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Synthesis, characterization and structure of lanthanide nitrate complexes with 2-azacyclononanone (AZA)

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Abstract

Complexes with composition [Ln(NO$_3$)$_3$(AZA)$_3$] (Ln=Nd, Eu, Gd, Tb, Ho and Er) were synthesized and characterized by CHN elemental analyses and lanthanide titration with EDTA. IR spectra show that they are anhydrous and the ligands (AZA) bonded through the carbonyl oxygen; nitrate counter-ions are bidentate, linked to the central ions. The emission spectrum of the europium complex was interpreted in terms of a D_{3h} distorted to C_{3v} symmetry. The structure, determined by X-ray single crystal studies is described as a distorted tricapped trigonal prism with the AZA ligands bonded to one of the bases of the prism and nitrates with one oxygen bonded to one of the bases of the prism and the other forming one of the caps. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Lanthanides; 2-Azacyclononanone; Structure

1. Introduction

Lanthanide complexes containing lactams as neutral ligands have been studied in our laboratories. Compounds with δ-valerolactam (VL) with formulas: Ln (TFMS)$_3$.8VL (TFMS=CF$_3$SO$_3^-$, Ln=La−Lu) [1]; Ln(ClO$_4$)$_3$.8VL (Ln=La−Ho), Ln(ClO$_4$)$_3$.7VL (Ln=Er−Lu) [2,3]; Ln (ReO$_4$)$_3$.8VL (Ln=Pr, Nd, Sm, Eu), Tb (ReO$_4$)$_3$.7VL [4] were synthesized and studied. Complexes with ϵ-caprolactam (CAP) with compositions: La (DCA)$_3$.3CAP (DCA=dichloroacetate), Ln (DCA)$_3$.1.5CAP (Ln=Ce, Gd) [5], Ln (pic)$_3$.3CAP (pic=picrate Ln=Gd, Tb, Dy, Eu) [6] and Ln (TFMS)$_3$.8CAP (Ln=La–Eu), Ln (TFMS)$_3$.7CAP (Ln=Gd, Tb, Dy, Yb, Lu) [7] were also prepared and characterized.

The 2-azacyclononanone (AZA) was used for the preparation of rare-earth picrate compounds Ln (pic)$_3$.3AZA (Ln=Nd, Eu) that were characterized by spectroscopic methods, X-ray structure determination [8] and thermal studies [9].

In this article the complexes formed by reaction of hydrated lanthanide nitrate and AZA with composition [Ln(NO$_3$)$_3$(AZA)$_3$] (Ln=Nd, Eu, Gd, Tb, Ho and Er) are described. They were characterized by microanalytical procedures, titration of the lanthanides with EDTA, IR spectra, emission spectra of the europium compound at room temperature and at 77 K and X-ray single crystal structural studies. The interest in such compounds is related to properties concerning bonding of the nitrate counter-ions, bonding of the aza ligands, thermal behaviour and correlations between structure and spectroscopy of the compounds.

2. Experimental

The complexes were prepared by reaction of the hydrated lanthanide nitrates with AZA in ethanol using a 1:3 molar ratio, filtered, washed with a small volume of ethanol and dried in vacuo over anhydrous calcium chloride.

IR spectra were performed on a FT-IR Prospect R-MIDAC apparatus, using KBr pellets. Emission spectra of the europium compound were recorded on a Hitachi-Perkin Elmer MPF-4 spectrofluorimeter using 394 nm excitation radiation at room temperature and at 77 K. The absorption spectrum of the neodymium compound was obtained at

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Table 1
Summary of analytical results (%) for [Ln$(NO_3)_3$(AZA)$_3$] compounds

Lanthanide	Ln		C		H		N	
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.
Nd	19.2	19.4	38.3	38.6	6.0	5.8	11.2	11.0
Eu	19.9	19.6	37.8	37.9	5.9	5.6	11.0	11.0
Gd	20.5	20.4	37.5	37.3	5.9	5.8	10.9	10.8
Tb	20.7	21.1	37.5	36.9	5.8	5.6	10.9	10.8
Ho	21.3	21.6	37.2	37.2	5.8	5.6	10.8	10.6
Er	21.5	21.6	37.1	37.2	5.7	5.5	10.8	10.5

room temperature on a Carl Zeiss DMR-10 spectrophotometer using silicone mull in a 0.5 mm optical path cell.

2.1. Crystal structure determination

Data were collected on a CAD-4 Mach 3 Enraf-Nonius diffractometer in the ω/2θ scan mode, using graphite-monochromated MoKα radiation. These data were corrected for Lorentz, polarization and absorption effects. The structure of the Er compound was solved by the standard Patterson heavy-atom method, followed by normal difference Fourier techniques. H-atoms were refined with fixed geometry, each riding on a carrier atom, with an isotropic displacement parameter amounting 1.2 times the values of the equivalent isotopic displacement of the atoms they are attached. The programs used were SHELXL-97 [10], SHELXS-86 [11] and ZORTEP [12]. Further details were deposited at the Cambridge Crystallographic Data Centre.

Table 2
Infrared data (cm^{-1}) for the [Ln$(NO_3)_3$(AZA)$_3$] compounds[a]

(a)

Ln	Attributions						
	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	$\nu_{C=O}$
Nd	1279s	1027m	737w	1446s	710w	812w	1616s
Eu	1284s	1028m	738w	1448s	709w	810w	1615s
Gd	1284s	1027m	739w	1449s	709w	812w	1616s
Tb	1286s	1030m	738w	1452s	700w	807w	1618s
Ho	1290s	1030m	741w	1453s	700w	807w	1618s
Er	1288s	1027m	744w	1452s	703w	810w	1618s
AZA	–	–	–	–	–	–	1647s

(b)

Ln	$\nu_2+\nu_3$	$\nu_2+\nu_5$	Δ	$\nu_4+\nu_1$
Nd	1764	1737	27	167
Eu	1766	1737	29	164
Gd	1766	1736	30	165
Tb	1768	1730	38	166
Ho	1771	1730	41	163
Er	1771	1730	41	164

3. Results and discussion

Table 1 contains a summary of the analytical results. According to the data the proposed stoichiometry was confirmed.

IR data are presented in Table 2. Shifts of νCO to lower frequencies as compared to those observed for the free

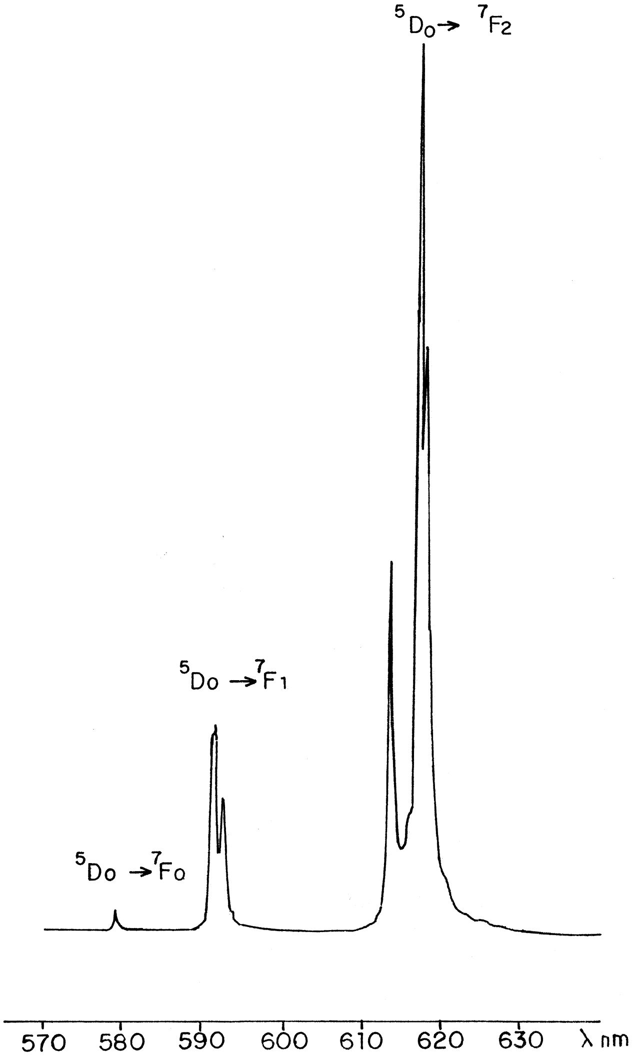

Fig. 1. Emission spectrum of [Eu$(NO_3)_3$(AZA)$_3$] at 77 K.

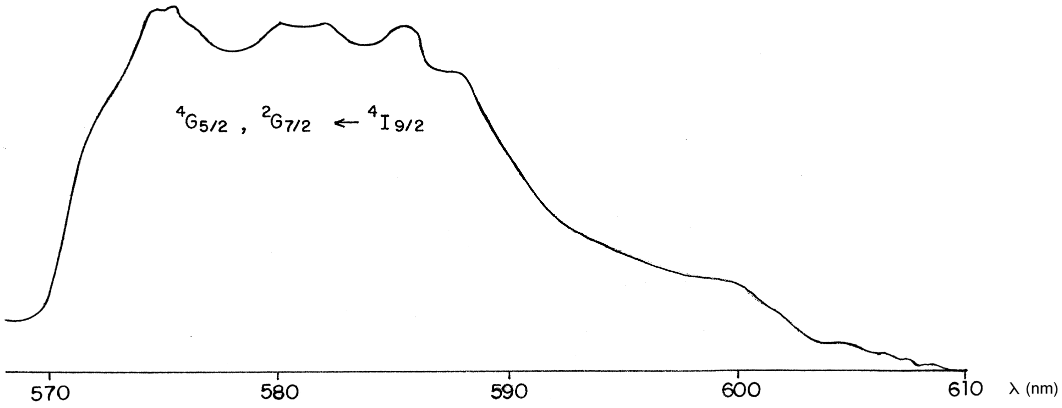

Fig. 2. Absorption spectrum of $[Nd(NO_3)_3(AZA)_3]$ at room temperature.

ligand were observed, indicating that AZA ligands are bonded through the carbonyl oxygen (Table 2).

The D_{3h} symmetry of the nitrate ion is lowered to C_{2v} or C_s when it behaves as monodentate or bidentate ligand bonded to a central ion or acts as a bridge. The number of bands increases in the infrared spectra due to the splitting of E species (ν_3 and ν_4) and IR activation of the ν_2 band [13]. In all cases several modes of coordination are possible. In this case six bands were identified indicating such symmetry lowering (Table 2a). Some considerations about infrared combination frequencies in complexes containing nitrate group are found in references [14,15]. By applying such criteria ($\nu_2+\nu_3$), ($\nu_2+\nu_5$)=($\nu_3-\nu_5$) and ($\nu_4-\nu_1$) and comparing with the data of [16] it is possible

Table 3
Crystal data collection and refinement

Empirical formula	C_{24} H_{45} Er N_6 O_{12}
Formula weight	776.92
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/a$
Unit cell dimensions	$a=14.0250(10)$ Å
	$b=12.665(2)$ Å
	$c=19.0650(10)$ Å
	$\beta=107.047(7)°$
Volume	3237.7(6) $Å^3$
Z	4
Density (calculated)	1.594 Mg m^{-3}
Absorption coefficient	2.658 mm^{-1}
F(000)	1580
Crystal size	0.30×0.20×0.20 mm
Theta range for data collection	2.21 to 25.50°
Index ranges	$-16\leq h\leq 16$, $-1\leq 5k\leq 0$, $0\leq l\leq 23$
Reflections collected	6205
Independent reflections	6014 [R(int)=0.0760]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6014/0/388
Goodness-of-fit on F^2	0.984
Final R indices [$I>2\sigma(I)$]	$R1=0.0522$, $wR2=0.1119$
R indices (all data)	$R1=0.1698$, $wR2=0.1420$
Largest diff. peak and hole[a]	1.53 and −1.42 e $Å^{-3}$

[a] These residuals are located at less than 1 Å from the Er ion.

Table 4
Distances (A) and angles (°) around Er^{3+}

Er-O(11B)	2.249(7)
Er-O(11C)	2.253(8)
Er-O(11A)	2.273(7)
Er-O(1C)	2.399(8)
Er-O(2A)	2.453(7)
Er-O(1B)	2.466(8)
Er-O(2B)	2.473(7)
Er-O(2C)	2.488(8)
Er-O(1A)	2.494(8)
O(11B)-Er-O(11C)	83.2(3)
O(11B)-Er-O(11A)	84.6(3)
O(11C)-Er-O(11A)	86.1(3)
O(11B)-Er-O(1C)	84.7(3)
O(11C)-Er-O(1C)	125.8(3)
O(11A)-Er-O(1C)	144.6(3)
O(11B)-Er-O(2A)	129.1(3)
O(11C)-Er-O(2A)	144.2(3)
O(11A)-Er-O(2A)	82.8(3)
O(1C)-Er-O(2A)	78.1(3)
O(11B)-Er-O(1B)	146.3(3)
O(11C)-Er-O(1B)	84.8(3)
O(11A)-Er-O(1B)	125.9(3)
O(1C)-Er-O(1B)	77.0(3)
O(2A)-Er-O(1B)	74.6(3)
O(11B)-Er-O(2B)	149.7(3)
O(11C)-Er-O(2B)	73.5(3)
O(11A)-Er-O(2B)	74.8(2)
O(1C)-Er-O(2B)	124.7(3)
O(2A)-Er-O(2B)	70.7(3)
O(1B)-Er-O(2B)	51.5(2)
O(11B)-Er-O(2C)	75.8(3)
O(11C)-Er-O(2C)	74.0(3)
O(11A)-Er-O(2C)	153.4(3)
O(1C)-Er-O(2C)	51.9(3)
O(2A)-Er-O(2C)	123.5(3)
O(1B)-Er-O(2C)	70.6(3)
O(2B)-Er-O(2C)	114.7(3)
O(11B)-Er-O(1A)	78.1(3)
O(11C)-Er-O(1A)	153.7(3)
O(11A)-Er-O(1A)	73.9(3)
O(1C)-Er-O(1A)	70.9(3)
O(2A)-Er-O(1A)	51.0(3)
O(1B)-Er-O(1A)	120.7(3)
O(2B)-Er-O(1A)	115.8(3)
O(2C)-Er-O(1A)	118.3(3)

to conclude for the existence of bidentate nitrates (Table 2b).

The emission spectra at room temperature and at 77 K are similar; the low temperature one is well resolved and presents a very weak ${}^5D_0 \rightarrow {}^7F_0$ band, three peaks due to ${}^5D_0 \rightarrow {}^7F_1$ (two peaks very close due to an E levels and one due to an A_1 level). The ${}^5D_0 \rightarrow {}^7F_2$ transition also presents three peaks (one due to an A level and two to an E levels (Fig. 1). The spectrum was interpreted in terms of a D_{3h} distorted to a C_{3v} symmetry [17].

Fig. 2 contains the absorption spectrum of the neodymium compound of the hypersensitive ${}^2G_{7/2}$, ${}^4G_{5/2} \leftarrow {}^4I_{9/2}$ transition, in the solid state. The nephelauxetic parameter ($\beta = 0.989$) [18] covalent factor ($b^{1/2} = 0.074$) [19] and Sinha's parameter ($\delta = 1.11$) [20] obtained from the spectrum at room temperature are indicative of an essentially electrostatic bonding with some covalent contribution between the metal ion and the oxygen donor ligands.

Table 3 presents the crystal data collection and refine-

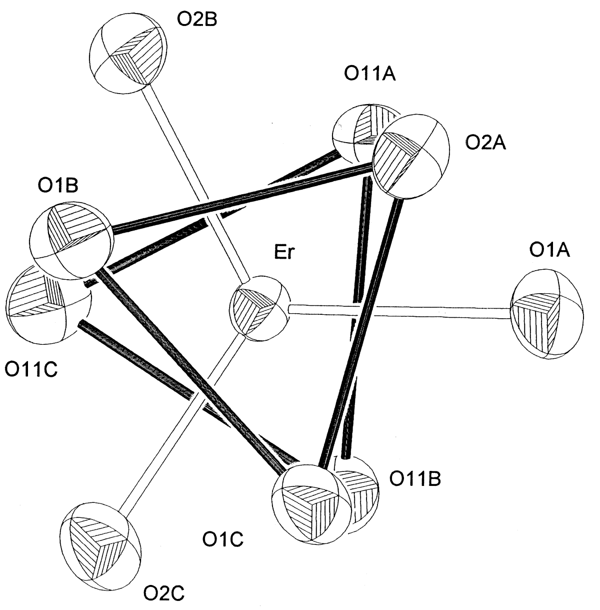

Fig. 3. View of the coordination polyhedron.

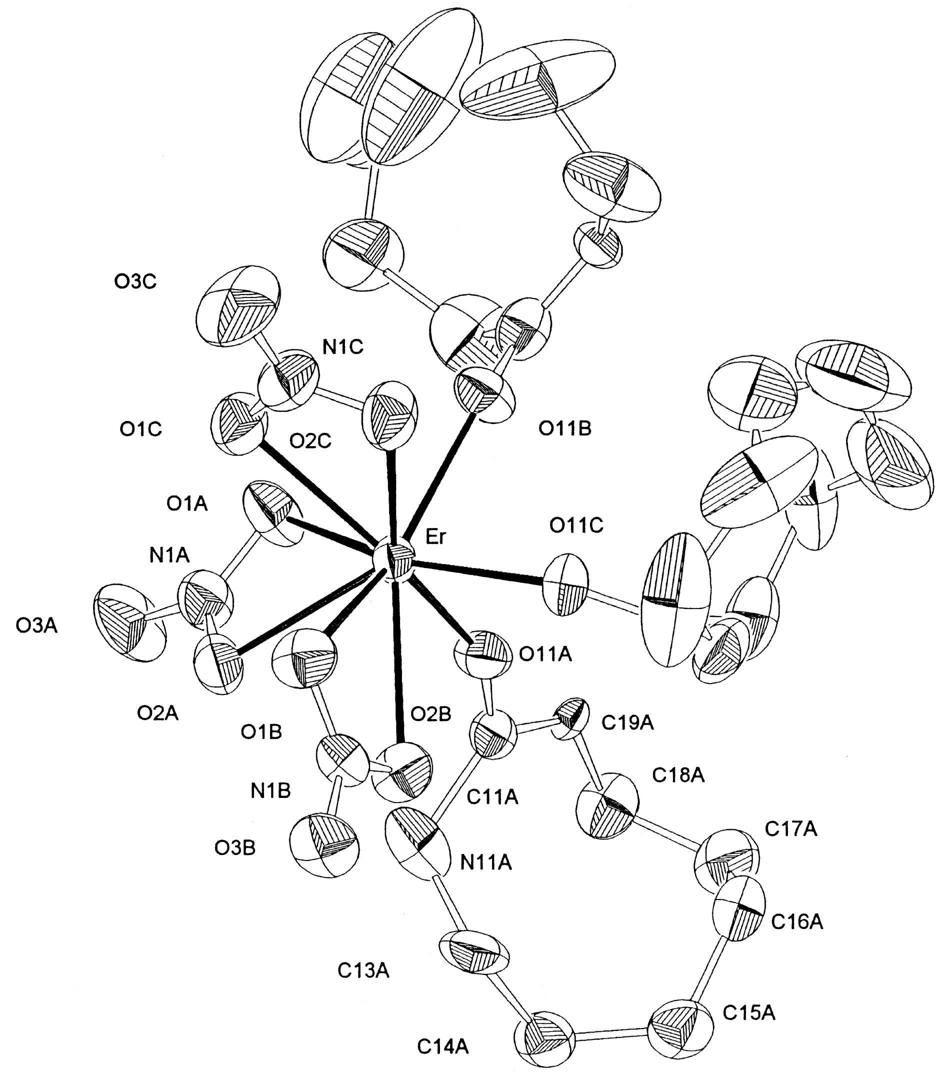

Fig. 4. Structure of $[Er(NO_3)_3(AZA)_3]$.

ment of the Er compound and Table 4 distances and angles around the Er^{3+} ion. Fig. 3 shows a ZORTEP view of the coordination polyhedron and Fig. 4 the structure of the complex.

The Er ion achieves a coordination number of nine by the bonding of three bidentate nitrate groups and three oxygens of three azacyclononanone moieties in a slightly distorted tricapped trigonal prism fashion. The Er ion is displaced from the caps' plane by 0.486(4) Å towards the 011A, 011B, 011C face.

Several geometric parameters to quantify the deformation of the coordination polyhedra, introduced by Balic Zunic and Makovicky [21] and implemented in IVTON [22], 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 the minimum. These are: the central atom-centroid distance (Δ) is 0.150 Å, the average distance from the centroid to the ligands, (r) is 2.384 Å, and the ''sphericity'' ($1 - \sigma_r/r$) is 0.975 (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 1.974 (the tabulated value is 1.988 [23]).

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