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Synthesis, structure and properties of lanthanide(III) picrate complexes with *trans*-1,4-dithiane-1,4-dioxide (TDTD)

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Abstract

A series of isomorphous lanthanide complexes, having general formula $M(pic)_3(TDTD)_{1.5}$ (M = Ce–Er, Yb and Y), was synthesized and characterized by microanalyses, infrared spectra and visible emission spectrum for the Eu complex. Crystal structures were determined for the Ce and Eu derivatives; for the other complexes only cell parameters were obtained and reported. The compounds crystallize with a monoclinic cell, space group $P2_1/c$ with $Z=4$. The metal ions are nine-coordinated with a tricapped trigonal prismatic coordination polyhedron, achieved via the bonding of three bidentate picrate units and three oxygens of the TDTD ligands. The TDTD moieties are shared by adjacent metal centers, forming three-dimensional polymers.

Introduction

The picrates of the lanthanides have been the object of fairly extensive investigations. The preparation, some properties and the structures of the ytterbium and yttrium picrates have been described [1–3]. Two different crystalline forms hydrated cerium picrate, $Ce(pic)_3 \cdot 12H_2O$, were obtained, having essentially the same coordination geometries; their coordination polyhedron was described as being intermediate between a tricapped trigonal prism (TCTP) and a monocapped square antiprism (CSAP) [4]. Various papers have reported the synthesis and characterization [5] and a thermogravimetric study [6] of complexes formed by lanthanide picrates with dimethyl sulfoxide, the thermal properties of some 4-picoline-*N*-oxide adducts [7] and complexes of 2-picoline-*N*-oxide [8]. Lanthanide picrate complexes with hexamethyl-phosphoramide (HMPA) have been obtained as two series of compounds, $M(pic)_3 \cdot 3HMPA$ (M = La–Nd) and $M(pic)_3 \cdot 2HMPA$ (M = Sm–Lu, Y): the isomorphous Ho and Y complexes were found to have a distorted dodecahedral geometry [9].

In this article we describe the preparation, characterization and a structural study on the lanthanide(III) picrate complexes with *trans*-1,4-dithiane-1,4-dioxide (TDTD) as additional ligand.

Experimental

Synthesis of the complexes and instrumental methods

The ligand (TDTD) was prepared by the method of Bell and Bennett [10]. The addition compounds were obtained by reaction of the corresponding hydrated lanthanide picrate with an excess of TDTD at room temperature in water solution. The yellow crystals that formed were washed with water and dried in air. They were characterized by lanthanide complexometric titration with EDTA using xylenol-orange as indicator [11]. Carbon, hydrogen and nitrogen were determined by microanalysis. Analytical data of the complexes are reported in Table 1. IR spectra of the complexes as KBr disks were recorded with a BOMEM FTIR model MB-102 instrument. The emission spectrum of the europium compound was determined on a Hitachi Perkin-Elmer MPF-4 spectrofluorimeter with 434 nm excitation at 77 K.

X-ray measurements and structure determination

The crystal and refinement data are summarized in Tables 2 and 3. The crystals were aligned on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo Kα radiation. The cell dimensions were taken from a least-square fit of 25 reflections in the range $16 \leq 2\theta \leq 24°$. The total observed reflections were measured in the $\omega/2\theta$ mode. As a check on the stability of the diffractometer and of the crystals, three

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TABLE 1. Analytical data (%) for the compounds of formula $M(pic)_3(TDTD)_{1.5}$

Compound	Metal ion		Carbon		Hydrogen		Nitrogen	
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.
Y[a]	8.27	8.73	28.27	28.82	1.98	1.70	12.36	12.07
Ce[a]	13.09	13.19	26.92	27.46	1.88	1.61	11.77	12.18
Pr	13.37	13.89	27.36	27.33	1.72	1.68	11.97	11.64
Nd	13.65	13.57	27.28	27.22	1.72	1.70	11.93	11.22
Sm	14.14	13.98	27.12	27.06	1.71	1.72	11.86	11.51
Eu	14.27	13.74	27.08	27.12	1.70	1.65	11.84	11.43
Gd	14.72	14.59	26.93	26.86	1.69	1.58	11.78	12.22
Tb	14.84	14.70	26.90	26.95	1.69	1.60	11.76	11.31
Dy	15.10	15.25	26.81	26.84	1.69	1.63	11.73	11.76
Ho	15.31	15.25	26.75	26.67	1.68	1.67	11.70	11.90
Er	15.49	15.52	26.69	27.02	1.68	1.72	11.67	11.86
Yb[a]	15.68	15.70	26.12	26.88	1.83	1.47	11.42	12.56

[a] $[M(pic)_3(TDTD)_{1.5}\cdot H_2O$.

TABLE 2. Cell parameters along the isostructural series $[M(C_6O_7N_3H_2)_3(S_2O_2C_4H_8)_{1.5}]$

M	FW	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)	D_{calc} (Mg m^{-3})	Ionic radii[a]
Ce[b]	1070.76	12.846(2)	17.390(5)	17.174(2)	110.53(2)	3593(1)	1.98	1.196
Pr	1053.53	12.842(7)	17.331(9)	17.212(8)	110.44(3)	3589(3)	1.95	1.179
Nd	1056.82	12.793(4)	17.292(2)	17.244(7)	110.36(2)	3576(2)	1.96	1.163
Sm	1063.02	12.788(1)	17.213(4)	17.275(5)	110.55(2)	3561(1)	1.98	1.132
Eu	1064.58	12.777(2)	17.178(2)	17.274(2)	110.63(1)	3548(1)	1.99	1.120
Gd	1069.82	12.763(1)	17.134(2)	17.235(12)	110.59(3)	3528(3)	2.01	1.107
Tb	1071.55	12.730(7)	17.063(3)	17.265(44)	110.72(6)	3508(9)	2.03	1.095
Dy	1075.15	12.723(5)	17.039(2)	17.305(12)	110.87(3)	3513(4)	2.03	1.083
Y[b]	1019.57	12.729(1)	16.973(5)	17.276(8)	110.99(2)	3485(2)	1.94	1.075
Ho	1077.55	12.739(4)	16.990(2)	17.341(5)	110.96(2)	3505(4)	2.04	1.072
Er	1079.82	12.734(5)	16.967(4)	17.354(2)	111.11(2)	3498(2)	2.05	1.062
Yb[b]	1085.62	12.744(3)	17.033(3)	17.279(8)	110.87(2)	3504(2)	2.06	1.042

[a] For nine-coordination, ref. 12. [b] Data for $[M(pic)_3(TDTD)_{1.5}\cdot H_2O$.

TABLE 3. Summary of the experimental conditions for data collections for $[Ln(C_6O_7N_3H_2)_3(S_2O_2C_4H_8)_{1.5}]$

	Ce	Eu
$F(000)$ (e)	2132	2112
Reflections measured	6370	4826
Unique observed reflections ($I \geqslant 3\sigma(I)$)	4767	3964
No. variables	559	550
2θ Range (°)	5.1–50	6.0–46
h Range	−15 to 13	0 to 10
k Range	0 to 20	0 to 15
l Range	0 to 20	−15 to 15
Crystal dimensions (mm)	0.15×0.13×0.08	0.10×0.15×0.10
μ(Mo Kα) (cm^{-1})	15.6	20.5
Empirical absorption (transmission range)	74.96–99,85	87.24–99,96
R[a]	0.037	0.026
R_w[b]	0.048	0.039
Goodness-of-fit[c]	1.91	1.76
$\lvert\Delta\rho\rvert$ (e Å^3)	1.05	1.07

[a] $R = (\Sigma[|F_o| - k|F_c|])/\Sigma|F_o|$. [b] $R_w = [(\Sigma w(|F_o| - k|F_c|)^2)/\Sigma w|F_o|^2]^{1/2}, w = [\sigma(|F_o|)^2]^{-1}$. [c] Goodness-of-fit $= [(\Sigma w||F_o| - k|F_c||^2)/(\text{no. of reflections} - \text{no. of variables})]^{1/2}$.

reflections were measured at 60 min intervals during data collection and no significant fluctuation in intensities was observed. The diffracted intensities were corrected for Lorentz and polarization effects and absorption with ψ-scan method [13]. The space group, $P2_1/c$, was determined by systematic absences. Of the reflections measured, those having $I \geqslant 3\sigma(I)$ were considered observed. The structures were solved using Patterson and Fourier methods and were refined by full-matrix least-squares procedures. The structure factor calculations included both f' and f'' anomalous dispersion terms for the lanthanide atoms [14]. Anisotropic thermal parameters were applied to the non-H atoms. The hydrogen atoms contributions were introduced in calculated positions (d(C–H) = 0.98 Å; $U_{iso} = 0.07$ Å^2 for the cerium derivative and 0.05 Å^2 for the europium complex). Data processing and computation were carried out using MOLEN [15] and PARST [16] programs. Final positional and equivalent B thermal parameters for Ce and Eu derivatives are reported in Table 4. See also ‘Supplementary material’.

Results and discussion

Selected IR absorptions of the M(pic)$_3$(TDTD)$_{1.5}$ complexes and of the parent salts, M(pic)$_3 \cdot n$H$_2$O, are reported in Table 5. The symmetric–NO$_2$ stretching mode appears as a single absorption in both series of compounds, with only minor frequency shifts. The antisymmetric NO$_2$ stretching, however, differs significantly, as it appears as a single absorption in the picrate salts and as two closely spaced bands in the TDTD complexes. Thus the –NO$_2$ absorptions in the TDTD complexes closely resemble those of picric acid [17] (ν_sNO$_2$ = 1343 cm^{-1}, ν_{as}NO$_2$ = 1560 and 1532 cm^{-1}), as would be expected for a monodentate coordination of the –NO$_2$ ligand in the M(pic)$_3$(TDTD)$_{1.5}$ species. For the TDTD ligands, the stretching absorption of the S=O group, which appears as a single band in the free ligand, is split into two components in most M(pic)$_3$(TDTD)$_{1.5}$ complexes, indicating a lower symmetry of the TDTD moiety.

Figure 1 shows the emission spectrum of the europium complex recorded at 77 K. The existence of a weak $^5D_0 \rightarrow {}^7F_0$ transition is indicative of a C_n, C_{nv} or C_s symmetry [18]. The three bands due to the $^5D_0 \rightarrow {}^7F_1$ transition and the five peaks attributed to two E species and one A$_1$ species for $^5D_0 \rightarrow {}^7F_2$ are indicative of C_{3v} symmetry for the EuO$_9$ coordination sphere [19].

The single-crystal X-ray analysis of [Ce(pic)$_3$(TDTD)$_{1.5}$]·H$_2$O showed that this complex is a tridimensional polymer. The nine-coordination polyhedron around the Ce atom is a tricapped trigonal prism resulting from the bonding of three bidentate picrates

TABLE 4. Final positional and equivalent B thermal parameters, with e.s.d.s in parentheses, for [Ce(pic)$_3$(TDTD)$_{1.5}$]·H$_2$O (a) and [Eu(pic)$_3$(TDTD)$_{1.5}$] (b)

Atom	x/a	y/b	z/c	B$_{eq}$ (Å^2)
(a)				
Ce	0.06470(3)	0.06121(2)	0.26726(2)	1.623(6)
S(1)	−0.0918(1)	−0.1212(1)	0.2351(1)	2.88(4)
S(2)	−0.0110(1)	0.2427(1)	0.3691(1)	3.14(4)
S(3)	0.1179(1)	−0.0260(1)	0.4780(1)	2.88(4)
O(w)	−0.0605(7)	−0.0675(6)	0.3674(6)	6.3(2)
O(1)	−0.0832(4)	0.1184(3)	0.1596(3)	2.6(1)
O(2)	0.2032(4)	−0.0314(3)	0.2694(3)	3.3(1)
O(3)	0.2013(4)	0.1488(3)	0.2536(3)	3.4(1)
O(4)	0.0418(4)	0.1765(3)	0.3411(3)	3.2(1)
O(5)	−0.0449(4)	−0.0540(3)	0.2044(3)	2.8(1)
O(6)	0.0618(4)	−0.0113(3)	0.3861(3)	2.4(1)
O(21)	−0.1377(4)	0.0633(3)	0.2855(3)	3.4(1)
O(22)	−0.3095(4)	0.0520(3)	0.2696(3)	3.7(1)
O(41)	−0.5979(5)	0.1503(4)	0.0418(4)	5.5(2)
O(42)	−0.5638(5)	0.2096(4)	−0.0567(4)	5.2(2)
O(61)	−0.0790(5)	0.2240(4)	0.0392(4)	4.9(1)
O(62)	−0.1752(5)	0.1555(4)	−0.0654(4)	5.5(2)
O(81)	0.1069(4)	0.0370(4)	0.1241(3)	4.0(1)
O(82)	0.1922(6)	0.0347(5)	0.0377(4)	7.3(2)
O(101)	0.5644(5)	−0.0433(4)	0.1052(4)	6.0(2)
O(102)	0.6433(5)	−0.1109(4)	0.2167(5)	6.9(2)
O(121)	0.3423(8)	−0.0847(6)	0.4124(5)	12.5(3)
O(122)	0.4215(9)	−0.1805(5)	0.3840(5)	9.6(3)
O(141)	0.2475(4)	0.0864(3)	0.4029(3)	3.6(1)
O(142)	0.4110(6)	0.0861(7)	0.4848(5)	10.7(3)
O(161)	0.6887(4)	0.2246(4)	0.2950(4)	5.0(1)
O(162)	0.7173(4)	0.1678(4)	0.4128(4)	4.9(2)
O(181)	0.3217(6)	0.2858(4)	0.1171(5)	7.0(2)
O(182)	0.1897(7)	0.2313(7)	0.1281(6)	20.3(3)
N(2)	−0.2360(4)	0.0724(3)	0.2437(3)	2.3(1)
N(4)	−0.5346(5)	0.1735(4)	0.0090(5)	4.1(2)
N(6)	−0.1563(5)	0.1816(4)	0.0042(4)	3.1(1)
N(8)	0.1901(5)	0.0227(4)	0.1068(4)	3.4(1)
N(10)	0.5670(5)	−0.0726(4)	0.1712(5)	4.8(2)
N(12)	0.3808(6)	−0.1195(5)	0.3689(4)	4.5(2)
N(14)	0.3439(5)	0.0982(4)	0.4166(4)	4.0(2)
N(16)	0.6554(5)	0.1917(4)	0.3448(4)	3.6(1)
N(18)	0.2832(5)	0.2441(5)	0.1536(4)	4.1(2)
C(1)	−0.1852(5)	0.1284(4)	0.1277(4)	2.0(1)
C(2)	−0.2674(5)	0.1085(4)	0.1630(4)	2.3(1)
C(3)	−0.3814(5)	0.1224(4)	0.1250(4)	2.7(1)
C(4)	−0.4178(6)	0.1558(4)	0.0475(4)	2.8(2)
C(5)	−0.3441(6)	0.1748(4)	0.0069(4)	3.0(2)
C(6)	−0.2336(5)	0.1616(4)	0.0461(4)	2.5(1)
C(7)	0.2825(6)	−0.0405(4)	0.2438(4)	2.7(2)
C(8)	0.2864(6)	−0.0125(4)	0.1667(4)	2.9(2)
C(9)	0.3787(6)	−0.0217(5)	0.1433(5)	3.2(2)
C(10)	0.4710(6)	−0.0608(5)	0.1961(5)	3.4(2)
C(11)	0.4723(6)	−0.0921(5)	0.2702(5)	3.5(2)
C(12)	0.3799(6)	−0.0820(4)	0.2917(5)	3.0(2)
C(13)	0.3032(5)	0.1610(4)	0.2768(4)	2.4(1)
C(14)	0.3826(6)	0.1326(4)	0.3538(4)	2.6(1)
C(15)	0.4978(6)	0.1417(4)	0.3761(5)	2.9(2)
C(16)	0.5378(6)	0.1811(4)	0.3221(4)	2.8(2)
C(17)	0.4664(6)	0.2129(5)	0.2488(5)	3.0(2)
C(18)	0.3545(6)	0.2047(4)	0.2284(4)	2.6(1)
C(19)	−0.1657(6)	−0.1734(4)	0.1426(6)	4.1(2)

(*continued*)

TABLE 4. (*continued*)

Atom	x/a	y/b	z/c	B_{eq} (Å^2)
(a)				
C(20)	0.0994(8)	0.3100(4)	0.4119(5)	4.1(2)
C(21)	−0.0858(6)	0.2958(4)	0.2781(5)	3.4(2)
C(22)	0.0205(7)	−0.1878(4)	0.2777(5)	3.3(2)
C(23)	0.0937(7)	0.0593(5)	0.5279(4)	3.7(2)
C(24)	0.0228(6)	−0.0877(4)	0.5036(4)	3.2(2)
(b)				
Eu	0.43448(1)	0.06241(1)	0.22873(1)	1.597(5)
S(1)	0.40869(8)	0.38275(6)	0.23826(6)	2.47(2)
S(2)	0.50363(9)	0.24422(6)	0.12956(6)	2.89(2)
S(3)	0.38230(8)	−0.02537(6)	0.02368(6)	2.62(2)
O(1)	0.5741(2)	0.1208(2)	0.3349(1)	2.41(6)
O(2)	0.3005(2)	−0.0303(2)	0.2239(2)	2.85(6)
O(3)	0.3018(2)	0.1456(2)	0.2476(2)	2.90(6)
O(4)	0.4496(2)	0.1770(2)	0.1578(2)	3.11(7)
O(5)	0.4563(2)	0.4518(1)	0.2076(2)	2.54(6)
O(6)	0.4417(2)	−0.0083(1)	0.1151(1)	2.25(6)
O(21)	0.6337(2)	0.0691(2)	0.2097(2)	3.27(7)
O(22)	0.8069(3)	0.0553(2)	0.2286(2)	3.46(7)
O(41)	1.0952(3)	0.1457(2)	0.4641(2)	5.5(1)
O(42)	1.0576(3)	0.2067(2)	0.5602(2)	4.88(9)
O(61)	0.5687(3)	0.2202(2)	0.4592(2)	4.60(8)
O(62)	0.6653(3)	0.1505(2)	0.5623(2)	5.19(9)
O(81)	0.4003(2)	0.0332(2)	0.3717(2)	3.65(7)
O(82)	0.3091(3)	0.0396(3)	0.4539(2)	7.9(1)
O(101)	−0.0638(3)	−0.0429(2)	0.3869(2)	5.21(8)
O(102)	−0.1444(3)	−0.1103(2)	0.2753(2)	5.9(1)
O(121)	0.0752(4)	−0.1824(3)	0.1089(3)	9.3(1)
O(122)	0.1628(4)	−0.0927(4)	0.0846(3)	13.2(1)
O(141)	0.2539(2)	0.0876(2)	0.0960(2)	3.46(7)
O(142)	0.0868(3)	0.0819(4)	0.0177(2)	11.7(2)
O(161)	−0.1885(3)	0.2285(2)	0.2038(2)	4.67(8)
O(162)	−0.2180(2)	0.1707(2)	0.0873(2)	4.46(8)
O(181)	0.1805(3)	0.2783(2)	0.3881(2)	6.5(1)
O(182)	0.3156(4)	0.2492(3)	0.3598(3)	14.5(1)
N(2)	0.7323(3)	0.0756(2)	0.2536(2)	2.18(7)
N(4)	1.0298(3)	0.1698(2)	0.4955(2)	3.77(9)
N(6)	0.6465(3)	0.1776(2)	0.4938(2)	2.95(8)
N(8)	0.3148(3)	0.0239(2)	0.3870(2)	3.38(9)
N(10)	−0.0658(3)	−0.0718(2)	0.3223(3)	4.5(1)
N(12)	0.1212(3)	−0.1232(3)	0.1267(2)	4.4(1)
N(14)	0.1555(3)	0.0969(2)	0.0840(2)	3.88(9)
N(16)	−0.1559(3)	0.1947(2)	0.1547(2)	3.58(9)
N(18)	0.2194(3)	0.2435(2)	0.3464(2)	3.71(9)
C(1)	0.6788(3)	0.1286(2)	0.3692(2)	2.07(8)
C(2)	0.7621(3)	0.1096(2)	0.3358(2)	2.14(9)
C(3)	0.8757(3)	0.1218(2)	0.3761(2)	2.65(9)
C(4)	0.9113(3)	0.1532(2)	0.4546(3)	2.9(1)
C(5)	0.8355(3)	0.1699(2)	0.4940(2)	3.0(1)
C(6)	0.7256(3)	0.1588(2)	0.4529(2)	2.38(9)
C(7)	0.2201(3)	−0.0400(2)	0.2494(2)	2.37(9)
C(8)	0.2152(3)	−0.0118(2)	0.3259(2)	2.39(9)
C(9)	0.1237(4)	−0.0213(2)	0.3495(3)	3.2(1)
C(10)	0.0310(4)	−0.0601(2)	0.2973(3)	3.1(1)
C(11)	0.0293(3)	−0.0928(3)	0.2236(3)	3.3(1)
C(12)	0.1220(3)	−0.0834(3)	0.2015(2)	2.68(9)
C(13)	0.1972(3)	0.1587(2)	0.2232(2)	2.21(9)
C(14)	0.1174(3)	0.1323(2)	0.1467(2)	2.37(9)
C(15)	0.0039(3)	0.1423(2)	0.1240(2)	2.8(1)
C(16)	−0.0364(3)	0.1816(2)	0.1777(2)	2.66(9)

(*continued*)

TABLE 4. (*continued*)

Atom	x/a	y/b	z/c	B_{eq} (Å^2)
(b)				
C(17)	0.0355(3)	0.2124(2)	0.2516(2)	2.66(9)
C(18)	0.1483(3)	0.2030(2)	0.2715(2)	2.50(9)
C(19)	0.3295(4)	0.3308(3)	0.1447(3)	3.9(1)
C(20)	0.3937(4)	0.3145(3)	0.0893(3)	3.7(1)
C(21)	0.5832(3)	0.2968(2)	0.2213(3)	2.9(1)
C(22)	0.5215(4)	0.3145(2)	0.2782(3)	2.9(1)
C(23)	0.4030(4)	0.0600(2)	−0.0296(3)	3.3(1)
C(24)	0.4779(4)	−0.0885(2)	−0.0006(2)	3.0(1)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$.

TABLE 5. Selected IR absorption (cm^{-1}) of the M(pic)$_3$(TDTD)$_{1.5}$ complexes and of M(pic)$_3\cdot n$H$_2$O

	ν_{SO}	ν_sNO$_2$		ν_{as}NO$_2$	
		Salt	Complex	Salt	Complex
TDTD	1019				
Picric Acid		1343		1532, 1560	
Y	999, 1030	1334	1341	1562	1514, 1549
Ce	995, 1018	1341	1341	1562	1513, 1541
Pr	995, 1019	1341	1340	1570	1513, 1541
Nd	996, 1020	1343	1342	1570	1513, 1542
Sm	996, 1020	1336	1340	1563	1513, 1541
Eu	1001	1344	1341	1570	1513, 1542
Gd	998, 1027	1343	1340	1569	1513, 1542
Tb	998, 1027	1343	1342	1570	1514, 1542
Dy	998, 1028,	1341	1341	1569	1514, 1542
Ho	998, 1029	1341	1342	1562	1512, 1544
Er	995, 1019	1340	1335	1570	1527, 1542
Yb	998, 1027	1334	1341	1574	1513, 1542

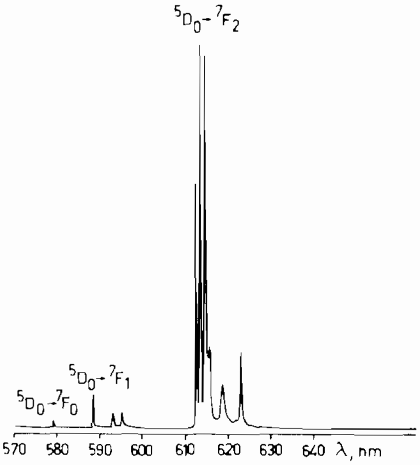

Fig. 1. Emission spectrum of the europium compound at 77 K.

and three oxygen atoms, one for each of the three TDTD ligands which form bridges with three adjacent Ce(pic)$_3$ units. The coordination of each picrate ligand occurs via the phenoxo oxygen and one of the two oxygens of an adjacent nitrate moiety. Four non-coordinated water molecules are present in each unit cell.

The compound [Eu(pic)$_3$(TDTD)$_{1.5}$] is also a tridimensional polymer and the coordination geometry of the Eu(III) center is the same as in Ce(III) analog. An ORTEP [20] view of the Eu asymmetric unit, with the atom numbering scheme, the same for the two compounds, is reported in Fig. 2. The two structures differ only in the absence of lattice water in the Eu derivative. The bond distances of the two coordination polyhedrons are reported in Table 6.

Figure 3 illustrates the polymeric arrangements common to the structures of the Ce and Eu complexes. Three types of oxygen bond distances can be distinguished in the coordination spheres. The averaged values are 2.381 Å for the Ce–O$_{\text{phenoxo}}$ distance, 2.441 Å for the Ce–O$_{\text{TDTD}}$ distance, and 2.719 Å for the Ce–O–NO distance. The longest distances correspond to the capping positions in the trigonal prisms. The same trend is observed in the Eu derivative, where the respective averaged values are Eu–O$_{\text{phenoxo}}$ = 2.309 Å, Eu–O$_{\text{TDTD}}$ = 2.360 Å and Eu–O–NO = 2.676 Å. The variations in the corresponding bond lengths for the Ce and Eu complexes are in agreement with the values of the respective ionic radii [12].

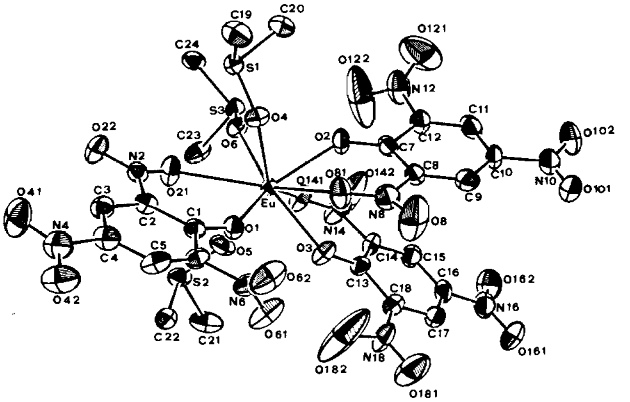

Fig. 2. Perspective view and atom labeling of the Eu(pic)$_3$(TDTD)$_{1.5}$. Thermal ellipsoids are given at the 50% probability level.

TABLE 6. Bond lengths (Å) in the coordination spheres of the complexes [Ln(pic)$_3$(TDTD)$_{1.5}$]

	Ce	Eu
Ln–O(1)	2.357(4)	2.288(2)
Ln–O(2)	2.390(5)	2.316(3)
Ln–O(3)	2.396(5)	2.324(3)
Ln–O(4)	2.444(5)	2.362(3)
Ln–O(5)	2.469(4)	2.382(2)
Ln–O(6)	2.410(5)	2.336(3)
Ln–O(21)	2.726(6)	2.677(3)
Ln–O(81)	2.729(6)	2.700(3)
Ln–O(141)	2.701(4)	2.651(2)

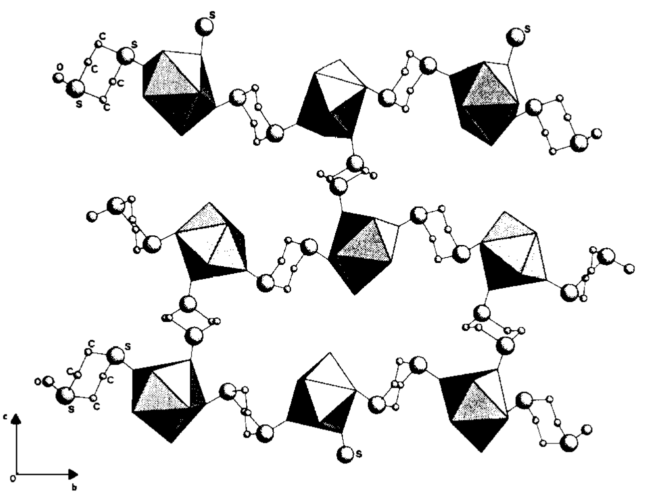

Fig. 3. Polymeric arrangements, viewed down the *a* axis, for the structures of Ce and Eu complexes. (The solids represent the coordination polyhedrons, while the TDTD ligands are fully in evidence.)

The conformation of the picrate ligands is only slightly influenced by chelation to the metal ions. In the picric acid molecule [21] an intramolecular hydrogen bond between the phenoxo oxygen and the adjacent oxygen of the nitro group stabilizes a rather planar arrangement of the nitro group with respect to the central aromatic system. In the complex the same effect is achieved by chelation to the lanthanide ion. The second adjacent nitro group, which is not involved in coordination, is rotated with respect to the ring with torsion angles of (O(61)–N(6)–C(6)–C(1)) −55.2° and O(62)–N(6)–C(6)–C(1)) 126.3°. These values are comparable to those reported for uncomplexed acid [21]. In contrast, a significant difference is observed between the C–O bond distance of the coordinated phenoxo group and that of the uncomplexed acid [21]. The C–O bond decreases from 1.327(3) Å for the acid to 1.246 and 1.264 Å (averaged values) for the cerium and europium complexes, respectively. This effect has been observed in the crystal structures of five other nitrophenolate derivatives [22], where the ionization of the phenol group results in a significant shortening of the C–O bonds. For example, in the 2,6-dinitrophenolate ion, the C–O distance is 1.249 Å whereas in the Ce(pic)$_3 \cdot 12H_2O$ complex [4], its average value is 1.26(2) Å considering both coordinated and uncoordinated picrates. The N–O distance for the oxygen atom coordinated to the metal ion is not influenced by chelation and has its usual value of 1.223 Å.

The TDTD ligands lie on the crystallographic inversion centers and the *trans* conformation of the ligand is maintained upon coordination. There is no significant change in bond lengths and angles with respect to the free molecule [23].

A comparison between the structure of the polymeric Ce complex discussed here and that of $Ce(pic)_3 \cdot 12H_2O$ [4] shows some interesting differences. The latter complex exists as two crystalline forms in which the very similar nine-coordinate complex cations, $[Ce(pic)_2(H_2O)_6]^+$, are well separated and contain two different picrate ligands, one bidentate via the phenoxo oxygen and the adjacent nitrate oxygen and the other monodentate via the phenoxo oxygen. The six water molecules complete the coordination sphere resulting in a geometry intermediate between TCTP and CSAP. It may be noted that the presence of the coordinated water molecules ($Ce–OH_2$ range is 2.49(1)–2.57(1) Å), affects markedly not only the coordination mode of the picrate ligands but also the bond distances of the coordinated nitrate oxygen in the bidentate picrate. In one form the Ce–O–NO distance is only slightly larger (2.75(1) Å) than the corresponding distance in the polymer ($Ce–O–NO_{av}$ 2.719 Å) whereas in the second form it is considerably larger (2.94(2) Å). These structural variations are clearly related to the different steric hindrance of the TDTD ligands compared to the water molecules, in the coordination spheres of the two complexes, suggesting that in these species, the metal–oxygen bonding is largely electrostatic.

The cell parameters reported in Table 2 indicate perfect isostructurality along this series of $M(pic)_3(TDTD)_{1.5}$ complexes. Except for some hydrate derivatives, the trend of the cell volume values agrees with the decrease in the metal ionic radii along the lanthanide series.

Supplementary material

Anisotropic thermal parameters, hydrogen positional parameters and observed as well as calculated structure factors (×10) are available from the authors on request.

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