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Luminescence and structure of europium compounds

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Contents

Abbreviations: *o*-ABA, *o*-aminobenzoate; AZA, 2-azacyclononanone; BCTP, bicapped trigonal prism; DEPP, α-(diethoxyphosphoryl)propanone; DMVP, diethyl-1-methylvinylphosphate; DMA, *N*,*N*-dimethylacetamide; DDPA, *N*,*N*-dimethyl-diphenylphosphinamide; DMF, *N*,*N*-dimethylformamide; DMOP, 2,9-dimethyl-1,10-phenantroline; DPM, dipivaloylmethanato; bipy, dipy = 2,2′-dipyridine; DTSO, 1,3-dithiane-1-oxide; HMPA, hexamethylphosphoramide; MS, methanesulfonate; MMNO, 4-methylmorpholine-*N*-oxide; ODA, oxydiacetate; PMG, *N*-phosphonomethylglycine; pic, picrate; L-pro, L-proline; 3-picNO, 3-picoline-*N*-oxide; 4-picNO, 4-picoline-*N*-oxide; pyzNO, pyrazine-*N*-oxide; pyNO, pyridine-*N*-oxide; SAP, square antiprism; $C_4O_4^{2-}$, squarate; TDTD, *trans*-1,4-dithiane-1,4-dioxide; TCTP, tricapped trigonal prism; TFMS, trifluoromethanesulfonate; TAN, 4,4,4-trifluoro-1-(2-naphthyl)-1,3-butanedionato; terpy, 2,2′:6′,2″-terpyridine; teof, triethyl-orthoformate; VL, δ-valerolactam.

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Abstract

Europium complexes in the +3 oxidation state, with coordination numbers six, seven, eight, nine and ten are under consideration. In most cases, single crystals or isomorphous compounds were studied by X-ray structural analyses. An attempt is made to correlate the results with the emission spectrum interpretation. Only articles containing both aspects are included in this review. Some general remarks concerning different coordination numbered complexes are also presented.

Keywords: Luminescence; Europium; Coordination number; Structure

1. Introduction

The element europium, atomic number 63 is one of most interesting among the lanthanides, especially in the +3 oxidation state. Its compounds present several important properties and applications. Due to narrow f–f transitions, a good sensitization of the Eu^{3+} luminescence can be achieved through the antenna effect. The lines of the emission spectra are generally sharp and dependent on the crystal field around the metal ions. This fact may be used in the determination of the symmetry and geometry of complex species, and in some cases in species containing other elements, when they are doped with europium acting as a structural probe. Considerable attention has been paid to the luminescence of europium compounds due to the possibility of acting as phosphors and development of materials with LASER properties. In most cases, single crystals of the Eu compound or some isomorphous compounds, were obtained and X-ray structural studies performed and correlated with the spectroscopic interpretation.

In 1967, Sinha published 'Europium' [1] containing, among other items, spectroscopic and structural data and also possible uses and applications of this element and its compounds. In 1975, Moeller in 'The Chemistry of the Lanthanides' [2] also considered europium properties and compounds. There are several publications related to the lanthanides containing topics devoted to aspects here concerned: books by Bünzli and Choppin [3], Cotton [4], Saez–Puche and Caro [5] and several publications edited by Gschneidner and Eyring [6]. A review article containing crystal-field calculations and scalar strength parameters for C_{3v}, D_3 and D_{3d} symmetries has also appeared [7].

The ionic nature of the lanthanide–ligand bonds due to the screening of 4f orbitals and the relatively large radii of the elements gives rise to large coordination numbers. Indeed the coordination number six is very scarce as a consequence of the large amount of space around the Ln^{3+} cations. Only articles including some recent results that contain both aspects are included in this review and were selected from about 300 publications collected in the literature. So, in this article, the description of several compounds, characterized by their emission spectra and X-ray structural studies, found in the literature and also those studied in our laboratories will be presented according to the different coordination numbers, with the main aim to correlate structure and visible emission spectra.

2. Compounds with coordination number six

The following compounds were obtained and characterized in our laboratories.

2.1. $[Eu(DDPA)_6](ClO_4)_3$

$[Ln(DDPA)_6](ClO_4)_3$ (Ln = La–Lu, Y) have been described by Vicentini and Dunstan [8]. The whole isomorphous series containing the elements from praseodymium to europium, characterized by X-ray powder patterns, has been considered.

The emission spectrum of the europium complex (Fig. 1) shows two strong bands corresponding to the $^5D_o \rightarrow {}^7F_{1,2}$ transitions. The O_h symmetry with a slight distortion to C_{4v} was attributed, since a very weak band due to $^5D_o \rightarrow {}^7F_o$ and three peaks at 77 K in the $^5D_o \rightarrow {}^7F_2$ region due to transitions A_1 to E and A_1 levels were observed.

According to these results the dynamic distortions of the O_h symmetry have been attributed to temperature effects. This view is further supported by the fact that the relative intensity of the 'forbidden' $^5D_o \rightarrow {}^7F_2$ band attributed to vibronic interactions decreases drastically with temperature.

X-ray single-crystal studies [9] indicate that in the europium complex the cation is coordinated to six oxygens of the DDPA groups in a crystallographic octahedral configuration.

The phosphoryl group is aligned with the europium atom along a twofold axis with an Eu–O interatomic distance of 2.27(2) Å. The high local symmetry of the

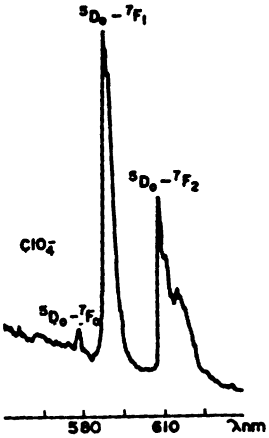

Fig. 1. Emission spectrum of the $[Eu(DDPA)_6](ClO_4)_3$ complex at 77 K (Ref. [8] p. 36).

special position for the europium atom enforces all DDPA atoms other than oxygen and phosphorus to be disordered. There are two independent positions with half occupation for one of the phenyl groups (the other is generated by the twofold axis) (Fig. 2).

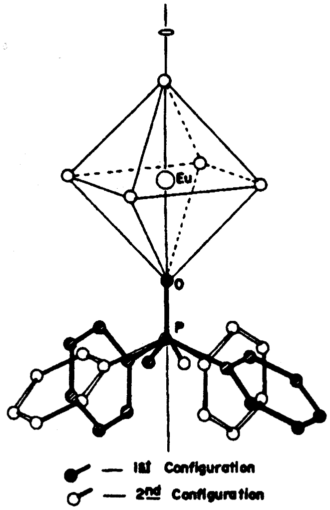

Fig. 2. Schematic representation of the Eu ion environment showing one of the independent DDPA groups of the $[Eu(DDPA)_6](ClO_4)_3$ complex in its two disordered occupation sites (Ref. [9] p. 36).

3. Compounds with coordination number seven

The following compounds were prepared and characterized in our laboratories.

3.1. [Eu(MS)$_3$]

$Ln(CH_3SO_3)_3$ [10] (Ln = La–Lu, Y) compounds were prepared by reaction of lanthanide basic carbonates and methanesulfonic acid. The hydrated salts lose the water molecules at 120–150°C, remaining as stable anhydrous salts. The compounds from Eu–Lu and Y form an isomorphous series.

The emission spectrum at 77 K of the europium salt presents an extremely weak $^5D_o \rightarrow {}^7F_o$ peak. Three peaks were observed for the $^5D_o \rightarrow {}^7F_1$. The $^5D_o \rightarrow {}^7F_2$ transition presents four peaks (transitions to E levels). The relative more intense band at ~ 620 nm compared with those at ~ 590 nm are indicative that the compound does not present an inversion center. The symmetries D_3 or D_{3h} have been suggested [10] (Fig. 3). Perhaps the above symmetries are overestimates and it is probably C_{2v}.

According to X-ray single-crystal structural studies [11] the methanesulfonate ions behave as bidentate ligands, giving rise to a polymeric tridimensional structure. Each ytterbium cation is coordinated to seven methanesulfonate anions and the polyhedron around the lanthanide ion is a distorted monocapped trigonal prism (Fig. 4).

The distortion of the polyhedron is due to the repulsions between the anions, due to steric requirements, thus producing small differences in the Ln–O distances. The capping oxygen is at a 2.160(2) Å distance and the remaining six oxygens are at distances between 2.260(3) and 2.308(7) Å.

4. Compounds with coordination number eight

Table 1 presents some complexes with coordination number eight. The following compounds were prepared and characterized in our laboratories.

4.1. [Ln(TDTD)$_2$(TFMS)(H$_2$O)$_3$]·2TDTD·2TFMS

An isostructural series of lanthanide complexes with the formula above (Ln = La–Lu, Y) was obtained [19]. The emission spectrum of the europium compound contains an extremely weak forbidden $^5D_o \rightarrow {}^7F_o$ band; two peaks due to $^5D_o \rightarrow {}^7F_1$ (one very sharp and an unresolved larger one) and three peaks due to a $^5D_o \rightarrow {}^7F_2$ transition (one A_2 level and two E level). D_{2d} symmetry was suggested for the complex species [20].

The X-ray structural study of the neodymium compound, isomorphous with the europium, shows that the structure of the complexes present the formula above. Neodymium is 8-coordinated by one oxygen from TFMS, by four oxygens from TDTD and by three water oxygens. One ‘free’ TFMS ion is disordered.

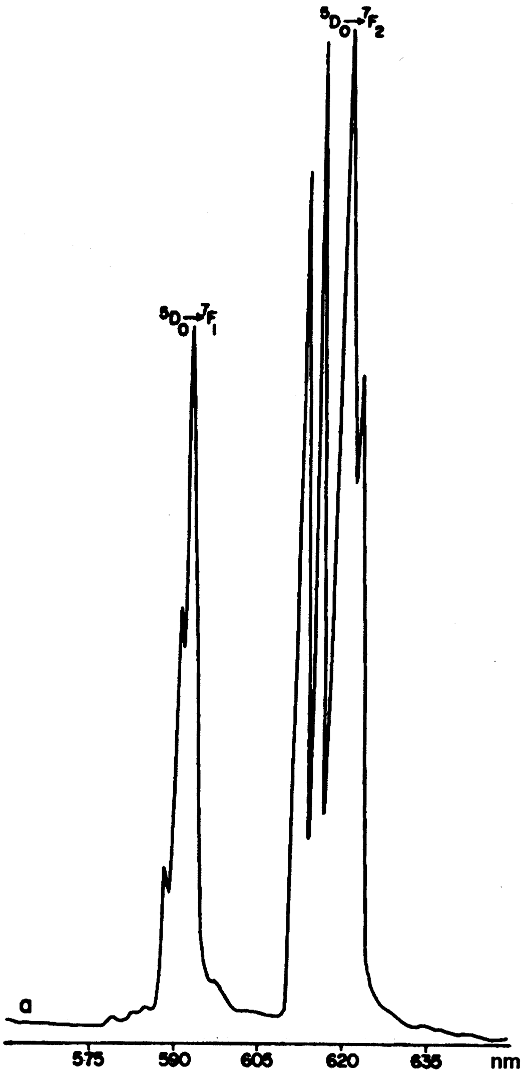

Fig. 3. Emission spectrum of the compound of formula $Eu(CH_3SO_3)_3$ at 77 K (Ref. [10] p. 720).

The 'free' and bonded TDTD molecules maintain the *trans* configuration. The coordination around neodymium is very much distorted from the three main idealized polyhedra: dodecahedron, square antiprism and bicapped trigonal prism.

4.2. $[Eu(4\text{-}picNO)_8](CF_3SO_3)_3$

Lanthanoid trifluoromethanesulfonates react in ethanol with 4-picoline-*N*-oxide (4-picNO) to form complexes with the compositions $[Ln(4\text{-}picNO)_8](CF_3SO_3)_3$

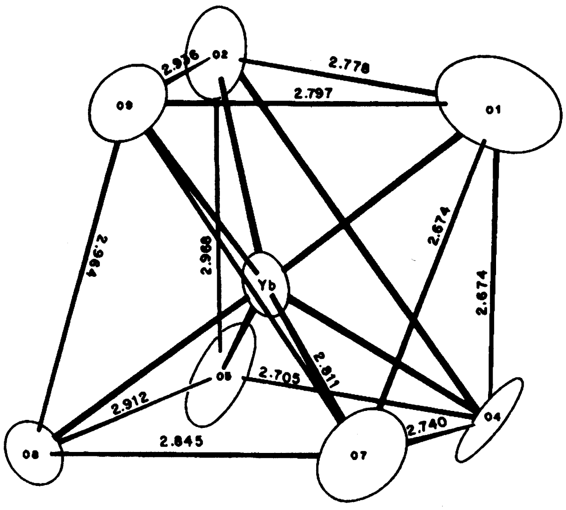

Fig. 4. Coordination polyhedron of the $Yb(CH_3SO_3)_3$ complex, isomorphous with that of europium (Ref. [11] p. 115).

(Ln = La–Gd) and $[Ln(4\text{-picNO})_7](CF_3SO_3)_3$ (Ln = Tb–Lu, Y) forming two isostructural series [21].

The emission spectrum shows an intense band with a weak shoulder due to $^5D_o \rightarrow {}^7F_1$ transition, two peaks, one of them very strong, due to $^5D_o \rightarrow {}^7F_2$ and also two peaks, one very strong, due to $^5D_o \rightarrow {}^7F_4$ transition. It was not possible to derive the point group symmetry since the spectrum is not well resolved.

The structure of the neodymium compound, isomorphous with that of europium, was determined, showing a square antiprismatic coordination. The distortions observed in relation to the ideal polyhedron are possible due to packing effects and may be rationalized by rotation of one square face of the polyhedron of ca. 37.6° away from the 45° projected angle characterizing the D_{4d} geometry, thus giving a coordination polyhedron of D_4 symmetry.

4.3. $[Eu(VL)_8](ClO_4)_3$

Complexes with formula $[Ln(VL)_8](ClO_4)_3$ (Ln = La–Ho) and $[Ln(VL)_7](ClO_4)_3$ (Ln = Er–Lu, Y) were synthesized and characterized [22]. The emission spectrum at 77 K does not present a $^5D_o \rightarrow {}^7F_o$ transition. Three peaks were obtained for the $^5D_o \rightarrow {}^7F_1$ transition: one at 588 nm (A_2 magnetically allowed level) and two at 593 and 594 nm (E_1 levels — doubly degenerate, electrically allowed); one peak and a shoulder at 612.5, 613 nm (E_1 levels, electrically allowed). The spectrum (Fig. 5) was interpreted in terms of D_{4d} symmetry according to calculations by Nascimento [23]. Nevertheless, Blasse [24] considers that, in this unusual symmetry, none of the $^5D_o \rightarrow {}^7F_2$ transitions are allowed whereas an intense transition is seen. However, he points out that observation of a $^5D_o \rightarrow {}^7F_2$ transition is due to the deviation from

Table 1
Selected compounds found in the literature with CN = 8

Formula	Geometry and/ or coordination	Symmetry	Fluorescence	Peaks	Ref.
$[Eu(pyNO)_8)](ClO_4)_3$	Approximate	C_{2v}	$^5D_o \rightarrow {}^7F_o$	1	[12]
	SAP		$^5D_o \rightarrow {}^7F_1$	3	
			$^5D_o \rightarrow {}^7F_2$	3	
$[Eu_2(C_4O_4)_3(H_2O)_8]$	Distorted SAP	D_{2d}/or	$^5D_o \rightarrow {}^7F_o$	1	[13]
(two non-equivalent	Dodecahedron	C_{2v}/or	$^5D_o \rightarrow {}^7F_1$	5	
Eu^{3+})	BCTP	C_2	$^5D_o \rightarrow {}^7F_2$	7	
$[Eu(DPM)_3(DMOP)]$	Distorted SAP	C_1	$^5D_o \rightarrow {}^7F_o$	2 (separat.)	[14]
(two geometrical			$^5D_o \rightarrow {}^7F_1$	6	
isomers)			$^5D_o \rightarrow {}^7F_2$	8	
$[Eu(o\text{-}ABA)_3bipy]$	Not attributed	C_1	$^5D_o \rightarrow {}^7F_o$	1	[15]
bipy	two Eu^{3+}		$^5D_o \rightarrow {}^7F_1$	3 + 1 vibr.	
	centers		$^5D_o \rightarrow {}^7F_2$	5 + 2 vibr.	
$[Eu_2(PMG)(H_2O)_8]$ (ClO_4)	BCTP(8)	C_{2v}	$^5D_o \rightarrow {}^7F_o$	2	[16]
CN 8(9) Polynuclear	SAP(9)	C_{4v}	$^5D_o \rightarrow {}^7F_1$	4	
			$^5D_o \rightarrow {}^7F_2$	5	
			Plates		
$[Eu(TAN)_3dipy]$	SAP	Not attributed	$^5D_o \rightarrow {}^7F_o$	2 (two sites)	[17]
Plates			$^5D_o \rightarrow {}^7F_1$	4	
(two forms) Blocks	BCTP		$^5D_o \rightarrow {}^7F_2$	3	
			Blocks		
			$^5D_o \rightarrow {}^7F_o$	1	
			$^5D_o \rightarrow {}^7F_1$	3 + sh	
			$^5D_o \rightarrow {}^7F_2$	3	
I-$[Eu_2(L\text{-}pro)_4(H_2O)_8]$	SAP	Distorted D_{4h}	$^5D_o \rightarrow {}^7F_o$	1 + sh	[18]
$(ClO_4)_6.4H_2O$			$^5D_o \rightarrow {}^7F_1$	4	
			$^5D_o \rightarrow {}^7F_2$	3	
II-$[Eu(L\text{-}pro)_3(H_2O)_8]$	Dodecahedron	Distorted D_{2d}	$^5D_o \rightarrow {}^7F_o$	1	
$(ClO_4)_3$			$^5D_o \rightarrow {}^7F_1$	6	
			$^5D_o \rightarrow {}^7F_2$	8	

exact D_{4d} symmetry. A distorted D_4 symmetry with A_2 and E levels for the $^5D_o \rightarrow {}^7F_1$ transition and an E level for $^5D_o \rightarrow {}^7F_2$ transition (all electric and magnetic allowed) [20] may be considered.

The neodymium compound was studied by X-ray single crystal analysis. Its structure consists of $[Nd(VL)_8]^{3+}$ complex cations (Fig. 6) and disordered ClO_4^- anions. The coordination sphere geometry is very close to that of an ideal square antiprism. The two square faces of the antiprism are roughly parallel.

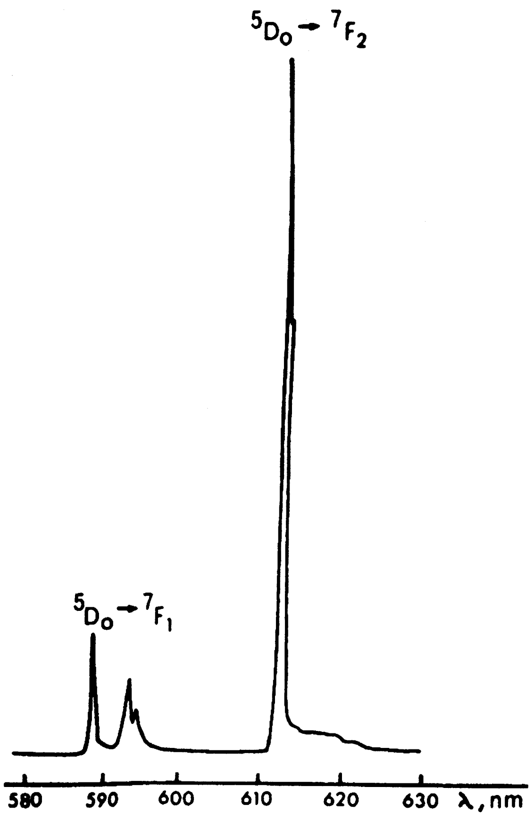

Fig. 5. Emission spectrum of the complex $[Eu(VL)_8](ClO_4)_3$ at 77 K (Ref. [22] p. 53).

4.4. $[Eu(VL)_8](ReO_4)_3$

The compound presents an identical emission spectrum to that of the ClO_4^- compound [25]. X-ray single crystal diffraction shows unit cell parameters with values that are very similar (within experimental error), showing that the compounds are isomorphous.

5. Compounds with coordination number nine

Table 2 presents some complexes with coordination number nine. The following compounds were prepared and characterized in our laboratories.

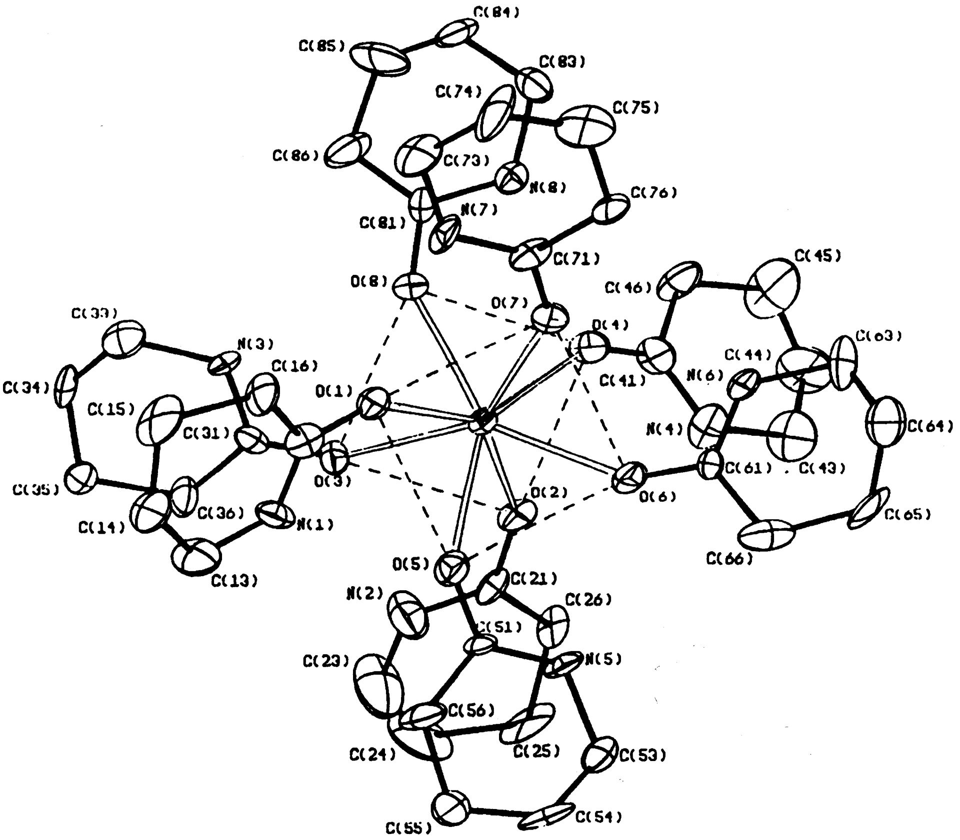

Fig. 6. Structure of the complex $[Nd(VL)_8](ClO_4)_3$ (Ref. [22] p. 54).

5.1. $[Eu(NO_3)_3 \cdot 3DMA]$

Compounds with the above composition (Ln = Nd–Lu, Y) have been described [35]. The emission spectrum of the europium compound was interpreted in terms of a C_{3v} symmetry with a tricapped trigonal prism geometry [36]. The structure of the samarium complex, isomorphous with that of europium, consists of monomeric molecules in which the central ion is surrounded by six ligands. The three DMA coordinate through the carbonyl oxygen and all nitrate ligands are attached in bidentate fashion. The coordination polyhedra is described as a distorted tricapped trigonal prism of oxygen atoms [37].

5.2. $[Ln(H_2O)_4(\eta'\text{-}TDTD)_2(\eta'\text{-}ReO_4)(\mu\text{-}\eta^2\text{-}TDTD)]_n(ReO_4)_{2n} \cdot nTDTD$

Compounds of the above composition (Ln = Pr, Nd, Eu) were synthesized [38]. They are essentially isomorphous. The emission spectrum of the europium compound contains a weak $^5D_o \rightarrow {}^7F_o$ band, three poorly resolved peaks due to

Table 2
Selected compounds found in the literature with CN = 9

Formula	Geometry and/or coordination	Symmetry	Fluorescence	Peaks	Ref.
$[Eu(terpy)_3](ClO_4)_3$	Distorted	Distorted	$^5D_o \rightarrow ^7F_1$	3	[26,27]
	TCTP	D_3	$^5D_o \rightarrow ^7F_2$	4	
$Na_3\ [Eu(ODA)_3]\cdot 6H_2O$	Approx.	D_3	$^5D_o \rightarrow ^7F_1$	2	[28]
	TCTP		$^5D_o \rightarrow ^7F_2$	2	
$[Eu(DPM)_3terpy]$	Distorted	C_1	$^5D_o \rightarrow ^7F_o$	1	[29]
	TCTP		$^5D_o \rightarrow ^7F_1$	6	
			$^5D_o \rightarrow ^7F_2$	9	
			(two emitting centers)		
$[Eu(H_2L)^{a}(NO_3)_2]NO_3$	Distorted	Not attributed	$^5D_o \rightarrow ^7F_o$	1	[30]
Two structural forms	TCTP		$^5D_o \rightarrow ^7F_1$	4	
			$^5D_o \rightarrow ^7F_2$	4	
$[Eu_2(L)_3{}^{b}](ClO_4)_6(CH_3CN)_9$	Slightly distorted	D_3	$^5D_o \rightarrow ^7F_1$	3	[31]
	TCTP		$^5D_o \rightarrow ^7F_2$	3 and a shoulder	
$[EuZn(L^2)^{c}{}_8](ClO_4)_5$	Slightly distorted		$^5D_o \rightarrow ^7F_o$	1	[32]
	TCTP		$^5D_o \rightarrow ^7F_1$	3	
			$^5D_o \rightarrow ^7F_2$	5	
			(10 K)		
$[Eu(L^5)_3{}^{d}](ClO_4)_3\cdot 4MeCN$	Slightly distorted	$D_{3h} \rightarrow C_{2v}$	$^5D_o \rightarrow ^7F_o$	1	[33]
	TCTP	or lower	$^5D_o \rightarrow ^7F_1$	2	
			$^5D_o \rightarrow ^7F_2$	1 + sh	
$[Co(sar)^{e}][Eu(dipic)_3{}^{f}]\cdot 3H_2O$	TCTP	D_3	$^5D_o \rightarrow ^7F_o$	Narrow	[34]
			$^5D_o \rightarrow ^7F_1$	2 A1–E	
			$^5D_o \rightarrow ^7F_2$	2 A1–E	

[a] H_2L = condensation of 2,6-diformyl-4-chlorophenol and diethylenetriamine.

[b] bis[1-methyl-2-(6′-[1″-(3,5-dimethoxybenzyl) benzimidazol-2″-yl) pyrid-2′-yl)benzimidazol-5-yl]methane.

[c] L^2 = 2-[6-(*N*,*N*′-diethylcarboxamido) pyridin-2-yl]-1,1′-dimethyl-5,5′-methylene-2″-(5-methylpyridin-2-yl)-bis[1H-benzimidazole].

[d] L^5 = 2,6-bis(1′-ethyl-5′methylbenzimidazol-2′-yl)pyridine.

[e] sar = sarcophagine (3,6,10,13,19-hexaazabicyclo [6,6,6]) icosane.

[f] dipic = pyridine-2,6-dicarboxylate.

$^5D_o \rightarrow {}^7F_1$ (transitions to A_2 and E levels) and a broad band with two shoulders attributed to a $^5D_o \rightarrow {}^7F_2$ transition. C_{4v} symmetry was proposed for the complex species [20].

The structure of the neodymium complex was completely resolved. The Nd and one of the Re atoms are sited on a twofold axis and coordinated through one of the perrhenate oxygen atoms, which is also sited on the twofold axis. The three other oxygen atoms of that anion are disordered. The second perrhenate group is in a general crystallographic position and not coordinated to the cation. The coordination polyhedron around the Nd ion is a distorted capped square antiprism, of an approximate C_{4v} point symmetry and actual (crystallographic) point symmetry C_2. The water molecules, related in pairs through the twofold axis, form the uncapped (approximate) square base; the capped face is formed from two crystallographically independent TDTD groups and their twofold axis equivalents; one of these groups is in a general position and has one of its oxygen atoms uncoordinated; the other TDTD group is on a center of symmetry and its oxygen atoms bridge between neighboring Nd cations, giving rise to infinite chains of polyhedra along the *c* direction of the crystal. The coordinated perrhenate oxygen forms the capping vertex of the polyhedron. The remaining TDTD group, sited on a center of symmetry, is uncoordinated to the Nd cation. A projection of the polyhedra chain is shown in Fig. 7. Fig. 8 is a projection down the twofold axis showing the oxygen polyhedra.

5.3. $[Eu(DMA)_3(H_2O)_6]\ (CF_3SO_3)_3$

Complexes with composition $[Ln(DMA)_3(H_2O)_6]\ (CF_3SO_3)_3$ (Ln–La–Tb) were described, constituting an isomorphous series [39]. The emission spectrum at 77 K (Fig. 9) does not present a $^5D_o \rightarrow {}^7F_o$ transition (forbidden for A_1' to A_1' transition) but shows one peak with a shoulder due to $^5D_o \rightarrow {}^7F_1$ transitions (allowed magnetic dipole A_1' and E'' levels) and two peaks owing to the $^5D_o \rightarrow {}^7F_2$ transition (electric dipole allowed E' and magnetic dipole allowed E'') and was interpreted in terms of an approximately D_{3h} symmetry. A small peak at about 585 nm was attributed to a $^5D_1 \rightarrow {}^7F_3$ transition. No other bands due to $^5D_1 \rightarrow {}^7F_J$ transitions were observed in this low-intensity spectrum. Compounds with the same stoichiometry containing DMF as a ligand have a C_{3v} symmetry. The structure of the Pr^{3+} complex was determined (Fig. 10). The cation is coordinated to oxygens of water molecules located at the vertices of a trigonal prism. The DMAs occupy the capping positions and are bonded through the carbonyl oxygens. The mean Pr–O(w) distance is 2.52 Å and Pr–O(DMA) = 2.43 Å. For $[Pr(H_2O)_9]\ (C_2H_5SO_4)_3$ the average Pr–O distance is 2.47 Å and the equatorial Pr–O distance 2.65 Å. When the equatorial water ligands are substituted by DMA the distances become shorter and the prismatic distances are enlarged [40,41]. The distances and angles involving the praseodymium ion indicate C_2 to be a more accurate representation of the coordination point symmetry.

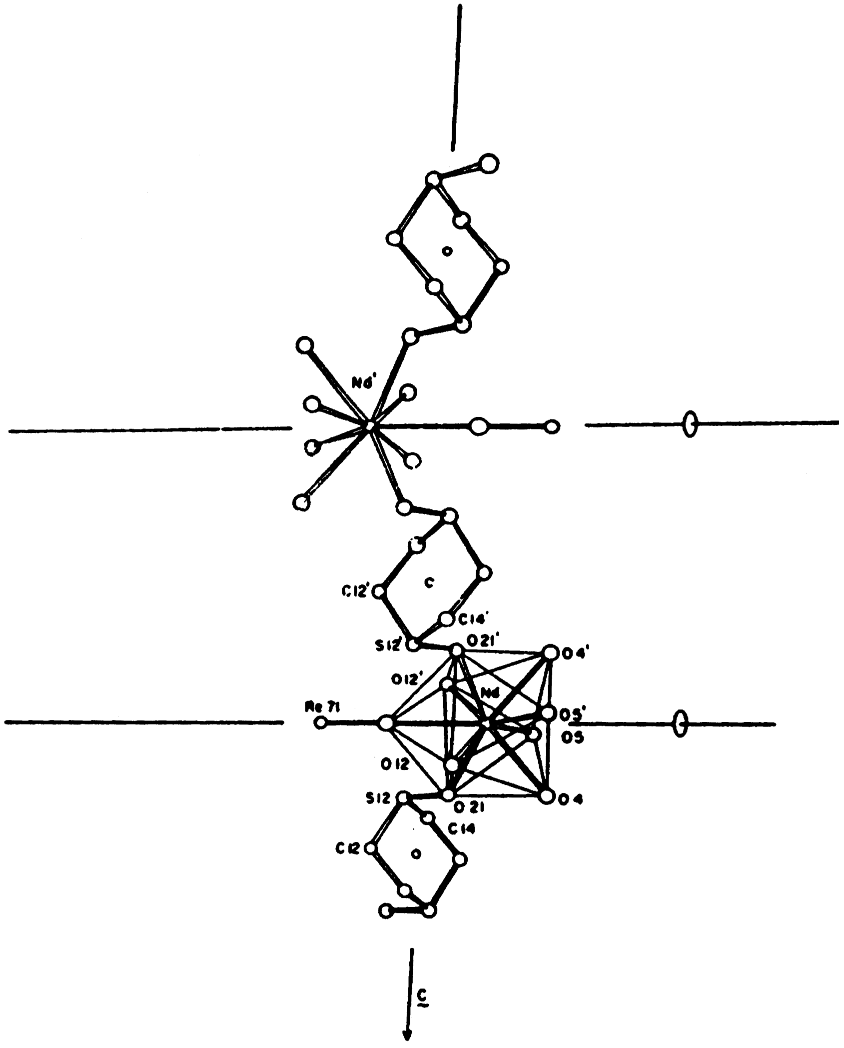

Fig. 7. Projection of the polyhedron chain of the complex of neodymium perrhenate with TDTD (primed names refer to symmetrically related atoms) (Ref. [38] p. 212).

5.4. $[Eu(DMF)_3(H_2O)_6](CF_3SO_3)_3$

Compounds with formula $[Eu(DMF)_3(H_2O)_6](CF_3SO_3)_3$ (Ln = La–Eu, Tb, Dy) are all isomorphous [42]. The emission spectrum obtained at 77 K contains a $^5D_o \rightarrow {}^7F_o$ band (the existence of this band indicates that only C_n, C_{nv} or C_s symmetries are possible [43]), one peak and shoulders due to $^5D_o \rightarrow {}^7F_1$ transition and two peaks and a shoulder due to $^5D_o \rightarrow {}^7F_2$. The spectrum was interpreted in terms of C_{3v} symmetry [20]. The structure of the neodymium complex indicates that

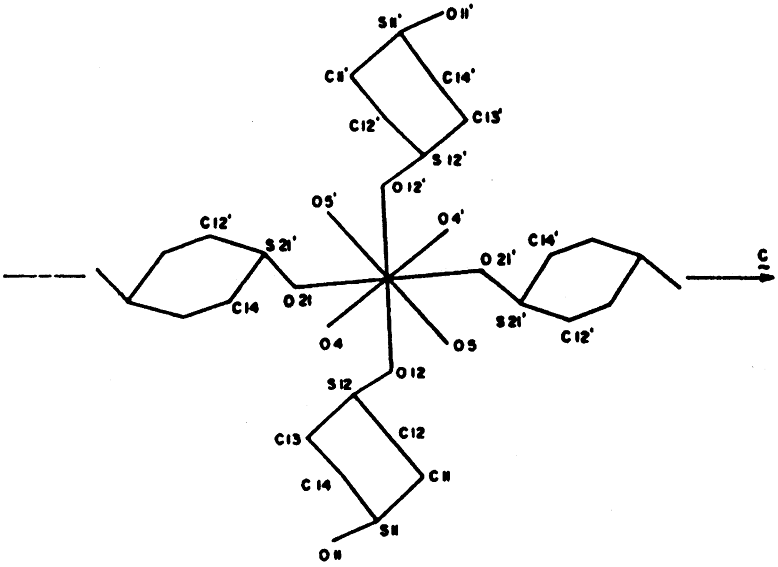

Fig. 8. Projection down *b*-axis showing the TDTD groups and the oxygen water molecules coordinated to the Nd^{3+} ions in the polyhedra of Fig. 7 (Ref. [38] p. 213).

the central ion is coordinated to six independent water molecules at a mean distance of Nd–Ow = 2.52(1) Å and to the oxygens of three independent DMF groups at a mean distance Nd–O = 2.40(2) Å. The coordination polyhedron is a tricapped prism of point symmetry C_{3v}. The water oxygen atoms are located at the corners of the prism and the oxygen atoms of the DMF groups at the vertices of the caps.

5.5. $[Eu(pic)_3(DMA)_3]$

The compounds $[Ln(pic)_3(DMA)_3]$ (Ln = La–Lu, Y) were prepared by the reaction of the hydrated lanthanide picrates and the ligand (molar ratio 1:3) using teof as interaction and dehydrating solvent [44]. The europium compound belongs to an isomorphous series containing the elements Nd–Yb and Y. The emission spectrum of the europium compound was described by Meira da Silva et al. [45]. The spectrum contains an extremely weak ${}^5D_o \rightarrow {}^7F_o$ band (for this reason was not considered in terms of interpretation of symmetry); three peaks due to ${}^5D_o \rightarrow {}^7F_1$ (A_2 and E levels at 589.5, 589.9 and 590.4 nm); three peaks for the ${}^5D_o \rightarrow {}^7F_2$ transition (A_1 and E levels at 613, 615 and 61 nm). According to the data an idealized D_{3h} symmetry consistent with a tricapped trigonal prism geometry was attributed [20]. The structure of the samarium compound, isomorphous with that of europium, was determined by single-crystal X-ray analysis. For the D_{3h} polyhedron, the main discordance is in the 4–7 (1.24 Å) normalized distance (in the notation of Guggenberger and Muetterties) [41] as compared to the theoretical value (1.42 Å). This is not in conflict with the approximate D_{3h} symmetry since this distance is

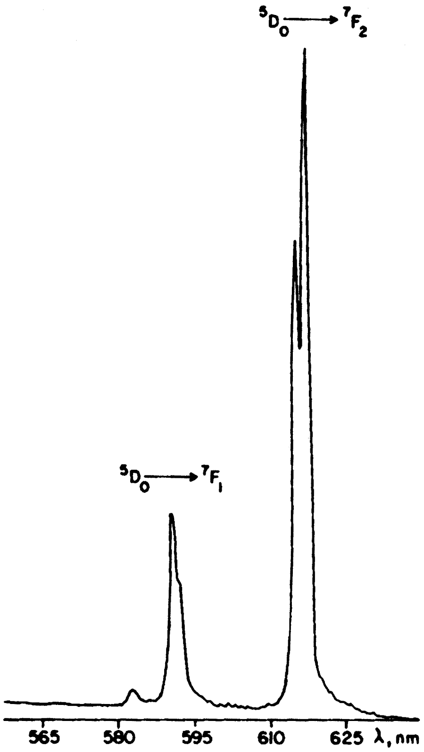

Fig. 9. Fluorescence spectrum of the compound of formula $[Eu(DMA)_3(H_2O)_6](CF_3SO_3)_3$ at 77 K (Ref. [39] p. 276).

parallel to the threefold axis. The occurrence of this short distance may be attributed to the three bite distances between the picrate moieties which bridge each of the capping atoms and three different corners of the trigonal prism. The distances (Å) are: Sm–O(11) 2.344(5); Sm–O(111) 2.736(7); Sm–O(21) 2.339(5); Sm–O(211) 2.767(6); Sm–O(31) 2.349(5); Sm–O(311) 2.657(6); Sm–O(4) 2.299(5); Sm–O(5) 2.332(5); Sm–O(6) 2.351(6).

5.6. $[Eu(pic)_3(AZA)_3]$

Complexes with composition $[Ln(pic)_3(AZA)_3]$ (Ln = Nd, Eu) were characterized by IR spectroscopy, elemental analysis and X-ray structural studies [46]. The emission spectrum of the europium compound shows a very small $^5D_o \rightarrow {}^7F_o$ peak indicating a slight distortion of the fundamental polyhedron. The $^7F_1$ level is split by the crystalline field into three components (one A_2 and one E levels, the latter split into two components). For the $^5D_o \rightarrow {}^7F_2$ transition five peaks were observed (two E levels and one A_2). All observations suggest a D_{3h} symmetry for the coordination polyhedron around Eu^{3+} [20] (Fig. 11). In this case the site symmetry

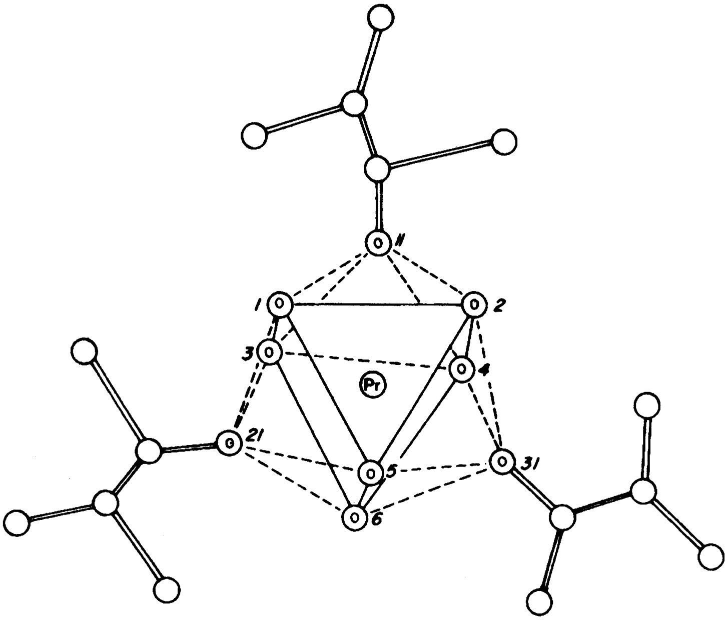

Fig. 10. Coordination polyhedron of the compound $[Pr(DMA)_3(H_2O)_6](CF_3SO_3)_3$, isomorphous with that of europium (Ref. [39] p. 277).

was overestimated. The spectrum can be interpreted in terms of C_{2v} symmetry (allowed transitions:1, 3 and 4 for $J = 0$, 1 and 2).

According to X-ray single-crystal diffraction analysis of the europium compound (Fig. 12) the coordination polyhedron is 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. The distances (Å) between Eu (III) and oxygens are: 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(7); Eu–O(6) 2.302(7).

5.7. $[Eu(pic)_3(HMPA)_3]$

The emission spectrum of the complex at 77 K [47] presents a $^5D_o \rightarrow {}^7F_o$ peak at 579 nm (transition to the A_1 level, electric dipole allowed), two peaks due to $^5D_o \rightarrow {}^7F_1$ at 590 and 596 nm (transitions to the A_2' and E'' levels, magnetic dipole allowed) and three peaks at 613, 615 and 617 nm (E' and E'' species electric and magnetic allowed, respectively). The spectrum was interpreted in terms of a D_{4h} distorted to C_{3v} symmetry [20].

The structure of the neodymium compound, isomorphous with that of europium was determined. The coordination polyhedron is an approximate tricapped trigonal prism. One base of the prism is formed by three oxygens of the HMPA ligands. The

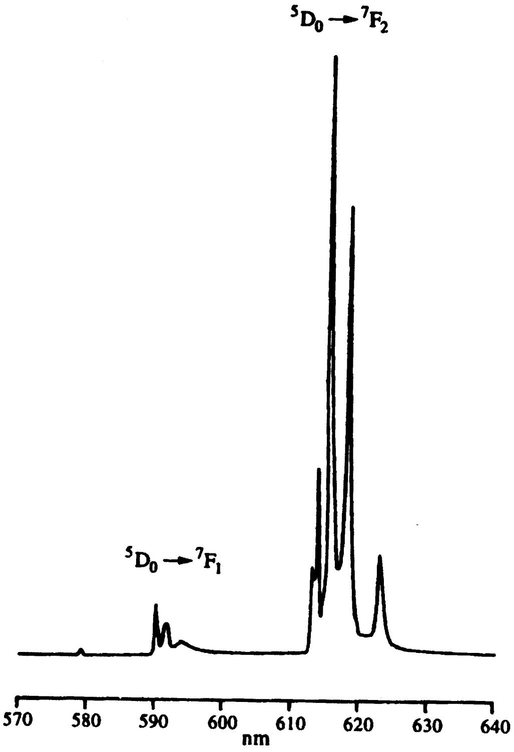

Fig. 11. Emission spectrum of the complex of formula $[Eu(pic)_3(AZA)_3]$ at 77 K (Ref. [46] p. 3520).

picrates are coordinated via the phenoxo-oxygen, forming the second base of the prism and the three ortho nitrogroups capping the square faces of the trigonal prism (Fig. 13).

5.8. $[Eu(pic)_3(3\text{-}picNO)_2H_2O]$

The emission spectrum presents two peaks due to $^5D_o \rightarrow {}^7F_o$ transitions (578, 579 nm) indicating the existence of two different Eu(III) coordination environments [48]. Four peaks were detected for the $^5D_o \rightarrow {}^7F_o$ (590, 592, 594, 595 nm) and seven peaks for the $^5D_o \rightarrow {}^7F_2$ transitions (612.5, 613, 614, 615, 617, 619, 622 nm). The large number of bands could certainly be due to the existence of two europium sites in the asymmetric unit. A band at 595 nm is attributed to a $^5D_1 \rightarrow {}^7F_n$ transition (Fig. 14). X-ray single crystal analyses showed that the complex contains two crystallographic non-equivalent Eu(III) ions. In both cases they are coordinated to nine oxygen atoms in the form of a distorted monocapped square antiprism, where one of the square faces is bent. The difference between the two environments is that in one of them the cap is over the square plane, whereas in the other it is over the distorted face of the antiprism. Fig. 15 shows the coordination polyhedra. In order to compare the Eu–O(cap) distances, they were corrected for the atomic motion [49]

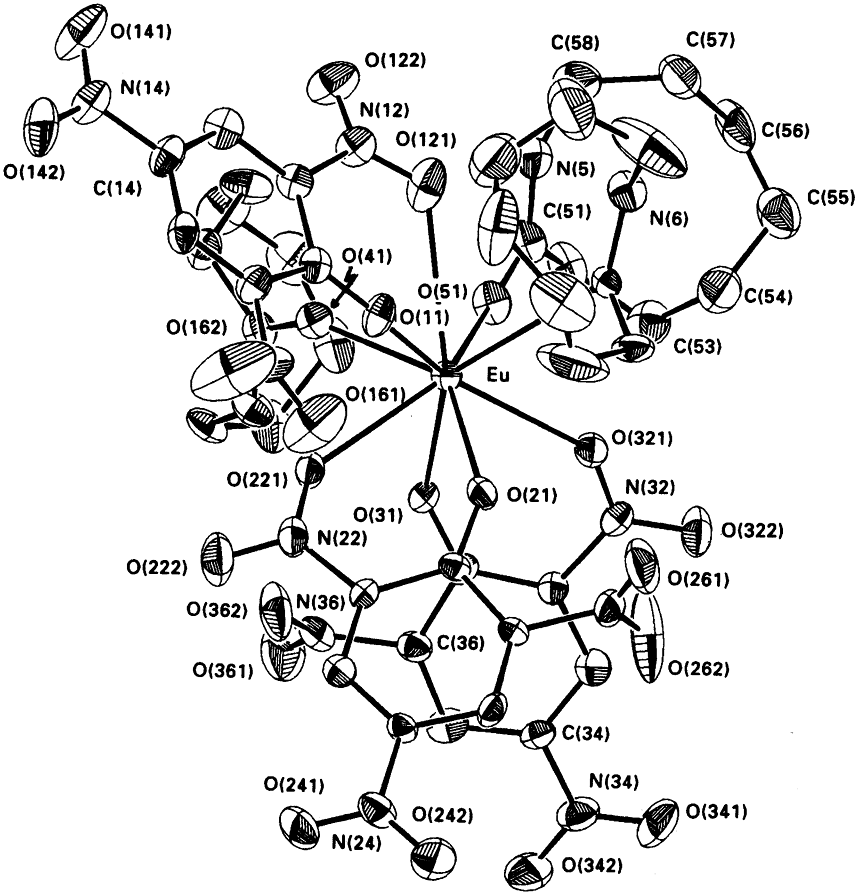

Fig. 12. Structure of the complex of formula [Eu(pic)$_3$(AZA)$_3$] (Ref. [46] p. 3521).

obtaining 2.682 and 2.905 Å for Eu1 and Eu2, respectively. Fig. 16 shows the structure of Eu1 with the respective label numbering.

5.9. [Eu(pic)$_3$(DEPP)$_3$] and [Eu(pic)$_3$(DMVP)$_3$](H$_2$O)

These compounds were obtained by reaction of the hydrated europium picrate and the liquid ligands in absolute ethanol (molar ratio 1:3) [50]. The solutions were left to crystallize at room temperature. The solids were filtered, washed with absolute ethanol and dried in air over filter paper. They were characterized by microanalytical procedures and IR spectra. Both complexes present intense luminescence and they may possibly be interesting phosphors. Peaks were found as follows: DEPP complex at 77 K displays one $^5D_o \rightarrow {}^7F_o$ at 579 nm, three $^5D_o \rightarrow {}^7F_1$ (589.5, 591.5 and 595 nm) and four peaks for $^5D_o \rightarrow {}^7F_2$ transition (614, 614.8, 615.7 and 617 nm). The DMVP complex at the same temperature shows one $^5D_o \rightarrow {}^7F_o$

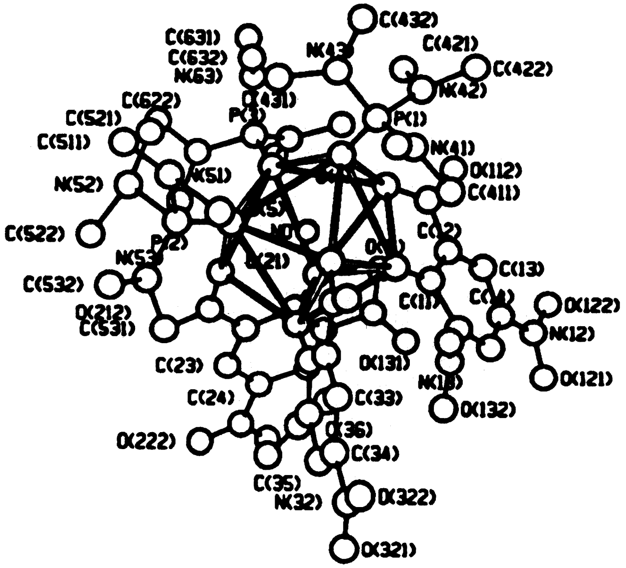

Fig. 13. Perspective view of the structure, showing the numbering scheme of the complex of formula [Nd(pic)$_3$(HMPA)$_3$] isomorphous with the europium complex (Ref. [47] p. 355).

peak (579 nm), three $^5D_o \rightarrow {}^7F_1$ (589.5, 591.5 and 596 nm) and four $^5D_o \rightarrow {}^7F_2$ (614, 615, 617 and a shoulder at 613.5 nm). Both emission spectra are very similar. The crystalline field causes a splitting of the $^7F_1$ level into three components (one A_2 and two E levels) and the $^7F_2$ into four (one A_1 and two 2E, one of the latter splits into two components). C_{3v} symmetry was proposed for both polyhedra [41] (Fig. 17). From X-ray single-crystal analyses it is apparent that both coordination polyhedra are very similar and are tricapped trigonal prisms, in agreement with luminescence data. One base of the prism is constituted by the phenolic oxygens of the picrate anions; the *o*-nitrogroup oxygens are the caps and the phosphoryl oxygens of the neutral ligands (DEPP and DMVP) form the other base of the prism (Figs. 18 and 19). Distances are given in Table 3.

5.10. [Ln(pic)$_3$(MMNO)(H$_2$O)$_2$]

The isomorphous complexes with the above composition (Ln = La, Nd, Eu) were obtained by crystallization of [Ln(pic)$_3$·3MMNO] from methanol.

The luminescence spectrum of the europium complex [51], determined at 77 K shows one band attributed to $^5D_o \rightarrow {}^7F_o$ at 577 nm. (A_1 levels electric dipole allowed), three peaks due to $^5D_o \rightarrow {}^7F_1$ at 586, 596, 599 nm (one A_2 levels, magnetic dipole allowed and E levels, magnetic and electrical allowed transitions) and three peaks due to $^5D_o \rightarrow {}^7F_2$ transition at 602, 603 and 616 nm (one A_1 levels, electrical allowed and two E levels magnetic and electrical allowed) the C_{3v} symmetry around the central ion was attributed to the complex [20].

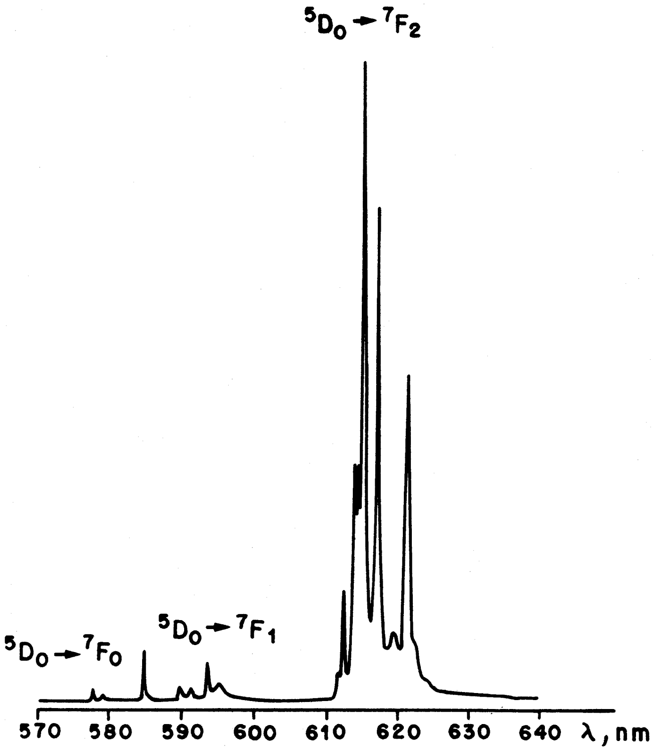

Fig. 14. Emission spectrum of $[Eu(pic)_3 \cdot (3\text{-}picNO)_2(H_2O)]$ complex at 77 K (Ref. [48] to be published in Inorg. Chim. Acta 292 (1999) 249).

According to X-ray single-crystal studies the complexes are coordinated by six oxygens of the bidentate picrate moieties, one MMNO bonded through the oxygen and two water molecules in a tricapped trigonal prism fashion. The dihedral angle between the trigonal faces is 5.40(6)° for the europium complex.

In the complexes the MMNO ring assumes an almost perfect chair conformation with the exocyclic oxygen atom being axial while the methyl group is equatorial. The water molecules are involved in intermolecular hydrogen bonds. The structure is presented in Fig. 20.

5.11. $[Eu(pic)(pyzNO)(H_2O)_6](pic)_2(pyzNO)H_2O$

The complex was prepared by reaction of the hydrated europium picrate with pyrazine-*N*-oxide in ethanol [52]. The emission spectrum contains an extremely weak $^5D_o \rightarrow {}^7F_o$ transition. The $^5D_o \rightarrow {}^7F_1$ transition contains three peaks (one A_2' level and two to E'' levels). The $^5D_o \rightarrow {}^7F_2$ transition shows an intense peak with a shoulder and two peaks due to E' and two E'' level. The spectrum was interpreted in terms of a D_{3h} distorted to C_{3v} symmetry [20]. The structure of the neodymium complex, isomorphous with that of europium, was determined and achieves a

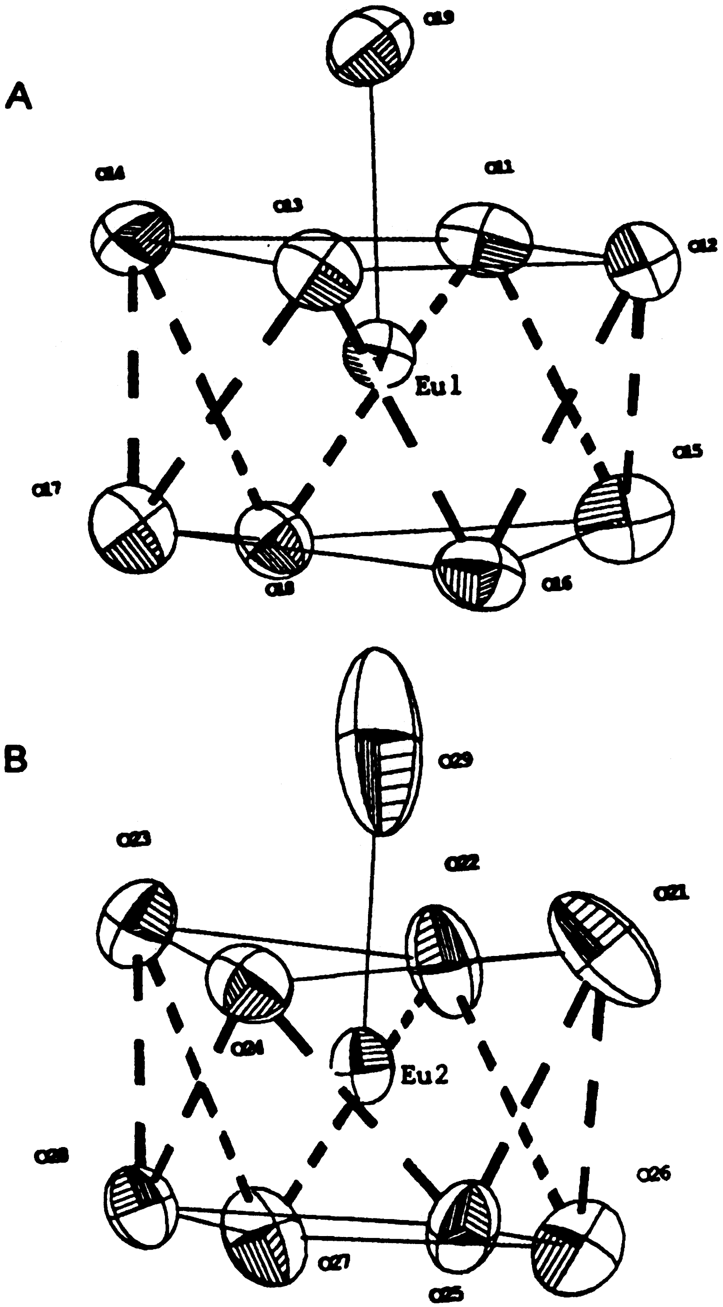

Fig. 15. Coordination polyhedra around Eu1 and Eu2 in the complex of formula [Eu(pic)$_3$·(3-picNO)$_2$(H$_2$O)] (Ref. [48]).

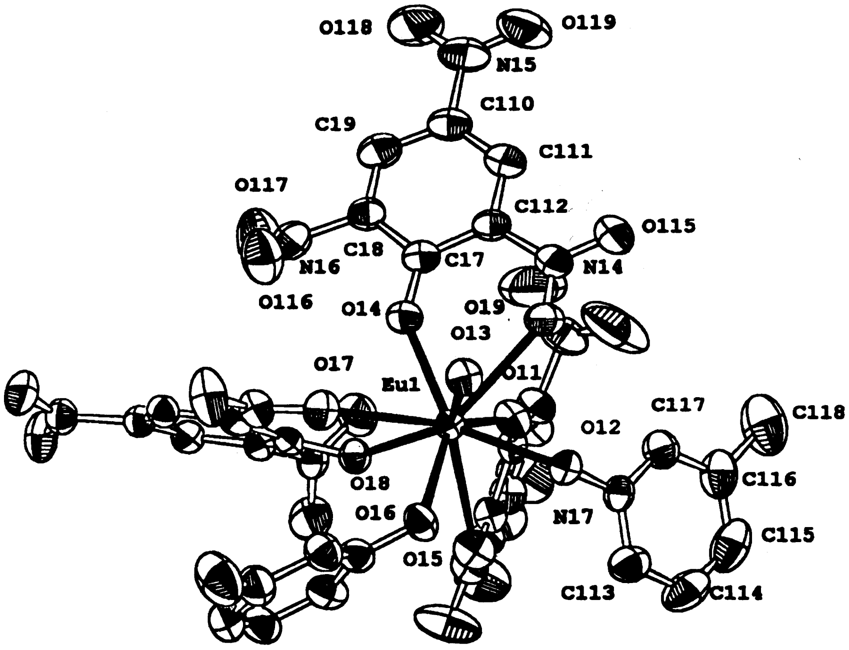

Fig. 16. Structure of Eu 1 in the complex of formula [Eu(pic)$_3$·(3-picNO)$_2$(H$_2$O)] (Ref. [48]).

coordination number nine by the bonding of one bidentate picrate via the phenoxo-oxygen and an oxygen of the adjacent nitro moiety, an oxygen of one pyrazine-*N*-oxide and six oxygens of water molecules, in a distorted tricapped trigonal prism fashion and contains two picrates, one pyzNO and one water molecule that are out of the Nd coordination sphere.

5.12. [Eu(pic)$_3$(DTSO)$_3$]

Lanthanide picrate complexes with DTSO, with composition [Ln(pic)$_3$(DTSO)$_3$] (Ln = La–Yb, Y) have been synthesized and form an isomorphous series [53]. The emission spectrum of the europium complex contains a weak peak due to $^5D_o \rightarrow {}^7F_o$ (transition to A$_1$ level), three peaks due to $^5D_o \rightarrow 7F_1$ (transition to one A$_2$ and two E levels, the latter splits into two peaks) and five peaks due to $^5D_o \rightarrow {}^7F_2$ (transition to one A$_1$ and two E levels) and was interpreted in terms of a C_{4v} symmetry [20]. Single crystal X-ray analysis of the Gd complex was carried out. The coordination polyhedron is a distorted monocapped square antiprism (C_{4v} symmetry). One base is planar and the other is slightly distorted and the cap is over the latter base.

5.13. [Eu(NO$_3$)$_3$(AZA)$_3$]

Complexes with composition [Ln(NO$_3$)$_3$(AZA)$_3$] (Ln = Nd, Eu, Gd, Tb, Ho, Er) were obtained by the reaction of the hydrated lanthanide nitrates with AZA in

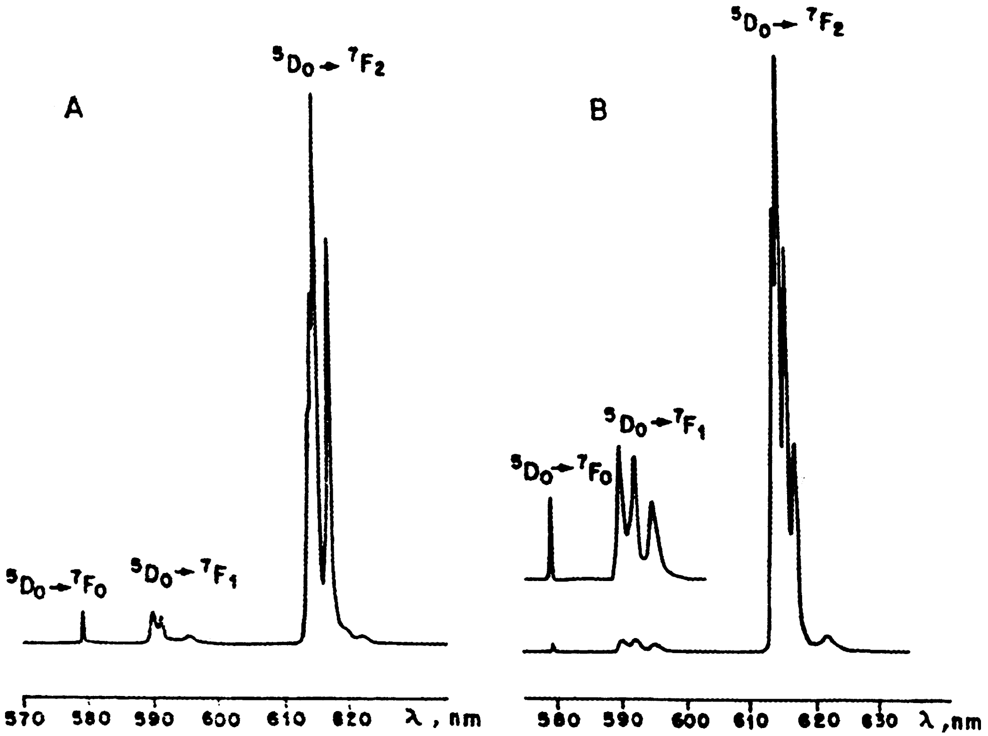

Fig. 17. Emission spectra of the complexes: A $[Eu(pic)_3{\cdot}3(DEPP)]$ and B $[Eu(pic)_3{\cdot}3(DMVP)](H_2O)$ at 77 K (Ref. [50]).

ethanol [54]. The luminescence spectrum presents a very weak $^5D_o \rightarrow {}^7F_o$ band, three peaks due to $^5D_o \rightarrow {}^7F_1$ (two peaks very close due to E level and one due to A_1 level). The $^5D_o \rightarrow {}^7F_2$ transition also presents three peaks (one due to transition to

Table 3
Distances (Å) between Eu(III) and oxygens in the complexes of formula $[Eu(pic)_3(DEPP)_3]$ and $[Eu(pic)_3(DMVP)_3](H_2O)$ [47]

	DEPP	DMVP
Eu 01	2.333(10)	2.351(7)
Eu 03	2.363(9)	2.369(8)
Eu 02	2.354(10)	2.353(7)
Eu 011	2.344(9)	2.354(6)
Eu 021	2.336(8)	2.332(5)
Eu 031	2.333(10)	2.345(7)
Eu 0111	2.608(10)	2.597(6)
Eu 0211	2.628(11)	2.621(7)
Eu 0311	2.605(13)	2.616(8)

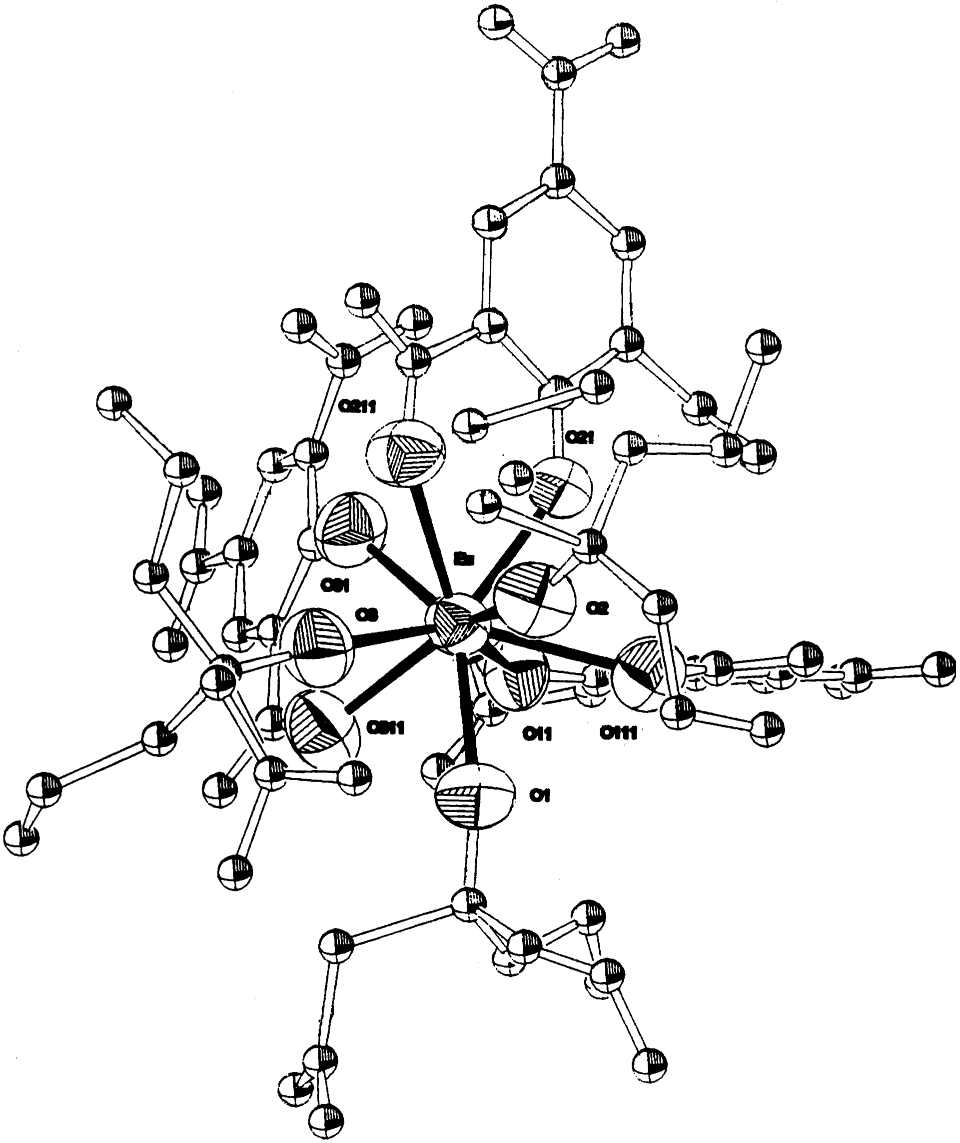

Fig. 18. Structure of the complex [Eu(pic)$_3$·3(DMVP)](H$_2$O). Thermal ellipsoids for Eu and O bonding atoms are drawn at 50% probability. For clarity, other atoms are in an arbitrary scale (Ref. [50]).

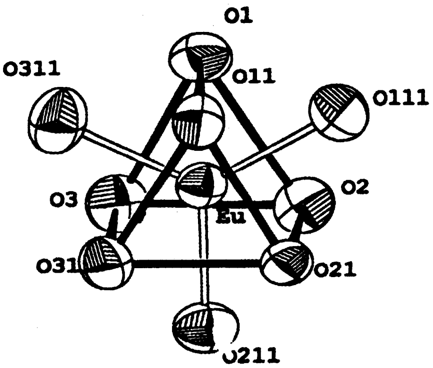

Fig. 19. Coordination polyhedron of [Eu(pic)$_3$·3(DMVP)] (Ref. [50]).

an A_1 level and two due to transitions to E levels). The spectrum was interpreted in terms of a D_{3h} distorted to C_{3v} symmetry [20].

The structure of the Er complex, isomorphous with that of europium, was determined. The Er ion achieves a coordination number nine by bonding three bidentate nitrate groups and three oxygens of three azacyclononanone moieties, in a slightly distorted trigonal prism fashion.

6. Compounds with coordination number 10

Table 4 presents some complexes with coordination number 10.

7. Final remarks

As shown in the previous sections the most frequent coordination number is nine in the form of a generally distorted, tricapped trigonal prismatic geometry. In the case of not too large ligands the symmetries found are close to D_{3h} or C_{3v}, whereas with the bulky polydentate ligands D_3 or lower symmetries are observed. The monocapped square antiprism polyhedron is rare. We could find one example with two crystallographically independent europium sites, and this is reflected in the luminescence spectrum.

Coordination number ten is also very common, specially when bulky polydentate ligands are involved, and low symmetries C_1, C_2 or D_2 are obtained. In most cases authors do not provide a local symmetry attribution but in some cases a bicapped dodecahedron, a distorted bipyramidal and bicapped square antiprism were attributed.

Coordination number eight is also frequent and the most common polyhedron found is a square antiprism, being also described as a bicapped trigonal prism and

Table 4
Selected compounds found in the literature with CN = 10

Formula	Geometry and/or coordination	Symmetry	Fluorescence	Peaks	Ref.
$[Eu(NO_3)_3 \cdot 12(crown\text{-}4)^{a}]$	Bicapped dodecahedron 3 bidentate nitrates 4 oxygens of the crown ether	D_2	$^5D_o \rightarrow {}^7F_o$ $^5D_o \rightarrow {}^7F_1$ $^5D_o \rightarrow {}^7F_2$	1	[55]
$[Eu(NO_3)_2(C_{12}H_{26}N_2O_4)^{b}]NO_3$	2 bidentate nitrates 6 donor atoms of the macrocycle	C_2	$^5D_o \rightarrow {}^7F_o$ $^5D_o \rightarrow {}^7F_1$ $^5D_o \rightarrow {}^7F_2$	1 3 5	[56]
$[Eu(NO_3)_2 \cdot Me_2(2,2)^{c}]$ $*[Eu(NO_3)_6]^{3-}$	Not attributed	C_2	Spectra recorded with several excit. energies	Several	[57]
$[Eu(NO_3)_2L^{d}_{B}]_{2d}[Eu(NO_3)_5]$ **I** **II**	**I** Local geometry not attributed **II** Distorted trigonal bipyramidal	Large deviation of D_{3h}	$^5D_o \rightarrow {}^7F_o$ $^5D_o \rightarrow {}^7F_1$ $^5D_o \rightarrow {}^7F_2$	2 two Eu sites 6 5	[58]
$[Eu(mbzimpy)^{e}(NO_3)_3(CH_3OH)]$	1 Tridentate mbzimpy 3 Bidentate nitrates 1 Methanol	Low	$^5D_o \rightarrow {}^7F_o$ $^5D_o \rightarrow {}^7F_1$ $^5D_o \rightarrow {}^7F_2$	1 3 3	[59]
$[EuL_2{}^{f}(NO_3)_2]NO_3 \cdot 2MeOH$	Bicapped SAP 2 Tridentate ligands 2 Bidentate NO_3^-	C_1	$^5D_o \rightarrow {}^7F_o$ $^5D_o \rightarrow {}^7F_1$ $^5D_o \rightarrow {}^7F_2$	1 vw 3 4	[60]
$[EuL^{f}(NO_3)_3 \cdot H_2O]L$	1 Tridentate ligand 3 Bidentate NO_3^- 1 Water	Low	$^5D_o \rightarrow {}^7F_o$ $^5D_o \rightarrow {}^7F_1$ $^5D_o \rightarrow {}^7F_2$	1 3 1	[61]

[a] 1,4,7,10-tetraozacyclododecane 12-crown-4.
[b] 1,7,10,16-tetraoxa-4,13-diazacyclooctadecane.
[c] Me(2,2) = 4,13-dimethyl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane.
[d] L_B = 2,4,8,15,18,21 hexaoxatricyclo [20.4.0.09.14] hexacosane.
[e] mbzimpy = 2,6-bis(1-methylbenzimidazol-2-yl) pyridine.
[f] L = 2,4-bis(3,5-dimethylpyrazol-1-yl)-6-methoxy-1,3,5-triazine.
* Coordination number 12.

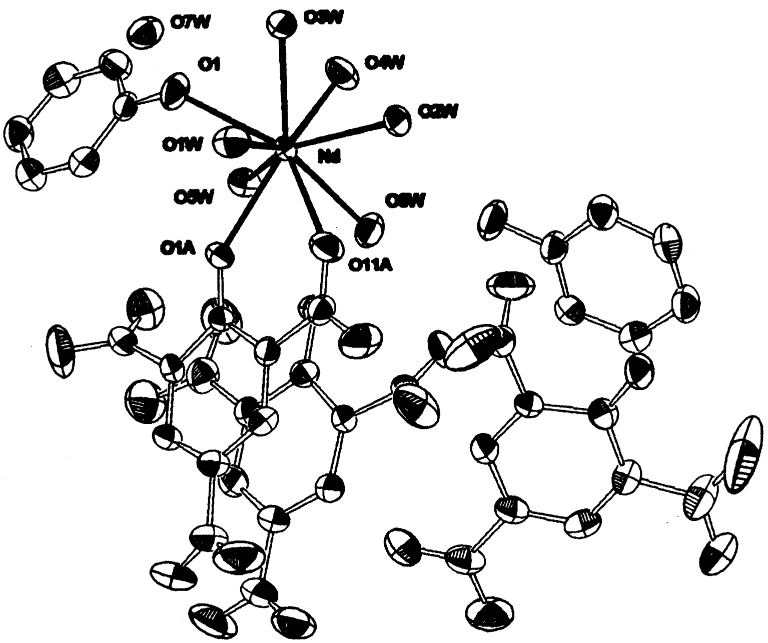

Fig. 20. Structure of the complex of formula [Nd(pic)$_3$·(MMNO)(H$_2$O)$_2$] isomorphous with that of europium (Ref. [51]).

one dodecahedron (D_{2d}). It is worth noting that in all the complexes synthesized in our laboratory the coordination polyhedron is close to the ideal D_{4d} symmetry.

Only a few examples of coordination numbers seven and six were found. In the case of coordination seven a monocapped trigonal prism with D_3 or D_{3h} symmetry has been suggested. For coordination number six the complex presented an O_h, distorted symmetry, with the central ion occupying the center of a crystallographically octahedral configuration.

Through the emission spectrum it is possible, in most cases, to establish an approximate microsymmetry around the central ion. Moreover, the existence of two peaks attributed to $^5D_o \rightarrow {}^7F_o$ and a large number of peaks due to $^5D_o \rightarrow {}^7F_{1,2}$ transitions, are indicative of the existence of two different europium sites. Another aspect to be emphasized is: when the $^5D_o \rightarrow {}^7F_{1,2}$ bands are large and poorly resolved, the existence of polymeric species may be predicted.

Generally, the peaks due to the $^5D_o \rightarrow {}^7F_2$ transition are more intense than those of $^5D_o \rightarrow {}^7F_1$, indicating the non-existence of an inversion center. In compounds with coordination number six, there is an inversion of the relative intensities indicating that the compound has a center of symmetry.

Another aspect that has to be considered is that practically all capping distances, except in compounds of coordination seven, are larger than that of the central atom to the corners of the fundamental polyhedron.

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