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Neodymium(III) and europium(III) picrate complexes with 2-azacyclononanone: spectroscopy and structure

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Abstract—Complexes with composition $Ln(pic)_3 \cdot 3(aza)$ (Ln = Nd, Eu; pic = picrate; aza = 2-azacyclononanone) were characterized by IR absorption spectroscopy and elemental analysis. Visible absorption spectra for the Nd compound and emission spectra for the Eu compound were also recorded. X-ray single crystal diffraction analysis of the Eu compound shows that the picrates are bidentate, bonded through the phenolic and one *o*-nitrogroup oxygens and the 2-azacyclononanones are bonded through the carbonyl oxygens, forming a tricapped trigonal prism with D_{3h} symmetry distorted towards C_{3v} around the Eu^{3+} ion, which is in agreement with the emission spectra evidence. © 1997 Elsevier Science Ltd

Keywords: neodymium; europium; picrate complexes; 2-azacyclononanone; X-ray diffraction; spectroscopy.

Complexes of lanthanide picrates with several organic sulfoxides [1–5], phosphine oxides [6], N-oxides [5,7,8], amides [9,10] and lactams [11], have been described previously. In this paper characterization and structure (for the Eu compound) of neodymium and europium picrate (pic) complexes with 2-azacyclononanone (aza), with composition $Ln(pic)_3 \cdot 3(aza)$ (Ln = Nd, Eu) are reported. These complexes were characterized by IR absorption spectrometry, absorption spectra of the Nd compound, emission spectra and X-ray single crystal analysis of the Eu compound.

EXPERIMENTAL

The synthesis and characterization of a series of complexes of lanthanide and yttrium picrates with 2-azacyclononanone and their thermal analysis will be described [12] elsewhere. The complexes were prepared by direct reaction of neodymium and europium picrates with the ligand in ethanolic solution. Single crystals of the Eu compound were obtained by slow evaporation of an ethanolic solution. Metal ion concentrations were determined by titrations with EDTA; CHN microanalysis were carried out on a Perkin–Elmer model 240 elemental analyzer. IR spectra were recorded on a Perkin–Elmer 1750 FTIR spectrometer, using Nujol mulls between KBr windows. Visible absorption spectra were recorded on a Zeiss DMR 10 spectrophotometer. Emission spectra were recorded on a Hitachi MPF-4 spectrofluorimeter at room temperature and 77K.

Crystal structure determination

The data was collected on a CAD-4 diffractometer, in the $\omega/2\theta$ scan mode with ω scan width $= 0.8+0.35 \tan \theta$, using graphite monochromated Mo–Kα radiation. Data was corrected for Lorentz and polarization effects. The structure was solved by the standard heavy-atom Patterson method, followed by

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Table 1. Infrared absorption frequencies for the Nd and Eu picrate complexes with 2-azacyclononanone (values are expressed in cm^{-1})

Ln	$\nu_{as}NO_2$	ν_sNO_2	νCO	νCN	δNO_2
Nd	1534 1566	1368 1324	1267	921 780	838
Eu	1536 1568	1367 1326	1269	921 781	839

normal difference Fourier techniques. Refinement was carried out by full-matrix least-squares. The programs used were: SHELX-76 [13], SHELXS-86 [14] and ORTEP [15]. Scattering factors for non-hydrogen atoms were taken from ref. [16] and corrections for anomalous dispersion from ref. [17] and for H-atoms from ref. [18]. Hydrogen atoms were included, as fixed contributors, on stereochemical ground with an overall isotropic temperature factor that refined to 0.121 (8) Å^2.

Further details were deposited with the Editor as supplementary material at the Cambridge Crystallographic Data Centre.

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

RESULTS AND DISCUSSION

Metal titrations with EDTA and CHN analysis showed evidence pointing towards a general composition Ln(pic)$_3$ · 3(aza) for the whole lanthanide and Y series. X-ray powder diffraction patterns shows that all compounds constitute one isomorphous series [12].

Infrared absorption spectral data for the Nd and Eu complexes are summarized in Table 1. Bands

Table 2. Summary of data collection and crystal parameters

Empirical formula	$C_{42}H_{48}EuN_{12}O_{24}$
Formula weight	1256.88
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 13.981(2) Å b = 24.065(3) Å c = 15.493(2) Å β = 91.70 (1)°
Volume	5210.4(12) Å^3
Z	4
Density (calculated)	1.602 Mg/m^3
Absorption coefficient	1.300 mm^{-1}
$F(000)$	2556
Crystal size	0.30 × 0.25 × 0.18 mm
θ range	1.56—25 deg
Index ranges	$-7 < h < 16, 0 < k < 28, -18 < l < 18$
Reflections collected	9541
Independent reflections	9142 [R(int) = 0.0331]
Observed reflections	3997
R indices [$I > 3\sigma(I)$]	R = 0.0536, wR = 0.0548

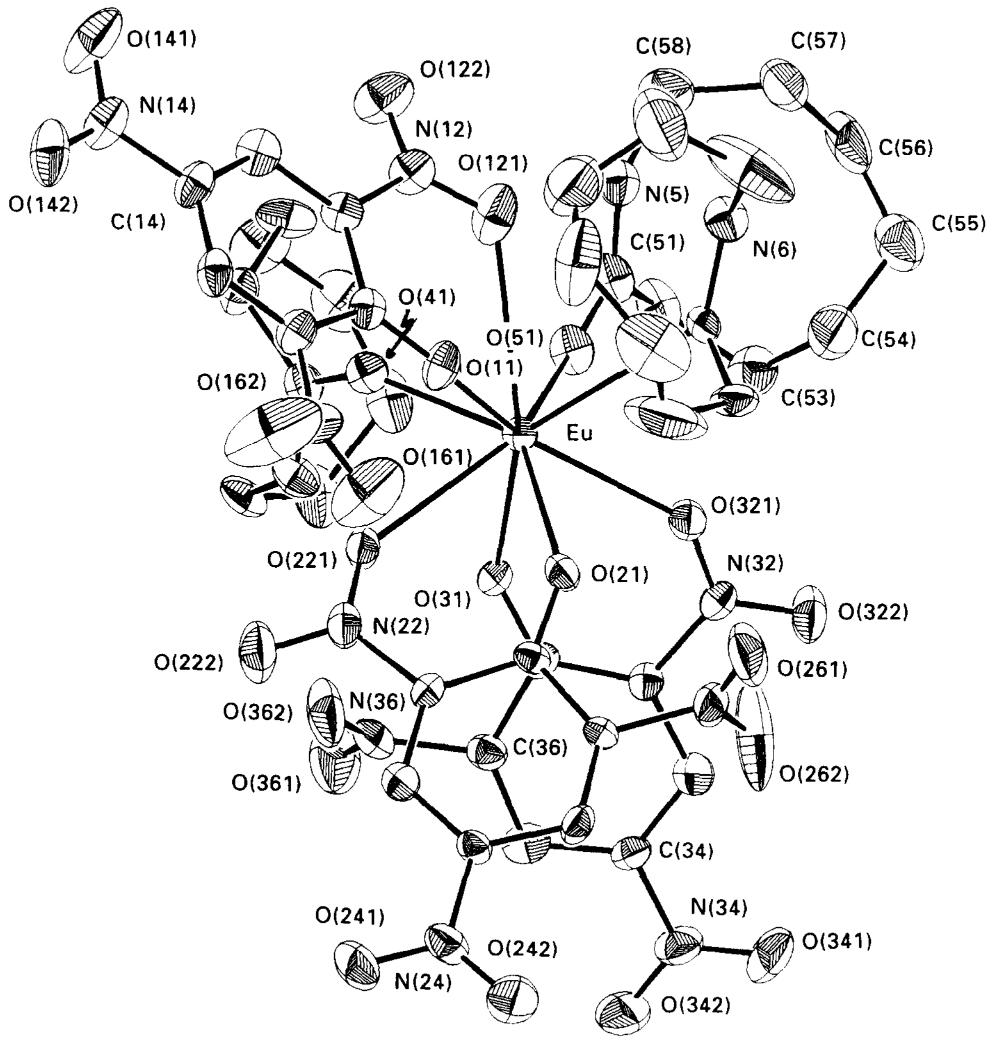

Fig. 2. ORTEP view of the complex.

related to the picrate ion ($\nu_{as}NO_2$, at *ca* 1560 and 1530 cm^{-1} and ν_sNO_2, at *ca* 1360 and 1320 cm^{-1}) suggest that these anions are coordinated through the phenolic oxygen and another *o*-nitrogroup oxygen [19]. Furthermore, νCO appears at 1260 cm^{-1}, while in the free ligand it appears at 1643 cm^{-1}, evidencing bonding of the 2-azacyclononanones through the carbonyl oxygens.

In the visible absorption spectra of the Nd compound the $^2G_{7/2}$, $^4G_{5/2} \leftarrow {}^4I_{9/2}$transitions appears, with baricenter at 17,071 cm^{-1}. The nephelauxetic parameter [20] ($\beta = 0.895$), covalent factor [21] ($b^{1/2} = 0.087$) and Sinha's parameter [22] ($\delta = 1.52$) were calculated. These values indicate that the metal–ligand bonds are essentially electrostatic, with a small covalent character. It is interesting to point out that both the spectrum and the values of the parameters are identical, within experimental accuracy, to those observed for Nd(pic)$_3$·3(DMA) (DMA = N,N-dimethylacetamide) [10], suggesting structural similarity.

The luminescence spectrum of the Eu compound at 77K is shown in Fig. 1. The appearance of the peaks in the $^5D_0 \rightarrow {}^7F_1$ transition, where $^7F_1$ is split by the crystalline field into three levels (one A_2 and one E, this latter split into two components) and five peaks in the $^5D_0 \rightarrow {}^7F_2$ transitions, where $^7F_2$ is split in two E and one A_2 species, suggest a D_{3h} symmetry for the coordination polyhedron around the Eu^{3+} ion [23,24]. The appearance of a very small $^5D_0 \rightarrow {}^7F_0$ peak indicates a slight distortion of this polyhedron towards C_{3v} symmetry.

Again, in this case this emission spectrum is almost identical to that of Nd(pic)$_3$·3(DMA) [10]. In both cases the proposed symmetries of the coordination polyhedra are in good agreement with those determined by single crystal X-ray diffraction.

Tables 2 and 3 present the crystallographic data and distances and angles around the Eu^{3+} ion, as determined from single crystal X-ray diffraction. The ORTEP view of the molecule is shown in Fig. 2 and the coordination polyhedron in Fig. 3.

Table 3. Distances (Å) and angles (°) around the europium

Eu—O(11)	2.339(7)
Eu—O(121)	2.88(1)
Eu—O(21)	2.325(7)
Eu—O(221)	2.641(7)
Eu—O(31)	2.370(8)
Eu—O(321)	2.581(8)
Eu—O(41)	2.331(7)
Eu—O(51)	2.337(8)
Eu—O(6)	2.302(7)
O(11)—Eu—O(121)	58.8(3)
O(11)—Eu—O(21)	84.2(3)
O(11)—Eu—O(221)	67.9(2)
O(11)—Eu—O(31)	137.5(3)
O(11)—Eu—O(321)	142.4(3)
O(11)—Eu—O(41)	78.9(3)
O(11)—Eu—O(51)	129.2(3)
O(11)—Eu—O(6)	80.6(3)
O(121)—Eu—O(21)	134.7(3)
O(121)—Eu—O(221)	114.9(2)
O(121)—Eu—O(31)	145.0(3)
O(121)—Eu—O(321)	123.4(3)
O(121)—Eu—O(41)	67.4(3)
O(121)—Eu—O(51)	70.8(3)
O(121)—Eu—O(6)	64.7(3)
O(21)—Eu—(221)	65.9(2)
O(21)—Eu—O(31)	79.9(3)
O(21)—Eu—O(321)	70.6(3)
O(21)—Eu—O(41)	134.0(3)
O(21)—Eu—O(51)	142.1(3)
O(21)—Eu—O(6)	85.9(3)
O(221)—Eu—O(31)	69.6(2)
O(221)—Eu—O(321)	121.5(2)
O(221)—Eu—O(41)	68.1(2)
O(221)—Eu—O(51)	137.0(3)
O(221)—Eu—O(6)	138.9(2)
O(31)—Eu—O(321)	65.9(3)
O(31)—Eu—O(41)	84.5(3)
O(31)—Eu—O(51)	83.2(3)
O(31)—Eu—O(6)	136.4(3)
O(321)—Eu—O(41)	138.6(3)
O(321)—Eu—O(51)	71.6(3)
O(321)—Eu—O(6)	70.5(3)
O(41)—Eu—O(51)	76.9(3)
O(41)—Eu—O(6)	131.9(3)
O(51)—Eu—O(6)	83.5(3)

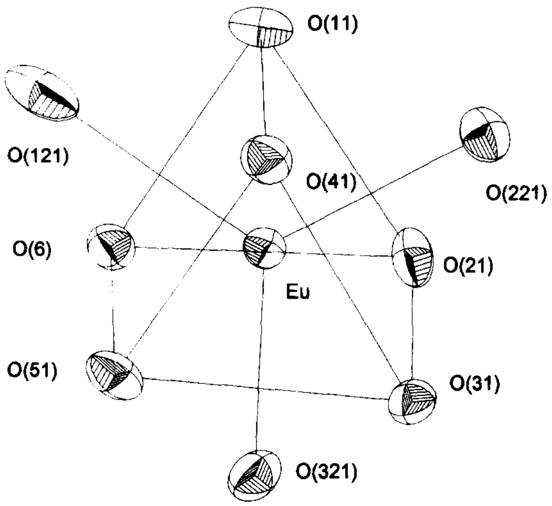

Fig. 3. Details of the coordination polyhedron.

The coordination polyhedron can be described as a slightly distorted tricapped trigonal prism, with three bidentate picrates coordinated through the phenoxy and *o*-nitrogroup oxygens and three 2-azacyclononanones coordinated through their carbonyl oxygens (as suggested by the IR spectra).

Concluding, it can be postulated that in the Nd and Eu compounds, spectroscopical behaviors are determined solely by the coordination polyhedra symmetries. Furthermore, in view of the structures determined for the aza and DMA complexes, emission spectra of the Eu compounds appears also to be a reliable method for indicating symmetries of coordination polyhedra for this type of compounds.

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