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Complexes of lanthanide picrates with 1,4-pyrazine-dioxide

M.C.C. Cardoso[a,*], L.B. Zinner[a,b], J. Zukerman-Schpector[c], D.M. Araújo Melo[a], G. Vicentini[a,b]

[a]*Departamento de Química, Universidade Federal do Rio Grande do Norte, C.P. 1661, CEP 59072-970, Natal, RN, Brazil*
[b]*Instituto de Química, Universidade de São Paulo, C.P. 26077, CEP 05513-970, São Paulo, SP, Brazil*
[c]*Departamento de Química, Universidade Federal de São Carlos, C.P. 676, CEP 13565-905, São Carlos, SP, Brazil*

Abstract

Complexes of hydrated lanthanide picrates with composition: $[Ln_2(pic)_2(pyzDO)(H_2O)_{12}](pic)_4\ (pyzDO)_2(H_2O)_4$ (Ln=Pr, Nd, Sm, Eu; pic=picrate; pyzDO=1,4-pyrazine-dioxide) were synthesized by reaction of the hydrated picrates in ethanolic solution with pyzDO in water solution. The compounds that are all isomorphous, as determined by X-ray powder patterns, were characterized by CHN elemental analyses and complexometric titration with EDTA. The crystal structure of the Eu compound has been solved by single crystal X-ray diffraction. IR absorption spectra were interpreted in terms of coordination of bidentate picrate counter-ions, bonded through the oxygen of the phenoxo group and one oxygen of an ortho-nitrogroup. The parameters obtained from the absorption spectrum of the neodymium compound suggest the existence of small covalent character of the metal–ligand bonds. The Eu ion achieves a coordination number of nine by the bonding to one bidentate picrate, six water molecules and an oxygen of bridging pyzDO moiety, in a tricapped trigonal prism fashion. The Eu ions linked in centrosymmetric dimers by bonded pyzDO and also more externally through two symmetry related bridges formed by two hydrogen bonded water molecules which are in turn hydrogen bonded to coordinated waters. Two picrate anions and one pyzDO molecule are out of the coordination sphere. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Chemical synthesis; Crystal structure; X-ray diffraction

1. Introduction

Complexes containing *N*-oxides as ligands [1–4] have been studied in our laboratories. Compounds with pyrazine-1,4 dioxide [5] and pyrazine-*N*-oxide with other counter-ions have been also investigated [6–9].

In this article we describe the complexes of hydrated lanthanide picrates containing pyrazine-1,4-dioxide. They were characterized by CHN microanalytical procedures, complexometric titration with EDTA, X-ray powder patterns, IR spectra, conductance measurements, visible absorption spectrum of the neodymium compound and X-ray single crystal studies of the europium complex.

2. Experimental

The pyzDO was obtained by oxidizing pyrazine (Aldrich) with 30% hydrogen peroxide, according to Koelsch and Grumprecht [10]. The compounds were prepared by mixing an ethanolic solution of the hydrated picrates with a water solution of pyrazine-1,4-dioxide (pyzDO) (molar ratio 1:2). The crystals were filtered and dried in air at room temperature. The compounds were characterized by microanalyses using a Perkin-Elmer 240 elemental analyzer and lanthanide titration with EDTA. The visible absorption spectrum of the Nd(III) compound was recorded on a Zeiss DMR 10 spectrophotometer, at room temperature, using a silicone mull in 0.50 mm path cell. IR spectra were recorded on a Midac Prospect spectrometer, using Nujol mulls between KBr plates. Conductance measurements were performed using a Quimis Q-450 conductivimeter at 25.0±0.2°C ($K_c=0.101\ cm^{-1}$).

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 Kα radiation. Data were corrected for Lorentz, polarization and absorption effects. This last correction was done using the 'ψ-scan' technique (maximum and minimum transmis-

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*Corresponding author.

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Table 1
Summary of data collection and crystal parameters

Formula	C_{24} H_{32} Eu N_{12} O_{32}
Molecular weight	1152.58
Crystal system	triclinic
Space group	$P1\bar{1}$
Cell constants	
a (Å)	7.944(1)
b (Å)	12.793(1)
c (Å)	20.224(2)
α (°)	75.129(4)
β (°)	81.932(4)
γ (°)	89.310(5)
Volume (Å^3)	1966.2(4)
Molecules per cell (Z)	2
Density (calcd.) D_c (g cm^{-3})	1.947
Radiation λ (Mo Kα) (Å)	0.71073
Crystal size	0.30×0.30×0.10 mm
T (K)	293
Linear absorption coeff. μ (mm^{-1})	1.726
θ range for data collection (°)	1.05–25.00
Reflections collected/unique	7124/6906 [R(int)$=0.0305$]
Reflections above $2\sigma(I)$	5821
Refinement method	Full-matrix least-squares on F^2
Data/parameters	6906/622
Goodness-of-fit on F^2	1.054
Final R indices [$I>2\sigma(I)$]	$R_1=0.0285$, $wR_2=0.0751$
R indices (all data)	$R_1=0.0426$, $wR_2=0.0805$
$h_{\min}$, $h_{\max}$; $k_{\min}$, $k_{\max}$; $l_{\min}$, $l_{\max}$	-9, 9; -14, 15; 0, 24
Max, min residuals (e Å^{-3})	0.67, -0.57

sion factors were: 0.846 and 0.625). 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 they are attached. A summary of crystallographic parameters is presented in Table 1. The programs used were SHELXS-86, [11] SHELXL-97 [12] and ZORTEP [13], PARST-95 [14] and IVTON [15].

4. Results and discussion

According to CHN analyses and titration with EDTA the following composition was evidenced: Ln(pic)$_3$ (pyzDO)$_{1.5}$ (H_2O)$_8$ (Ln=Pr, Nd, Sm, Eu; pic=picrate; pyzDO=1,4-pyrazine-dioxide). X-ray powder patterns indicate that they are isomorphous.

IR absorption spectral data show small shifts of νNO (~1252 cm^{-1}) and δ NO (854$_w$ cm^{-1}), of pyzDO to lower frequencies when compared with that of the free ligand (1258$_s$, 882$_w$ cm^{-1}), indicating coordination through the oxygen. Picrate ion bands [ν_{as}(NO_2) at ca. 1570$_s$ and 1545$_s$, and ν_s(NO_2) at ca. 1370$_s$ and 1340$_s$ cm^{-1}], suggest that these ions are coordinated through the phenolic oxygen and another *o*-nitrogroup oxygen. Water bands were also noted.

The visible absorption spectrum of the neodymium compound was determined from the $^2G_{7/2}$, $^4G_{5/2} \leftarrow {}^4I_{9/2}$ transitions and the following parameters were calculated: nephelauxetic parameter [16] ($\beta=0.985$), covalent factor [17] ($b^{1/2}=0.087$) and Sinha's parameter [18] ($\delta=1.52$); these values indicate the existence of a small covalent character in the metal–ligand bonds.

Bond distances and selected bond angles around the Eu(III) ion are shown in Table 2. Fig. 1 shows a ZORTEP plot of the coordination polyhedron. The Eu(III) ion

Table 2
Bond lengths [Å] and angles [°] around the Eu atom

Eu–O(1A)	2.359(3)
Eu–O(11A)	2.702(3)
Eu–O(1D)	2.399(3)
Eu–O(1W)	2.419(3)
Eu–O(2W)	2.489(3)
Eu–O(3W)	2.426(3)
Eu–O(4W)	2.428(3)
Eu–O(5W)	2.417(3)
Eu–O(6W)	2.433(3)
O(1A)–Eu–O(11A)	63.52(9)
O(1A)–Eu–O(1D)	85.40(11)
O(1A)–Eu–O(1W)	128.94(10)
O(1A)–Eu–O(2W)	143.42(10)
O(1A)–Eu–O(3W)	135.93(10)
O(1A)–Eu–O(4W)	80.13(10)
O(1A)–Eu–O(5W)	80.32(11)
O(1A)–Eu–O(6W)	68.31(10)
O(1D)–Eu–O(11A)	130.86(12)
O(1D)–Eu–O(1W)	136.97(10)
O(1D)–Eu–O(2W)	66.23(9)
O(1D)–Eu–O(3W)	91.40(12)
O(1D)–Eu–O(4W)	145.84(11)
O(1D)–Eu–O(5W)	73.65(12)
O(1D)–Eu–O(6W)	73.51(11)
O(1W)–Eu–O(11A)	66.18(10)
O(1W)–Eu–O(2W)	71.25(9)
O(1W)–Eu–O(3W)	80.23(11)
O(1W)–Eu–O(4W)	73.79(10)
O(1W)–Eu–O(5W)	86.32(11)
O(1W)–Eu–O(6W)	137.68(11)
O(2W)–Eu–O(11A)	118.29(9)
O(2W)–Eu–O(3W)	70.31(10)
O(2W)–Eu–O(4W)	136.09(10)
O(2W)–Eu–O(5W)	70.13(10)
O(2W)–Eu–O(6W)	120.38(10)
O(3W)–Eu–O(11A)	137.54(10)
O(3W)–Eu–O(4W)	78.35(11)
O(3W)–Eu–O(5W)	140.43(10)
O(3W)–Eu–O(6W)	68.67(10)
O(4W)–Eu–O(11A)	68.15(11)
O(4W)–Eu–O(5W)	132.85(11)
O(4W)–Eu–O(6W)	72.41(11)
O(5W)–Eu–O(11A)	64.71(11)
O(5W)–Eu–O(6W)	135.78(11)
O(6W)–Eu–O(11A)	121.26(9)

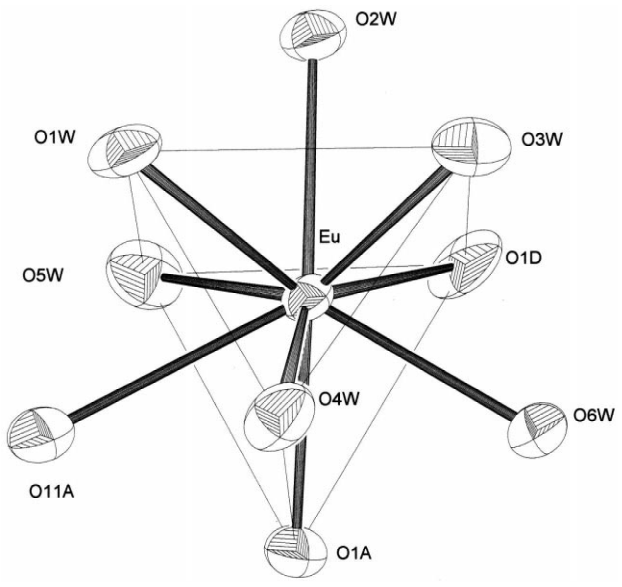

Fig. 1. Coordination polyhedron. Atoms are shown as 50% probability ellipsoids.

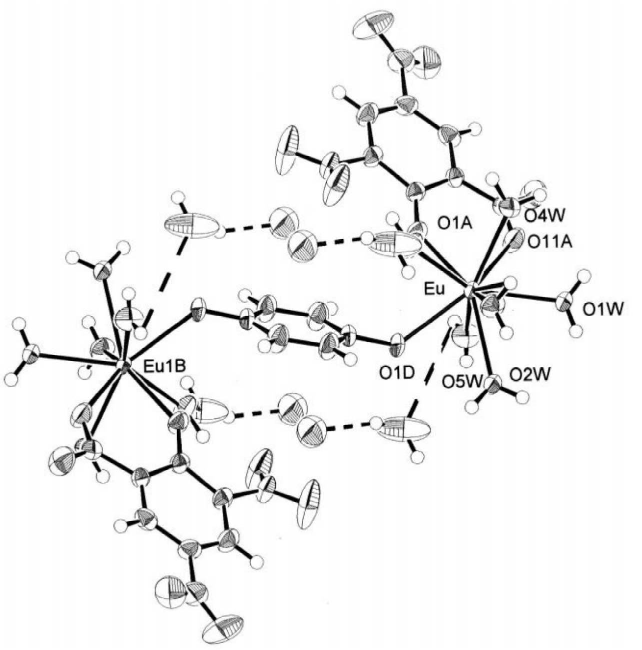

Fig. 2. The dimeric moiety. Atoms are shown as 50% probability ellipsoids.

achieves a coordination number of nine by the bonding of six water molecules, one bidentate picrate and one oxygen of a pyzDO, that is also bonded to a symmetry related Eu(III) ion, in a slightly distorted tricapped trigonal prism, the dihedral angle between the trigonal bases being of 6.5(2)°. Several geometric parameters to quantify the deformation of the coordination polyhedra, introduced by Balic Zunic and Makovicky [19] and implemented in IVTON [14], 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 atom–centroid distance (Δ) is 0.087 Å, the average distance from the centroid to the ligands (r) is 2.45 Å, and the ‘sphericity’ ($1-\sigma_r/r$) is 0.965 (σ_r is the standard deviation of the distances from the centroid to the ligands). Moreover, the Eu bond-valence parameter calculated for this structure is 2.056. The tabulated value is 2.076 [20].

The europium dimers, linked by the pyzDO molecule, are also related by hydrogen bonds through non coordinated water molecules, as can be seen in Fig. 2. O7W was found to be disordered occupying two different positions, so that it was refined with an s.o.f of 0.5. The water molecules are involved in a complex net of hydrogen bonds (Table 3).

Table 3
Hydrogen bond parameters[a]

D–H . . . A	D–H (Å)	D . . . A (Å)	H . . . A (Å)	D–H . . . A (°)
O4W–H24W . . . O1B(0)	0.92	2.759(4)	1.84	171.2
O6W–H16W . . . O31A(0)	0.89	2.854(4)	2.04	151.2
O8W–H18W . . . O7W(0)	0.78	2.499(11)	1.75	162.0
O1W–H1W1 . . . O1C(1)	0.83	2.711(4)	1.89	169.9
O2W–H22W . . . O1C(1)	0.85	2.721(4)	1.92	157.7
O1W–H2W1 . . . O1E(2)	0.84	2.785(5)	2.00	155.8
O4W–H14W . . . O1E(2)	0.87	2.775(4)	1.99	150.2
O3W–H23W . . . O2E(3)	0.90	2.707(4)	1.81	172.6
O2W–H12W . . . O22A(3)	0.95	2.963(4)	2.03	168.0
O3W–H13W . . . O21C(4)	0.89	2.984(4)	2.28	135.9
O5W–H15W . . . O1B(5)	0.84	2.781(4)	2.02	150.3
O5W–H25W . . . O8W(6)	0.76	2.892(6)	2.39	134.9
O6W–H26W . . . O8W(7)	0.85	2.687(6)	1.87	162.3
O8W–H28W . . . O21B(8)	0.83	2.906(6)	2.09	164.5

[a] Equivalent positions: (0): x, y, z; (1): $x+1, y-1, z$; (2): $-x-2, -y+2, -z+2$; (3): $x, y-1, z$; (4): $-x-2, -y+1, -z+2$; (5): $x+1, y, z$; (6): $-x, -y+1, -z+1$; (7): $-x-1, -y+1, -z+1$; (8): $-x-1, -y+2, -z+1$.

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