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Synthesis and structure of lanthanide(III) picrate complexes with 1,3-dithiane-1-oxide

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Abstract

Lanthanide picrate complexes with 1,3-dithiane-1-oxide (DTSO) were synthesized by reaction of the hydrated lanthanide picrates (pic) with DTSO in absolute ethanol. Conductance measurements in acetonitrile solutions show that the complexes behave as non-electrolytes. The parameters obtained (β=0.988, $b^{1/2}$=0.0762 and δ=1.17) from the absorption spectrum of the solid Nd compound for the $^2G_{7/2}$, $^4G_{5/2} \leftarrow {}^4I_{9/2}$ transition indicate that the metal–ligand bonds present weak covalent character. The bands $^5D_0 \rightarrow {}^7F_J$ (J=1,2,3) transitions for the emission spectra of the Eu compound were interpreted in terms of a C_{4v} symmetry. X-ray single-crystal data of the gadolinium compound showed that the crystal system is monoclinic, a=10.5577(10) Å, b=20.221(3) Å, c=21.4802(12) Å, β=93.969(6)°, space group $P2_1/c$, Z=4, V=4574.8(8) Å^3. The Gd ion achieves a coordination number of nine by the bonding of three bidentate picrate groups via their phenoxo-oxygen and an oxygen of the adjacent nitro moiety and three oxygens of the three DTSO molecules, in a distorted monocapped square antiprism fashion. X-ray powder patterns show only one isomorphous series.

Keywords: Lanthanides; Picrates; 1,3-Dithiane-1-oxide; X-ray structure determination; Spectroscopy

1. Introduction

The preparation and properties of lanthanide picrates have been described [1,2]. Several lanthanide picrate complexes with oxygen containing neutral ligands have been studied in our laboratories. Complexes with sulfoxides [3–14], phosphine oxides [15,16], *N*-oxides [17–21], amides [18,22–24], phosphoramides [25,26] and lactams [27] have been synthesized and characterized. Some of them had their structures studied by single-crystal X-ray diffraction and have shown to crystallize in the monoclinic system as $Nd(pic)_3$ $(TDTD)_{1.5}$, whose spatial group $P2_1/c$ [7], $La(pic)_3$ $(DMA)_3$, $P2_1/n$ [8], and the hydrated salt $Ce(pic)_3 \cdot 12H_2O$, $P2_1/n$ [28].

This article describes the preparation, characterization by microanalytical procedures and EDTA titrations, infrared absorption spectroscopy, emission and absorption spectroscopy and structural study of the gadolinium(III) picrate complex with 1,3-dithiane-1-oxide.

2. Experimental

The ligand 1,3-dithiane-1-oxide (DTSO) was prepared by oxidation of 1,3-dithiane with sodium metaperiodate as described by Carlson and Helquist [29]. The complexes were obtained by reaction in absolute ethanol of $Ln(pic)_3$ (Ln=La–Yb, Y) and DTSO in 1:3 molar ratio. The yellow crystals formed were washed with ethanol and dried under vacuum over anhydrous calcium chloride.

Lanthanide ions were determined by complexometric titration with EDTA using xylenol-orange as indicator. Analyses of carbon, hydrogen and nitrogen were performed using a Perkin-Elmer Model 240 elemental analyzer.

IR spectra were recorded on a Nicolet FTIR-8100 spectrometer using KBr pellets. The emission spectrum of the europium complex at 77 K was recorded on a Hitachi Perkin-Elmer MPF-4 spectrofluorimeter. The absorption spectrum of the neodymium compound was obtained on a Zeiss DMR-10 spectrophotometer. Conductance measurements were performed at 25.00±0.02°C, using an apparatus composed of a resistance box, a pointer gal-

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Table 1
Analytical data (%) for the compounds of formula $Ln(pic)_3 \cdot 3$ DTSO

Compound Ln	% Ln		% C		% H		% N	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
La	11.3	11.3	29.2	29.4	2.4	2.7	10.2	10.5
Ce	11.4	11.4	29.2	29.5	2.4	2.5	10.2	10.3
Pr	11.4	11.5	29.2	29.6	2.4	2.6	10.2	10.5
Nd	11.7	11.7	29.1	29.4	2.4	2.5	10.2	10.2
Sm	12.1	12.1	29.0	29.1	2.4	2.4	10.1	10.1
Eu	12.2	12.3	28.9	29.0	2.4	2.5	10.1	10.1
Gd	12.6	12.7	28.8	29.2	2.4	2.7	10.1	10.1
Tb	12.7	12.7	28.8	29.1	2.4	2.6	10.1	10.2
Dy	12.9	13.1	28.7	29.1	2.4	2.6	10.0	10.2
Ho	13.1	13.2	28.6	28.7	2.4	2.6	10.0	9.8
Er	13.3	13.3	28.6	28.9	2.4	2.5	10.0	8.8
Tm	13.4	13.4	28.5	26.7	2.4	2.4	10.0	9.2
Yb	13.7	13.7	28.5	28.6	2.4	2.5	10.0	10.0
Y	7.5	7.7	30.5	30.7	2.6	2.8	10.7	10.6

vanometer and a cell ($k_{\mathrm{cell}}=0.1233$ cm^{-1}) from Leeds and Northrup.

X-ray powder patterns were determined on a Rigaku Denke RU-200B instrument, using Cu Kα radiation.

3. Crystal structure determination

Data were collected on a CAD-4 Mach3 Enraf-Nonius diffractometer in the $\omega/2\theta$ scan mode, using graphite

Table 2
Selected IR absorption bands (cm^{-1}) of $Ln(pic)_3 \cdot 3$ DTSO complexes[a]

Compounds	ν_{as} NO$_2$	ν_s NO$_2$	ν SO	ν CO	ν CN	ν CC	δ NO$_2$
DTSO			1049 vs				
Picric acid	1556 w 1535 vs	1344 vs 1314 s		1269 s	920 s	1610 vs	784 s
La	1570 s 1538s	1365 m 1333 vs	986 vs	1273 vs	919 s	1613 vs	789 s
Ce	1571 s 1538 s	1364 m 1333 vs	985 vs	1274 vs	920 s	1613 vs	789 s
Pr	1570 s 1538 s	1365 m 1333 vs	986 s	1274 s	919 s	1613 s	789 s
Nd	1575 s 1541 vs	1364 m 1327 vs	987 s	1275 s	920 s	1613 s	789 s
Sm	1575 s 1542 vs	1364 m 1327 vs	989 s	1276 s	920 s	1612 s	788 s
Eu	1574 s 1541 vs	1363 m 1325 vs	985 s	1276 vs	920 s	1613 vs	788 s
Gd	1567 s 1538 m	1365 m 1333 vs	984 s	1277 s	920 s	1613 s	788 s
Tb	1571 s 1538 m	1364 m 1332 vs	984 s	1277 s	920 s	1613 s	788 s
Dy	1574 s 1541 vs	1361 m 1328 vs	986 vs	1276 s	920 s	1614 s	788 s
Ho	1574 m 1542 vs	1362 w 1329 s	985 vs	1278 s	921 s	1614 s	788 s
Er	1574 s 1547 vs	1363 w 1331 vs	986 vs	1276 s	919 s	1615 s	788 s
Tm	1574 m 1546 vs	1362 w 1330 vs	986 vs	1277 s	919 s	1614 s	789 s
Yb	1574 m 1545 vs	1362 w 1330 vs	986 vs	1277 s	919 s	1614 s	788 s
Y	1571 w 1551 vs	1363 w 1334 vs	990 vs	1275 s	917 s	1618 s	789 s

[a] Band intensities: vs, very strong; s, strong; m, medium; w, weak.

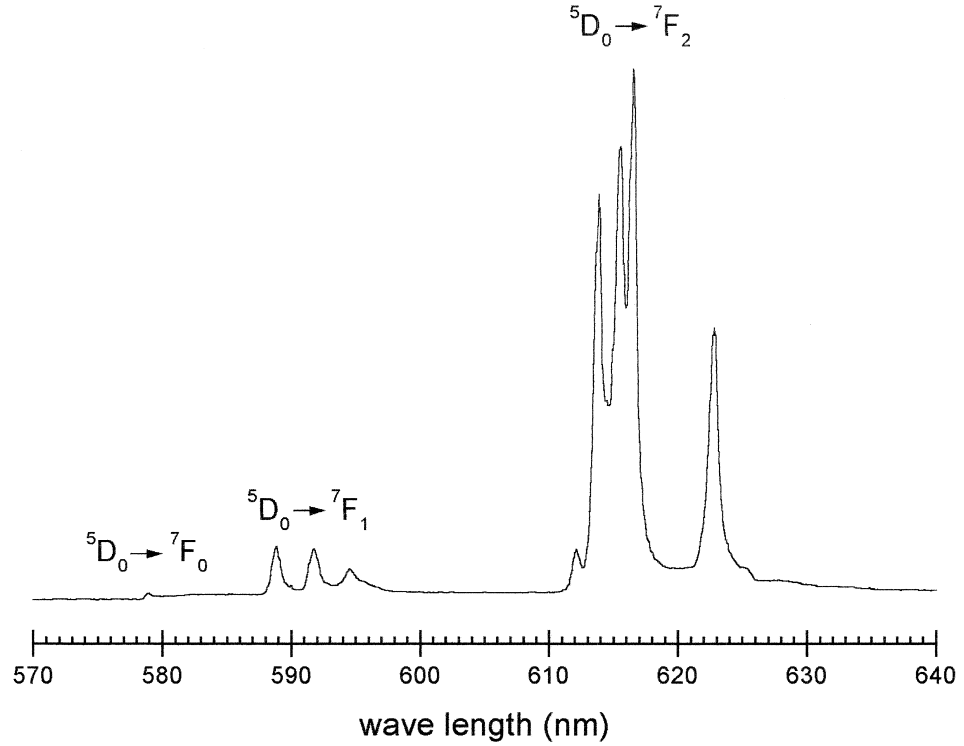

Fig. 1. Emission spectrum of the $Eu(pic)_3 \cdot 3$ DTSO at 77 K.

monochromated Mo Kα radiation. These data were corrected for Lorentz, polarization and absorption effects. The structure of Gd compound was solved by the standard Patterson heavy atom method, followed by normal difference Fourier techniques. H atoms were refined with fixed geometry, each riding on a carrier atom, with an isotropic displacement parameter amounting to 1.2 times the values of the equivalent isotropic displacement parameters of the atoms they are attached to. Data processing and computation were carried out using SHELXL-97 [30], SHELXS-86 [31], and ZORTEP [32].

4. Results and discussion

The results of microanalyses of the ligand DTSO, $C_4H_8S_2O$: C (35,5%), H (5,8%) agree with the calculated: 35.3 and 5.9%, respectively.

The contents lanthanide of (Ln=La–Yb and Y) C, H and N found in the complexes (Table 1) are in agreement with the proposed stoichiometry: $Ln(pic)_3 \cdot 3$ DTSO.

Table 2 shows relevant IR absorption bands of the complexes. According to the spectra, shifts of νSO (1049 cm^{-1}) in the free ligand to lower frequencies in the complexes (~985 cm^{-1}) indicate coordination of DTSO through the oxygen. The bands due to picrate, ν_{as} NO_2 and ν_s NO_2, suggest coordination through the phenolic and one oxygen of an ortho nitrogroup [2,33–35].

Conductance measurements in acetonitrile (27 S cm^2 mol^{-1}) show that the complexes behave as non-electrolytes [36].

Absorption spectra of the neodymium compound were registered in the solid state, at room temperature for the $^2G_{7/2}$, $^2G_{7/2} \leftarrow {}^4I_{9/2}$ transition. The calculated parameters ($\beta = 0.988$, $b^{1/2} = 0.0762$ and $\delta = 1.17$) indicate that the metal–ligand bonds present some covalent character [37–39].

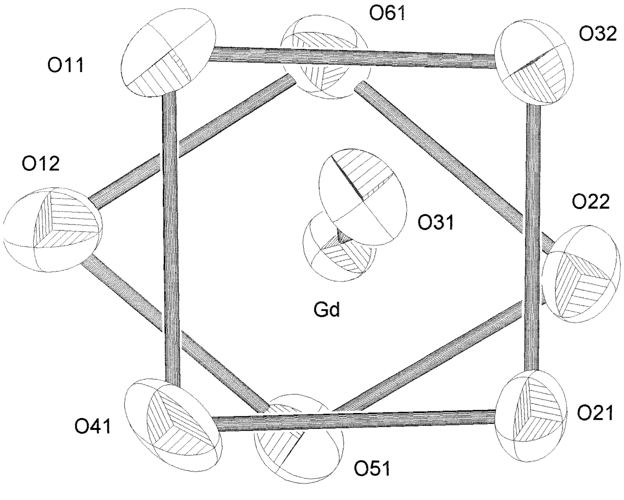

Fig. 2. Coordination polyhedron around the Gd^{3+} ion.

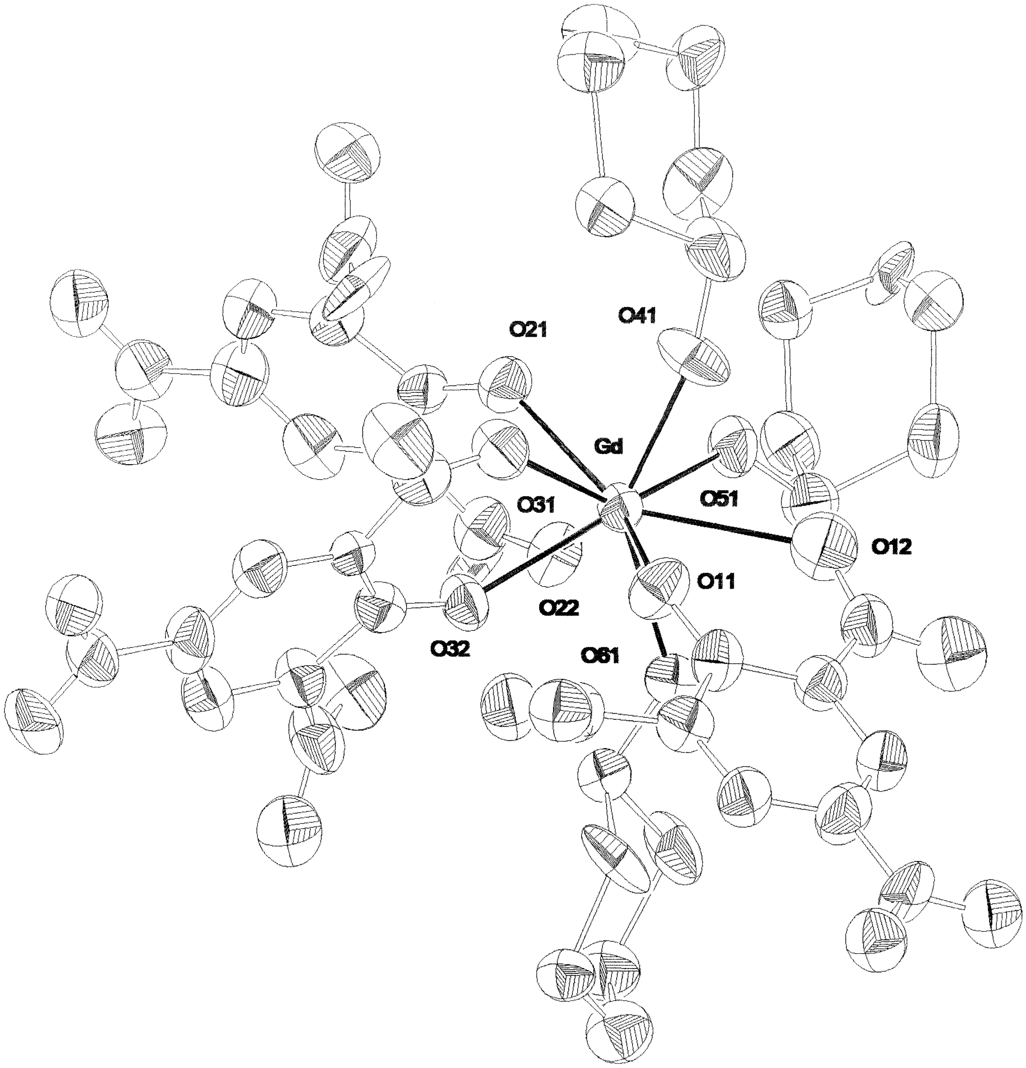

Fig. 3. ORTEP view of the Gd(pic)$_3$·3 DTSO.

Fig. 1 shows the emission spectrum of the europium complex recorded at 77 K. The spectrum contains a weak peak due to $^5D_0 \rightarrow {}^7F_0$ (A_1 species) transition that indicates the existence of a C_n, C_{nv} or C_s symmetry, three peaks due $^5D_0 \rightarrow {}^7F_1$ (one A_2 and one E species, the latter split into two peaks) and five peaks due to $^5D_0 \rightarrow {}^7F_2$ (one A_1 and two E species, the latter also split) transition; it was interpreted in terms of a C_{4v} symmetry [40].

X-ray powder patterns show only one isomorphous series. Single-crystal X-ray analysis of the Gd complexes was carried out. Table 3 presents the crystal collection and refinement data. The crystal system is monoclinic ($P2_1/c$). Fig. 2 shows the structure, and Fig. 3 the coordination polyhedron. The coordination polyhedron is a distorted monocapped square antiprism (C_{4v} symmetry) in agreement with emission data. Base 1, formed by O11, O21, O32 and O41 atoms, is planar to within 0.02 Å; base 2, formed by O12, O22, O51 and O61, is slightly distorted, being planar to within 0.15 Å, forming a dihedral angle of 3.17° (Table 4). The cap is over base 1, one nitro group oxygen, O31, and the coordination number is nine. The coordination polyhedron observed in this work is not common in this type of complexes, which usually are tricapped trigonal prisms [5,7,14,22,23,25,27]. The dihedral angle between the square faces is slightly different from those observed in square-antiprismatic complexes [21].

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Table 3
Crystallographic data and details of the structure refinement

Empirical formula	C_{30} H_{30} $GdN_9O_{24}S_6$
Formula weight	1250.24
Crystal system, space group	monoclinic, $P2_1/c$
Unit cell dimensions	
a (Å)	10.5577(10)
b (Å)	20.221(3)
c (Å)	21.4802(12)
α (°)	90.00
β (°)	93.969(6)
γ (°)	90.00
Volume (Å^3)	4574.8(8)
Molecules per cell (Z)	4
Calculated density, (D_c, g cm^{-3})	1.815
Absorption coefficient (μ, mm^{-1})	1.820
$F(000)$	2500
Crystal size (mm)	0.25×0.20×0.20
θ range for data collection (°)	2.18–25.50
Limiting indices	$-12\leq h\leq 12$, $-24\leq k\leq 0$, $-26\leq l\leq 0$
Reflections collected/unique	8751/8512 [$R_{int}=0.0473$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8512/0/631
Goodness-of-fit (S) on F^2	1.010
Final R indices [$I>2\sigma(I)$]	$R_1=0.0596$, w$R_2=0.1569$
R indices (all data)	$R_1=0.1697$, w$R_2=0.1968$
Max, min residual ρ (e Å^{-3})[a]	1.11 and -1.22

[a] This peak and hole are at less than 1 Å from the Gd atom.

Table 4
Distances (Å) and angles (°) around the Gd ion

Gd O21 2.308(6)
Gd O11 2.321(7)
Gd O41 2.331(7)
Gd O61 2.338(7)
Gd O51 2.332(7)
Gd O32 2.340(6)
Gd O31 2.575(7)
Gd O22 2.632(8)
Gd O12 2.723(9)

O21 Gd O11 139.2(2)
O21 Gd O41 82.9(3)
O11 Gd O41 84.2(3)
O21 Gd O61 133.9(3)
O11 Gd O61 77.1(3)
O41 Gd O61 138.2(3)
O21 Gd O51 85.2(2)
O11 Gd O51 129.0(3)
O41 Gd O51 77.2(3)
O61 Gd O51 86.1(3)
O21 Gd O32 78.8(2)
O11 Gd O32 85.1(3)
O41 Gd O32 137.5(3)
O61 Gd O32 78.1(2)
O51 Gd O32 138.0(2)
O21 Gd O31 72.9(2)
O11 Gd O31 66.3(2)
O41 Gd O31 72.5(3)
O61 Gd O31 129.4(2)
O51 Gd O31 144.3(3)
O32 Gd O31 65.5(2)
O21 Gd O22 66.1(2)
O11 Gd O22 141.0(3)
O41 Gd O22 134.2(3)
O61 Gd O22 68.7(2)
O51 Gd O22 67.8(2)
O32 Gd O22 70.3(2)
O31 Gd O22 123.8(2)
O21 Gd O12 144.5(3)
O11 Gd O12 62.5(3)
O41 Gd O12 70.6(3)
O61 Gd O12 67.7(3)
O51 Gd O12 66.6(2)
O32 Gd O12 136.6(2)
O31 Gd O12 118.4(3)
O22 Gd O12 117.3(2)

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