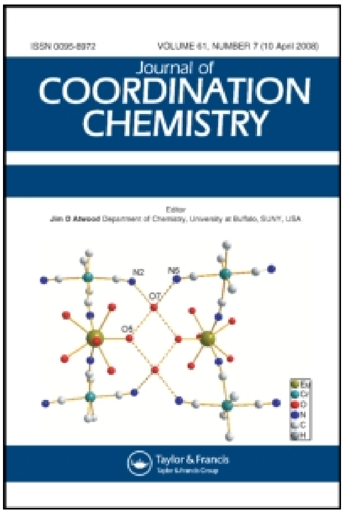

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Synthesis and Crystal Structure of Complexes of Lanthanide Picrates With *N,N'*-Dimethyl-*N,N'*-Diphenyl-1,2-PhenylenediOxydiacetamide

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SYNTHESIS AND CRYSTAL STRUCTURE OF COMPLEXES OF LANTHANIDE PICRATES WITH *N,N′*-DIMETHYL-*N,N′*-DIPHENYL-1,2-PHENYLENEDIOXYDIACETAMIDE

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Lanthanide picrate complexes with the ligand N,N′-dimethyl-N,N′-diphenyl-1,2-phenylenedioxydiacetamide (L) [Ln(Pic)$_3$L] (Ln = La, Gd, Er, Y) have been prepared in nonaqueous medium and characterized by elemental analysis, IR and ^{1}H spectra. The Gd(III) complex [Gd(Pic)$_3$L] · 3CH$_3$CN is triclinic, space group $P\bar{1}$, with $a = 14.292(1)$, $b = 14.976(2)$, $c = 16.571(2)$ Å, $\alpha = 97.855(9)$, $\beta = 111.439(9)$, $\gamma = 113.070(9)°$, $v = 28706(6)$ Å^3, $D_c = 1.584$ g/cm^3 for $Z = 2$. The structure was refined to R = 0.0318 based on 8409 observed reflections.

Keywords: Lanthanide; Picrate; Complex; X-ray structure; Polyethers

INTRODUCTION

Acyclic polyethers offer many advantages over the use of crown ether in the extraction and analysis (ion-selective electrodes) of the rare earths [1 – 5]. *N,N′*-diaryl-1,2-phenylenedioxydiacetamide can be used in ion-selective electrodes. For example, *N,N′*-dimethyl-*N,N′*-diphenyl-1,2-phenylenedi(oxy)diacetamide (ETH157) is a useful ionophore in electrode membranes and sensors [6 – 10]. A change of terminal group could affect the selectivity to the metal ion [11]. In order to investigate the effect of the terminal groups

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on selectivity and to find a novel and more selective ligand in extracting rare earths, we synthesized a series of the above ligands with various terminal groups and their complexes of rare earths. In the present work, we report the synthesis, characterization and structure of lanthanide picrate complexes with *N*,*N*′-dimethyl-*N*,*N*′-diphenyl-1,2-phenylenedioxydiacetamide (L).

EXPERIMENTAL

Reagents

The lanthanide picrates [12] and L [13] were prepared according to literature methods. All solvents used were purified by standard methods.

Chemical and Physical Measurements

The metal ion was determined by EDTA titration using xylenol orange as indicator. C, N and H were determined using an Elementar Vario EL instrument. IR spectra were recorded on a Nicolet AVATAR 360 FT-IR instrument using KBr discs in the 400–4000 cm^{-1} region. ^{1}H NMR spectra were measured on a Brucker AC 200 spectrometer in $CDCl_3$ solutions with TMS as internal standard.

Synthesis of [Ln(pic)$_3$L]

A solution of 0.1 mmol L in 10 cm^3 of anhydrous ethanol was added dropwise to a solution of 0.1 mmol lanthanide picrate in 8 cm^3 of anhydrous ethanol. The mixture was stirred at room temperature for 5 h. The precipitated solid complex was filtered, washed with anhydrous ethanol and dried *in vacuo* over P_4O_{10} for 48 h. All the complexes were obtained as yellow powders. Analytical data are given in Table I. The solid Gd(III)

TABLE I Analytical data for the complexes

	Analysis (%)^a			
Complex	*C*	*H*	*N*	*Ln*
La(pic)$_3$L · C_4H_6O	41.94(41.49)	2.84(2.85)	12.08(12.10)	11.23(10.90)
Gd(pic)$_3$L	40.52(40.48)	2.71(2.43)	12.42(12.37)	12.52(12.62)
Er(pic)$_3$L	40.19(40.16)	2.36(2.41)	12.52(12.27)	13.02(13.32)
Y(pic)$_3$L	42.82(42.83)	3.23(28.57)	13.09(13.08)	7.70(7.55)

^{a} Calculated values in parentheses.

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for $[\mathrm{Gd(pic)_3L}] \cdot 3\mathrm{CH_3CN}$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x/a	y/b	z/c	U_{eq}
Gd	– 258(1)	– 2510(1)	7508(1)	36(1)
O(1)	1427(3)	– 1016(2)	7883(2)	46(1)
O(2)	660(3)	– 1122(2)	9070(2)	37(1)
O(3)	– 1233(3)	– 2792(2)	8541(2)	39(1)
O(4)	– 2235(3)	– 3685(2)	6804(2)	48(1)
O(5)	– 976(3)	– 1387(2)	7297(2)	40(1)
O(6)	– 2899(4)	– 1869(3)	7613(3)	69(1)
O(7)	– 4237(4)	– 3050(3)	6343(3)	72(1)
O(8)	– 4826(5)	– 1401(4)	3945(4)	110(2)
O(9)	– 3338(5)	– 337(4)	3862(3)	98(2)
O(10)	398(4)	– 298(3)	5923(3)	79(1)
O(11)	632(4)	508(3)	7219(3)	70(1)
O(12)	830(3)	– 2932(2)	8641(2)	47(1)
O(13)	3025(4)	– 1487(3)	9802(4)	108(2)
O(14)	3601(5)	– 2053(4)	10903(4)	111(2)
O(15)	3563(6)	– 5272(4)	9858(5)	138(3)
O(16)	2226(4)	– 6396(3)	8577(4)	91(2)
O(17)	– 888(4)	– 5896(3)	6883(3)	107(2)
O(18)	– 771(3)	– 4412(3)	7040(3)	63(1)
O(19)	– 625(3)	– 2671(2)	6033(2)	48(1)
O(20)	– 2537(4)	– 3228(4)	4496(3)	92(1)
O(21)	– 2127(4)	– 2119(4)	3815(3)	94(2)
O(22)	799(5)	– 2004(4)	2952(3)	100(2)
O(23)	2408(6)	– 1668(4)	4039(4)	111(2)
O(24)	2608(5)	– 2254(5)	6817(3)	110(2)
O(25)	1164(3)	– 2859(3)	7060(2)	60(1)
N(1)	3021(4)	486(3)	8749(3)	52(1)
N(2)	– 3742(4)	– 4997(3)	6759(3)	49(1)
N(3)	– 3355(4)	– 2232(3)	6783(4)	50(1)
N(4)	– 3784(6)	– 905(4)	4226(4)	74(2)
N(5)	37(4)	– 102(3)	6443(3)	50(1)
N(6)	3033(5)	– 2175(4)	10105(4)	73(2)
N(7)	2701(6)	– 5558(4)	9155(5)	75(2)
N(8)	– 347(5)	– 4966(4)	7304(4)	70(2)
N(9)	– 1873(5)	– 2627(4)	4288(3)	69(1)
N(10)	1410(7)	– 1922(4)	3737(4)	76(2)
N(11)	1621(5)	– 2502(4)	6591(3)	60(1)
C(1)	3717(5)	2208(4)	9725(4)	58(2)
C(2)	4439(6)	2990(4)	10547(5)	71(2)
C(3)	5194(6)	2873(5)	11254(5)	77(2)
C(4)	5244(6)	1973(5)	11134(5)	79(2)
C(5)	4540(5)	1188(4)	10314(4)	63(2)
C(6)	3773(4)	1311(3)	9612(4)	45(1)
C(7)	3370(6)	493(4)	8015(4)	92(2)
C(8)	2040(4)	– 279(3)	8602(3)	41(1)
C(9)	1712(4)	– 213(3)	9362(3)	40(1)
C(10)	276(4)	– 1272(3)	9726(3)	34(1)
C(11)	821(4)	– 594(3)	10599(3)	45(1)
C(12)	379(5)	– 823(4)	11205(4)	52(1)
C(13)	– 612(5)	– 1707(4)	10927(4)	55(1)
C(14)	– 1185(5)	– 2391(3)	10042(3)	48(1)
C(15)	– 735(4)	– 2168(3)	9441(3)	36(1)

TABLE II (Continued)

	x/a	y/b	z/c	U_{eq}
C(16)	−2359(4)	−3638(3)	8208(3)	44(1)
C(17)	−2788(4)	−4123(3)	7193(3)	40(1)
C(18)	−4172(6)	−5530(4)	5795(4)	88(2)
C(19)	−4400(5)	−5472(4)	7211(4)	53(1)
C(20)	−4329(5)	−6284(4)	7474(5)	83(2)
C(21)	−5010(7)	−6756(5)	7879(6)	100(3)
C(22)	−5692(7)	−6393(6)	8014(5)	102(3)
C(23)	−5758(6)	−5591(4)	7760(4)	79(2)
C(24)	−5106(5)	−5123(4)	7351(4)	61(2)
C(25)	−1636(5)	−1245(3)	6615(3)	37(1)
C(26)	−2819(5)	−1654(3)	6288(3)	40(1)
C(27)	−3537(5)	−1580(4)	5502(3)	49(1)
C(28)	−3040(5)	−1006(4)	5047(4)	51(1)
C(29)	−1887(5)	−529(4)	5342(4)	49(1)
C(30)	−1205(5)	−631(3)	6109(3)	40(1)
C(31)	1278(5)	−3522(3)	8722(3)	40(1)
C(32)	2359(5)	−3229(4)	9463(4)	51(1)
C(33)	2812(5)	−3874(4)	9617(4)	60(2)
C(34)	2236(5)	−4853(4)	9012(4)	55(2)
C(35)	1222(5)	−5201(4)	8249(4)	55(2)
C(36)	737(5)	−4549(4)	8097(4)	47(1)
C(37)	−170(5)	−2566(3)	5498(3)	43(1)
C(38)	−733(5)	−2524(4)	4605(3)	49(1)
C(39)	−249(6)	−2322(4)	4035(4)	58(2)
C(40)	854(6)	−2168(4)	4320(4)	56(2)
C(41)	1467(5)	−2206(3)	5162(4)	53(1)
C(42)	950(5)	−2431(3)	5729(3)	43(1)
N(12)	−1306(7)	−5189(6)	8969(6)	152(3)
C(43)	−1022(9)	−6811(6)	8883(7)	160(5)
C(44)	−1204(8)	−5922(6)	8899(6)	109(3)
N(13)	−5513(10)	−1599(9)	6179(10)	204(6)
C(45)	−3871(10)	222(8)	7315(8)	225(7)
C(46)	−4790(10)	−789(9)	6704(9)	147(5)
N(14)	1810(30)	−4960(30)	6611(17)	220(12)
C(47)	2060(15)	−4520(20)	5208(12)	93(4)
C(48)	1770(10)	−4766(6)	5933(7)	179(6)
N(14′)	1020(20)	−4960(30)	6140(20)	220(12)
C(47′)	2522(13)	−4480(20)	5508(12)	93(4)
C(48′)	1770(10)	−4766(6)	5933(7)	179(6)

complex was recrystallized from MeCN by slow evaporation to give transparent yellow crystals of $[Gd(pic)_3L] \cdot 3CH_3CN$.

X-ray Structure Determination of $[Gd(Pic)_3L] \cdot 3CH_3CN$

Crystal Data

$C_{48}H_{39}N_{14}O_{25}Gd$, $Mr = 1369.18$, triclinic, space group $P\bar{1}$, $a = 14.292(1)$, $b = 14.976(2)$, $c = 16.571(2)$ Å, $\alpha = 97.855(9)$, $\beta = 111.439(9)$,

$\gamma = 113.070(7)^\circ$, $V = 2870.6(6)\,\text{Å}^3$, $Z = 2$, $Dc = 1.584\,\text{g/cm}^{-3}$, $\lambda(\text{MoK}\alpha) = 0.71073\,\text{Å}$, $F(000) = 1378$. Intensity data for a crystal of size $0.66 \times 0.60 \times 0.12$ mm were measured at 12°C on a P4 four-circle diffractometer with graphite-monochromated MoKα radiation, using a $\omega/2\theta$ scan. Lorentz and polarization corrections were applied, but no absorption correction was made.

The structure was solved by the Patterson method and subsequent difference Fourier techniques, and refined by block-matrix least-squares procedures. Non-hydrogen atoms were refined anisotropically. The weighing scheme was $w = 1/\{\sigma^2(F_0^2) + [0.0462(\max(F_0^2, 0) + 2F_0^2/3)]^2\}$, final R = 0.039, wR = 0.074. The highest peak in the final difference Fourier was $0.806\,\text{eÅ}^{-3}$. All calculations were performed on an Eclipses/S 140 computer with the SHELXTL program. Final atomic coordinates are given in Table II. Tables of anisotropic thermal parameters, hydrogen atom coordinates and structure factors are available as supplementary data from W.L. upon request.

RESULTS AND DISCUSSION

Analytical data for the complex conform to a 1 : 3 : 1 metal to picrate to L stoichiometry Ln(Pic)$_3$L (see Tab. I). All complexes are soluble in DMSO, DMF, MeCN, acetone and THF, slightly soluble in MeOH and AcOEt, and sparingly soluble in benzene, Et$_2$O and cyclohexane.

IR Spectra

The IR spectrum of free L shows bands at 1677 and 1119 cm^{-1} which may be assigned to ν(C=O) and ν(C—O—C), respectively. In the IR spectra of La(III) and Er(III) complexes, the two bands shift by *ca.* 45 and 37 cm^{-1} towards lower wave numbers, thus indicating that all the C=O and ether O atoms take part in coordination to the metal ions. The larger shifts for ν(C=O) in the spectra of the complexes suggest that the Ln—O (carbonyl) bond is stronger than the Ln—O (ether) bond [14]. These results are consistent with the ^{1}H NMR and the crystal structure determination.

The OH out-of-plane bending vibration of free Hpic at 1151 cm^{-1} disappears in the spectra of the complexes [14], indicating that the H-atom of the OH group is replaced by Ln(III). The ν(C—O) vibration at 1265 cm^{-1} is shifted towards higher frequency by *ca.* 10 cm^{-1} in the complexes. This is due to the following two effects. First, the hydrogen atom of the OH group is replaced by Ln(III), increasing the π-bond character of the C—O bond. Secondly, coordination of the oxygen atom of O—C (Pic$^-$) to Ln(III) causes the π-character to be weakened. Free Hpic has $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ at 1555 and 1342 cm^{-1}, respectively, which splits into two bands at *ca.* 1588, 1540 cm^{-1}, and *ca.* 1360, 1326 cm^{-1}, respectively, in the complexes. This indicates that some of the nitronyl O atoms take part in coordination [12].

^{1}H NMR Spectra

The spectrum of the ligand exhibits an unresolved multiplet at 7.4 ppm, a doublet at 6.8 and two singlet at 4.5 and 3.4 ppm assigned to —C_6H_5, —C_6H_4—, —C(O)CH_2— and —CH_3 protons, respectively. Upon coordination, the singnals of —C(O)CH_2— are shifted by 0.4 ppm and these of —C_6H_4— protons by only 0.1 ppm. This is probably due to the inductive effect of Ln—O(L) bonds and change in the conformation of the ligand in the complexes. The larger shift for —C(O)CH_2— protons than —C_6H_4— ones indicates the Ln—O(C=O) bond is stronger than the Ln—O(C—O—C) bond [14].

The ^{1}H signal of OH group in free Hpic disappears in the complexes, indicating that the H atom of the OH group is replaced by Ln(III). The benzene ring protons of the free Hpic exhibit a singlet at 9.12 ppm. Upon coordination, the signal moves to higher field. Only one singlet is observed for the benzene ring protons of the three-coordinated picrate groups, indicating fast exchange among the groups in solution [15].

Crystal Structure [Gd(Pic)$_3$L] · 3CH_3CN

The structure of [Gd(pic)$_3$L]·3CH_3CN is shown in Figure 1. Selected bond distances and angles are given in Table III. The crystal structure is composed of [Gd(Pic)$_3$L] and three CH_3CN molecules linked by weak van der Waals' forces. The Gd(III) ion is 9-coordinated by four oxygen atoms of L and five oxygen atoms of two bidentate and one unidentate picrates. The coordination polyhedron is a tricapped trigonal prism. The L molecule wraps around the metal ion with its oxygen atoms and forms a ring-like coordination structure together with the bidentate picrate [O(19)] situated at the open side of the L chain (Fig. 2). The four oxygen atoms of L[O(1), O(2), O(3), O(4)] are not quite coplanar, their deviation from the mean plane

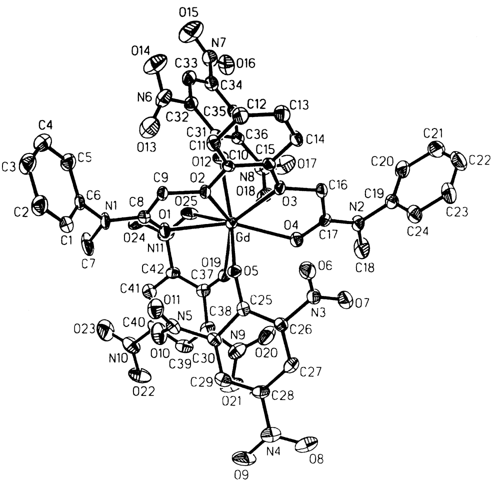

FIGURE 1 Molecular structure of [Gd(pic)$_3$L] · 3CH$_3$CN, showing the atom labeling scheme.

TABLE III Selected bond lengths (Å) and bond angles (deg) for [Gd(pic)$_3$L] · 3CH$_3$CN

Gd—O(1)	2.344(3)	Gd—O(12)	2.302(3)
Gd—O(2)	2.579(3)	Gd—O(18)	2.569(3)
Gd—O(3)	2.556(3)	Gd—O(19)	2.261(3)
Gd—O(4)	2.361(3)	Gd—O(25)	2.606(4)
Gd—O(5)	2.293(3)		
Mean lengths			
Gd—O(C—O, Pic)	2.285	Gd—O(NO$_2$, Pic)	2.588
Gd—O(C═O, L)	2.352	Gd—O(C—O—C, L)	2.568
O(1)—Gd—O(2)	62.80(10)	O(1)—Gd—O(4)	158.62(11)
O(5)—Gd—O(1)	80.47(11)	O(1)—Gd—O(3)	123.34(10)
O(5)—Gd—O(4)	80.51(11)	O(3)—Gd—O(2)	60.56(9)

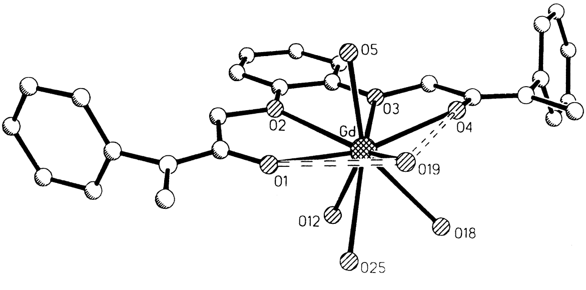

FIGURE 2 Ring-like coordination structure of [Gd(pic)$_3$L] · 3CH$_3$CN.

being the range 0.0401 – 0.1793 Å. The mean absolute deviation is 0.1074 Å. The Gd atom lies out of this plane by 0.4472 Å. Obviously L is distorted to some extent in order to maintain the Gd—O distances at suitable lengths for coordination.

The average distance between the Gd atom and the coordinated oxygen atom is 2.430 Å, where Gd—O(19) is the shortest, probably due to the higher electron density on the oxygen anion of the picrate. Gd—O(C═O) distances (mean 2.352 Å) are significantly shorter than Gd—O(C—O—C) (mean 2.568 Å). This suggests that the Gd—O(C═O) bond is stronger than the Gd—O(C—O—C) bond, in agreement with the IR data.

The structure shows that L acts as a multidentate ligand forming a ring-like coordination structure. Because of its superior flexibility, L exhibits a stable conformation that provides a coordination cavity. The internal cavity formed by the coordinating oxygen atoms is suited for the uptake of a cation, while the non-polar groups form a lipophilic shell around the coordination sphere. The L molecule therefore shows high coordination ability and lipophilicity, both of which could make it a useful component in sensors. Furthermore, it can be shown experimentally that the structures and properties of the open-chain crown ether complexes are closely dependant on counter anion and terminal group effects [16, 17]. A further study concerned with these will be reported in a following communication.

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