)—Gd—O(8)	120.7(1)
O(1)—Gd—O(10)	150.3(1)	O(2)—Gd—O(10)	83.3(1)
O(3)—Gd—O(10)	124.6(1)	O(4)—Gd—O(10)	121.3(1)
O(5)—Gd—O(10)	74.7(1)	O(7)—Gd—O(10)	78.0(1)
O(8)—Gd—O(10)	72.8(1)	O(1)—Gd—O(11)	151.7(1)
O(2)—Gd—O(11)	77.6(1)	O(3)—Gd—O(11)	73.7(1)
O(4)—Gd—O(11)	115.4(1)	O(5)—Gd—O(11)	70.9(1)
O(7)—Gd—O(11)	123.6(1)	O(8)—Gd—O(11)	118.2(1)
O(10)—Gd—O(11)	50.0(4)	O—N(4)—O(5)	117.4(4)
O(4)—N(4)—O(6)	112.4(6)	O(5)—N(4)—O(6)	121.2(6)
O(7)—N(5)—O(8)	115.9(4)	O(7)—N(5)—O(9)	122.8(5)
O(8)—N(5)—O(9)	121.4(5)	O(10)—N(6)—O(11)	116.0(5)
O(10)—N(6)—O(12)	122.4(6)	O(11)—N(6)—O(12)	121.5(5)

Selected bond lengths (Å) and angles (°) are shown in Table 4.

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