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Hydrated lanthanides picrate complexes with *cis*-1,3-dithiane-1,3-dioxide (*cis*-DTSO$_2$). Structure of the Ho compound

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Abstract

Compounds with composition [Ln(*cis*-DTSO$_2$)$_4$(H$_2$O)$_2$](pic)$_3$ (pic=picrate, Ln=Pr–Lu and Y) were obtained by reaction of hydrated lanthanide picrate with *cis*-DTSO$_2$ in absolute ethanol. The adducts were characterized by elemental analyses and IR spectra. The parameters obtained from the absorption spectrum of the solid Nd compound indicate that the metal–ligand bonds present weak covalent character. The low intensity emission spectrum obtained at 77 K for the Eu compound indicates the existence of dimeric species. X-ray powder patterns show only one isomorphous series. X-ray single-crystal data of the holmium compound showed that the crystal system is triclinic, space group $P\bar{1}$, $a=13.387(1)$ Å, $b=14.243(1)$ Å, $c=14.965(1)$ Å, $\alpha=99.879(8)°$, $\beta=102.063(9)°$, $\gamma=101.620(1)$. The Ho ion achieves a coordination number of eight by the bonding of two oxygens of one bidentate *cis*-DTSO$_2$, four oxygens of four monodentate *cis*-DTSO$_2$, one of which acts as a bridge between two neighboring Ho ions, and two water molecules, giving rise to a distorted square antiprism polyhedron. The picrate anions are not bonded to the Ho(III) ion. The crystal packing is governed by an intricate net of hydrogen bonds.

Keywords: Chemical synthesis; Crystal structure and symmetry; X-ray diffraction; Luminescence

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1. Introduction

The coordination chemistry of lanthanides is an area of increasing interest due to the wide range of applications of these compounds as luminescent probes, solid-state lasers, contrast agents in MRI, catalysts and other uses [1].

Adducts between lanthanide picrates and sulfoxides are under investigation in our laboratories. Complexes with the following compositions were obtained: Ln(pic)$_3$·3DTSO (DTSO=1,3-dithiane-1-oxide) [2]; Ln(pic)$_3$·nL (L=dibenzylsulfoxide, Ln=La, Eu; $n=3$; Ln=Yb, $n=2$) [3]; Ln(pic)$_3$·4L (L=benzyl-*t*-butylsulfoxide, Ln=Nd, Eu, Tb) [4]; Ln(pic)$_3$·3TMSO (TMSO=tetramethylenesulfoxide) [5,6]; Ln(pic)$_3$·3DMSO (DMSO=dimethylsulfoxide) [7–9]; Ln(pic)$_3$·2(rac-besm) (rac-besm=D,L-bis(ethylsufinyl)methane) [10,11]; Ln(pic)$_3$·1.5TDTD (TDTD=*trans*-1,4-dithiane-1,4-dioxide) [12,13].

This article describes the preparation, characterization by microanalytical procedures and EDTA titrations, infrared absorption spectroscopy, emission and absorption spectroscopy, X-ray powder analyses and structural study of the holmium(III) complex.

2. Experimental

The ligand *cis*-1,3-dithiane-1,3-dioxide was prepared together with the *trans* isomer by oxidation of *cis*-1,3-dithiane-1-oxide (DSTO) [1,14] with *m*-chloroperoxybenzoic acid [15]. A 10 mmol DTSO solution in 50 ml of dichloromethane at 0°C was treated dropwise at low temperature, under stirring, with a 10 mmol solution of the oxidant, for 30 min. The mixture was stirred for 4 h and left standing for 48 h at 0°C. The solvent was then completely removed and the solid washed with 200 ml of ethyl ether. The white solid was a mixture of *cis* and *trans*-DTSO$_2$. The insoluble *cis*-compound was separated

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from the soluble *trans* by treatment with ethanol. The *cis* compound was washed three times with ethanol. It was characterized by CHN microanalytical procedures: C: 35.4 (35.3), H: 5.8 (5.9), S: 46.9 (47.1) for experimental and calculated values, respectively; melting range 228–230°C and IR spectra. The complexes were prepared by reaction of the hydrated picrate dissolved in absolute ethanol and treatment with a warm ligand solution in the same solvent (molar ratio 1:4). The crystals were separated and maintained under vacuum over anhydrous calcium chloride.

Lanthanide ions were determined by complexometric titration with standard 0.01 mol l^{-1} EDTA using an acetic acid/sodium acetate buffer (pH = 5.8) and xylenol-orange as indicator. CHN microanalytical procedures were performed using a Perkin-Elmer 240 elemental analyzer.

Melting range was determined in a Quimis model Q.340.21/3 apparatus. IR spectra were recorded on a Nicolet FTIR-8100 spectrometer using KBr pellets. Conductance measurements were performed at 25.00±0.02°C, using an apparatus composed of a resistance box, a pointer galvanometer and a cell ($k_{cell} = 0.1233$ cm^{-1}) from Leeds and Northrup. The absorption spectrum of the Nd complex in nitromethane solution at room temperature was obtained on a Carl Zeiss DMR-10 spectrophotometer. The emission spectrum of the europium complex at 77 K was recorded on a Hitachi Perkin-Elmer MPF-4 spectrofluorimeter using 394 nm excitation radiation. X-ray powder patterns were obtained on a Rigaku Denke RU-200B instrument, using CuKα radiation.

2.1. Crystal structure determination

X-ray crystallographic data were recorded on an Enraf-Nonius CAD-4 Mach 3 diffractometer. Cell parameters were determined on the basis of 25 reflections; intensity data were obtained in the $\omega/2\theta$ scan mode, using graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å) at room temperature (293 K). During data collection the intensity of three standard reflections were monitored every 30 min of X-ray exposure time showing no significant decay. Data were corrected for Lorentz, polarization and absorption effects. The structure of the Ho compound was solved by the standard Patterson heavy atom method, followed by normal difference Fourier techniques. All non-H atoms were refined anisotropically on F^2. The H-atoms were located on stereochemical grounds, except those of the water molecules that were found in difference Fourier maps, but all were refined riding on a carrier atom, with an isotropic displacement parameter amounting to 1.2 the value of B_{eq} of the atom they are attached to. Programs used were SHELXS-86 [16], SHELXL-97 [17] and ZORTEP [18].

3. Results and discussion

The complexes with composition [Ln(*cis*-DTSO$_2$)$_4$(H$_2$O)$_2$](pic)$_3$, where Ln = Pr–Lu and Y, were characetrized by CHN mycroanalytical procedures confirming the proposed stoichiometry. Lanthanide contents were determined by EDTA titration. The IR spectra showed three bands at ca. 1046, 1011 and 974 cm^{-1}, indicating that the *cis*-DTSO$_2$ ligands are not coordinated in the same fashion. The free ligand shows νSO at 1055 and 1011 cm^{-1}. The bands due to the picrate anions, ν_{as} NO$_2$ and ν_s NO$_2$ at ca. 1559 and 1346 cm^{-1} indicate that they are not coordinated.

Conductance measurements in nitromethane ($\Lambda_M^- = 60$ S cm^2 mol^{-1}) show that the complexes behave as non-electrolytes [19].

Absorption spectra of the Nd complex were registered in the solid state and in nitromethane solution, at room temperature for the $^2G_{7/2}$, $^4G_{5/2} \leftarrow {}^4I_{9/2}$ transitions. The calculated specroscopic parameters: nephelauxetic ($\beta = 0.991$), covalent factor ($b^{1/2} = 0.069$) and Sinha's ($\delta = 0.96$) indicate that the metal–ligand bonds present some covalent character [20–22]. The oscillator strength in acetonitrile solution ($P \times 10^6 = 15.6$) was also determined. The low intensity emission spectrum, Fig. 1, obtained at 77 K for the Eu compound shows a weak peak due to $^5D_0 \rightarrow {}^7F_0$ (A_1 species), three peaks due to $^5D_0 \rightarrow {}^7F_1$ (one A_2 and one E species, the latter split into two peaks), a rather broad $^5D_0 \rightarrow {}^7F_2$ band indicating the existence of at least dimeric species and two broad weak peaks due to $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$, respectively.

X-ray powder patterns show only one isomorphous series. The structure of the holmium compound was determined by single crystal X-ray analysis. Table 1 presents the crystal data collection and refinement data, Table 2 presents the non-H atomic coordinates. Fig. 2 shows the coordination polyhedron, and Fig. 3 the structure.

The Ho^{+3} ion achieves a coordination number of eight by the bonding of two oxygens of one bidentate *cis*-DTSO$_2$, four oxygens of four monodentate *cis*-DTSO$_2$, one of which acts as a bridge between two neighboring Ho

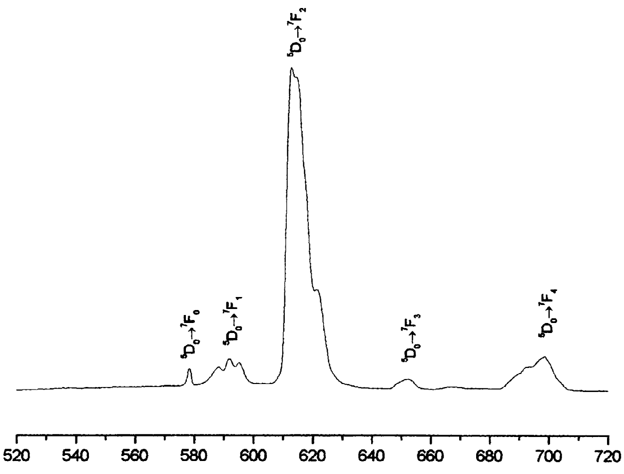

Fig. 1. Emission spectrum of the Eu complex.

Table 1
Crystallographic data and details of the structure refinement

Empirical formula	$C_{34}H_{42}N_9HoO_{31}S_8$
Formula weight	1494.18
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system,	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	13.387(1)
b (Å)	14.243(1)
c (Å)	14.965(1)
α (°)	99.879(8)
β (°)	102.063(9)
γ (°)	101.620(1)
Volume (Å^3)	2664.3(3)
Molecules per cell, Z	2
Calculated density, D_c, (g cm^{-3})	1.862
Absorption coefficient, μ (mm^{-1})	1.903
$F(000)$	1504
Crystal size (mm)	0.15×0.25×0.45
θ range for data collection (°)	1.43–25.44
Reflections collected	10175
Reflections collected/unique	9872 [R(int)=0.0341]
Data/restraints/parameters	9772/12/767
Goodness-of-fit (S) on F^2	1.039
Limiting indices	$-16 \leq h \leq 15$, $-17 \leq k \leq 16$, $0 \leq l \leq 18$
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0278$, $wR_2 = 0.0685$
R indices (all data)	$R_1 = 0.0462$, $wR_2 = 0.0742$

atoms, in agreement with the mentioned broad band in the emission spectrum, and two oxygens of two water molecules, in a distorted square antiprism fashion. The dihedral angle between the square faces is 3.3(1)°. The picrate anions are not bonded to the Ho(III) ion. The crystal packing is governed by an intricated net of hydrogen bonds as shown in Table 3.

Several geometric parameters to quantify the deformation of the coordination polyhedron, introduced by Balic Zunic and Makovicky [23] and implemented in IVTON [24], 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) of 0.029 Å, the average distance from the centroid to the ligands (r) is 2.348 Å, and the 'sphericity' ($1 - \sigma_r/r$) is of 0.982 (σ_r is the standard deviation of the distances from the centroid to the ligands). Moreover, the bond-valence parameter calculated for this structure is 2.021 (the tabulated value is 2.023) [25].

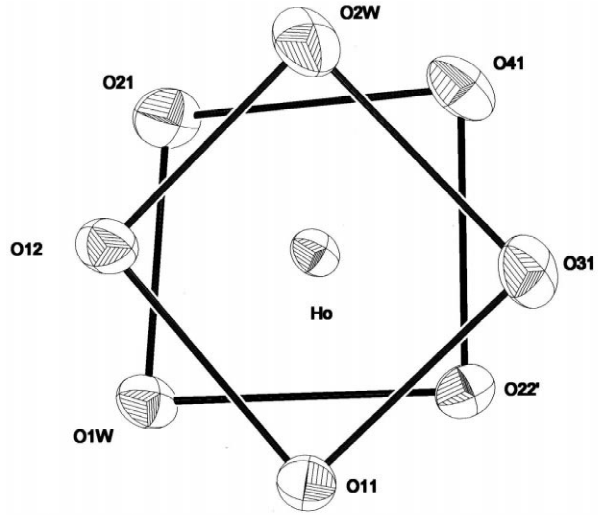

Fig. 2. View of the coordination polyhedron. Atoms are shown as 50% probability ellipsoids.

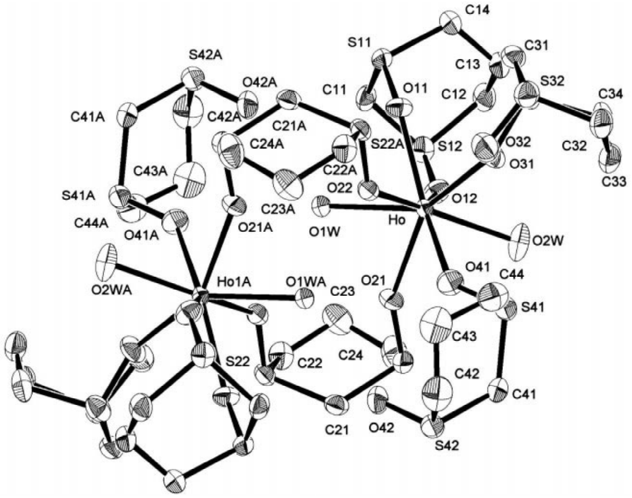

Fig. 3. Structure of the holmium complex. Atoms are shown as 50% probability ellipsoids.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$)

	x	y	z	U(eq)[a]
Ho	1698(1)	−268(1)	1227(1)	20(1)
S(11)	3440(1)	2213(1)	1707(1)	26(1)
S(12)	4082(1)	624(1)	443(1)	30(1)
S(21)	777(1)	−2263(1)	−889(1)	32(1)
S(22)	−449(1)	−1345(1)	−2370(1)	26(1)
S(31)	2985(1)	514(1)	3697(1)	35(1)
S(32)	1322(1)	514(1)	4898(1)	36(1)
S(41)	272(1)	−2339(1)	1917(1)	33(1)
S(42)	−1799(1)	−3444(1)	377(1)	36(1)
O(11)	2588(2)	1376(2)	1806(2)	30(1)
O(12)	3187(2)	−100(2)	625(2)	33(1)
O(21)	976(2)	−1286(2)	−221(2)	37(1)
O(22)	335(2)	434(2)	1614(2)	27(1)
O(31)	2101(2)	−52(2)	2847(2)	39(1)
O(32)	420(2)	94(2)	4047(2)	45(1)
O(41)	386(2)	−1535(2)	1382(2)	38(1)
O(42)	−1677(2)	−2632(2)	−144(2)	39(1)
O(1W)	1223(2)	599(2)	−5(2)	29(1)
O(2W)	2635(2)	−1484(2)	1496(2)	45(1)
O(1A)	385(3)	−6603(2)	3693(2)	69(1)
O(14A)	−100(30)	−5471(17)	2514(14)	65(7)
O(11A)	−490(20)	−5491(16)	2684(18)	77(5)
O(12A)	350(30)	−3960(13)	2974(16)	63(5)
O(13A)	−70(30)	−3995(12)	3148(14)	72(6)
O(21A)	2207(3)	−2316(2)	6083(2)	56(1)
O(22A)	2905(3)	−3118(3)	7043(2)	55(1)
O(31A)	2220(4)	−6667(3)	6142(4)	101(2)
O(32A)	727(4)	−7380(3)	5202(4)	99(2)
O(1B)	2992(2)	−2586(2)	2842(2)	44(1)
O(11B)	4922(3)	−1978(2)	4289(3)	62(1)
O(12B)	4236(3)	−2435(3)	5368(2)	71(1)
O(22B)	2695(3)	−6909(2)	3326(2)	57(1)
O(21B)	3835(3)	−6106(3)	4611(3)	73(1)
O(32B)	1126(3)	−5212(3)	1163(3)	72(1)
O(31B)	1942(3)	−3758(3)	1132(2)	69(1)
O(1C)	4462(3)	−1774(2)	751(2)	56(1)
O(11C)	5124(4)	−940(3)	2632(3)	82(1)
O(12C)	6501(3)	−1445(3)	3177(3)	76(1)
O(21C)	5474(4)	−5036(3)	2859(3)	80(1)
O(22C)	4698(3)	−5918(2)	1457(3)	73(1)
O(31C)	3688(3)	−3024(3)	−915(3)	78(1)
O(32C)	3069(4)	−4535(3)	−890(3)	102(2)
N(1A)	149(3)	−4776(3)	3197(2)	44(1)
N(2A)	2363(3)	−3085(3)	6288(2)	39(1)
N(3A)	1483(4)	−6659(3)	5533(3)	56(1)
N(1B)	4330(3)	−2569(2)	4565(2)	37(1)
N(2B)	3243(3)	−6138(3)	3851(3)	43(1)
N(3B)	1824(3)	−4444(3)	1516(2)	41(1)
N(1C)	5645(3)	−1560(3)	2623(3)	54(1)
N(2C)	5049(3)	−5120(3)	2033(3)	54(1)
N(3C)	3590(3)	−3701(3)	−501(3)	55(1)
C(11)	3759(3)	1799(3)	614(3)	29(1)
C(12)	5181(3)	876(3)	1457(3)	35(1)
C(13)	4920(3)	1197(3)	2381(3)	35(1)
C(14)	4631(3)	2186(3)	2505(3)	33(1)
C(21)	−391(3)	−2347(3)	−1777(2)	28(1)
C(22)	785(3)	−1191(3)	−2694(3)	34(1)
C(23)	1760(3)	−1122(3)	−1930(3)	43(1)
C(24)	1732(3)	−2057(4)	−1562(3)	47(1)
C(31)	2415(3)	1165(3)	4511(3)	34(1)
C(32)	1855(4)	−493(3)	5209(3)	40(1)
C(33)	2294(4)	−1041(3)	4478(3)	41(1)
C(34)	3273(3)	−419(3)	4311(3)	42(1)
C(41)	−507(3)	−3442(3)	1053(3)	34(1)
C(42)	−2334(4)	−3034(4)	1347(4)	51(1)
C(43)	−1715(4)	−2050(4)	1973(3)	52(1)
C(1A)	802(3)	−5823(3)	4269(3)	39(1)
C(2A)	766(3)	−4856(3)	4096(3)	33(1)
C(3A)	1261(3)	−3985(3)	4740(3)	32(1)
C(4A)	1861(3)	−4002(3)	5605(3)	31(1)
C(5A)	1957(3)	−4887(3)	5842(3)	36(1)
C(6A)	1431(3)	−5750(3)	5217(3)	36(1)
C(1B)	3066(3)	−3396(3)	3021(3)	30(1)
C(2B)	3701(3)	−3480(3)	3910(3)	31(1)
C(3B)	3754(3)	−4331(3)	4191(3)	33(1)
C(4B)	3181(3)	−5222(3)	3575(3)	34(1)
C(5B)	2561(3)	−5232(3)	2703(3)	34(1)
C(6B)	2510(3)	−4362(3)	2439(3)	31(1)
C(1C)	4608(3)	−2522(3)	1030(3)	36(1)
C(2C)	5196(3)	−2510(3)	1967(3)	37(1)
C(3C)	5365(3)	−3322(3)	2296(3)	41(1)
C(4C)	4927(3)	−4244(3)	1701(3)	38(1)
C(5C)	4352(3)	−4345(3)	794(3)	41(1)
C(6C)	4204(3)	−3526(3)	462(3)	39(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Hydrogen bonds parameters[a]

D–H . . . A	D . . . A (Å)	H . . . A (Å)	D–H . . . A (°)
O2W–H12W···O1C	2.963(5)	2.18	157.1
O2W–H22W···O1B	2.780(5)	1.92	174.0
O1W–H21W···O22^{i}	2.785(3)	1.93	156.5
O1W–H11W···O42^{i}	2.795(4)	1.95	161.0
C11–H11B···O31C^{ii}	3.408(6)	2.53	150.8
C21–H21B···O14A^{iii}	3.360(3)	2.55	140.9
C21–H21B···O1A^{iii}	3.000(5)	2.19	140.0
C43–H43B···O12C^{iv}	3.433(7)	2.48	168.4

[a] Symmetry operations: (i) $-x, -y, -z$; (ii) $-x+1, -y, -z$; (iii) $-x, -y-1, -z$; (iv) $x-1, +y, +z$.

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