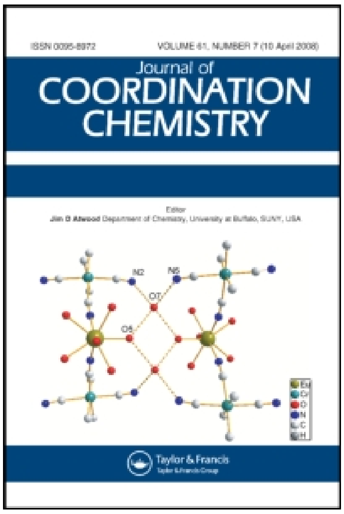

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SYNTHESIS, CRYSTAL STRUCTURE AND LUMINESCENCE STUDIES OF A LANTHANIDE COORDINATION POLYMER WITH A NEW DOUBLE BETAINE LIGAND

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SYNTHESIS, CRYSTAL STRUCTURE AND LUMINESCENCE STUDIES OF A LANTHANIDE COORDINATION POLYMER WITH A NEW DOUBLE BETAINE LIGAND

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A novel europium(III) coordination polymer with a new double betaine derivative, $\{[Eu(L^1)(NO_3)(H_2O)_3](NO_3)_2 \cdot 3.5H_2O\}_n$ (L^1 = 1,3-*bis*(pyridinio-4-carboxylato)-propane) has been synthesized and its structure determined. Its luminescence properties have also been studied. The title metal carboxylate coordination polymer contains centrosymmetric dimeric units in which each pair of metal ions is linked by a pair of *syn–anti* carboxylato-*O,O′* groups, and each pair of such dimeric units is bridged by the backbones of L^1 ligands to form infinite double chains in the *b* direction. These metal carboxylate chains are further cross-linked by hydrogen bonds among both coordinated and discrete nitrate anions, aqua ligands and lattice water molecules to form a three-dimensional network. Luminescent data show that the L^1 ligand is a good energy donor and the complex has a relatively long luminescent lifetime.

Keywords: Crystal structure; coordination polymer; europium(III); double betaine

INTRODUCTION

Lanthanide carboxylate complexes have been widely studied,[1,2] and most are found to exhibit a variety of dimeric or infinite chain structures. Recent

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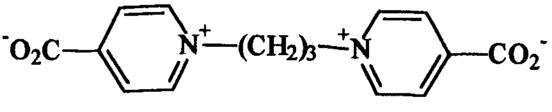
studies in our laboratory have demonstrated that the prototype tertiary amine betaine ($Me_3N^+CH_2CO_2^-$), its derivatives, and structural analogues of the corresponding carboxylate anions, are useful in the generation of lanthanide carboxylate complexes with new structural features due to their overall charge neutrality and possible inclusion of various of counter anions in the structure.[3–6] The lanthanide complexes isolated so far have been found to be mononuclear in which the carboxylate group is unidentate,[3] dimeric with the two lanthanide ions bridged by four *syn–syn* carboxylato-*O,O′* groups,[4] and polynuclear.[5,6] Since a double betaine contains two carboxylato groups, its linkage with the metal ion is expected to be much more complicated, as compared to a betaine. However, reports on the synthesis and crystal structure of their lanthanide complexes are thus far rather limited.[7,8] In this paper, we report the synthesis and crystal structure determination of a novel europium(III) coordination polymer of a new double betaine derivative, $\{[Eu(L^1)(NO_3)(H_2O)_3](NO_3)_2 \cdot 3.5H_2O\}_n$ (L^1 = 1,3-*bis*-(pyridinio-4-carboxylato)-propane), whose main structural feature is a metal carboxylate chain. Its luminescence properties have also been studied.



1,3-*bis*(pyridinio-4-carboxylato)-propane, L^1.

EXPERIMENTAL

IR spectra were obtained from KBr pellets with a Nicolet Magna-IR 550 spectrophotometer. Electronic spectra in the UV-visible range were recorded at room temperature with a Hitachi U-2000 spectrophotometer. Excitation and emission spectroscopic measurements were performed on a Hitachi MPF-4 fluorescence spectrophotometer at room temperature in the solid state.

Synthesis of the L^1 Ligand

1,3-Dibromopropane (10 cm^3, 0.1 mol) was dissolved in 100 cm^3 of acetone to give a colourless solution. To this solution ethyl isonicotinate (33 cm^3, 0.22 mol) was added. Refluxing the mixture gave a white precipitate which was collected by filtration. Hydrolysis of the product in 50 cm^3 of 5% w/v hydrochloric acid and then removal of the solvent yielded a white powder (25.2 g, yield 72%). Removal of the bromide and chloride ions with moist silver(I) oxide, finally yielded colourless microcrystals of L^1 (17.4 g, yield 61%). *Anal.* for $C_{15}H_{14}N_2O_4$ calculated (%): C, 62.9; H, 4.9; N, 9.8.

Found: C, 63.1; H, 4.8; N, 9.7. IR data (KBr) (cm^{-1}): 1641s, 1567s, 1509w, 1470m, 1453w, 1371s, 1338m, 1247m, 1214m, 1187m, 1152m, 1070w, 853m, 795s, 749m, 699s, 664m, 627m, 548w, 517w.

Synthesis of the Complex $\{[Eu(L^1)(NO_3)(H_2O)_3](NO_3)_2 \cdot 3.5H_2O\}_n$

Hydrated europium(III) nitrate and L^1 ligand were dissolved in distilled water at a 1 : 1 molar ratio. The mixture was stirred at 60°C for 10 min and then filtered. Slow evaporation of the filtrate afforded colourless blocky crystals of the title complex, yield 54%. *Anal.* for $C_{15}H_{27}N_5O_{19.5}Eu$ calculated (%): C, 24.2; H, 3.6; N, 9.4; Eu, 20.5. Found: C, 24.3; H, 3.7; N, 9.3; Eu, 20.4. IR data (cm^{-1}): 3381s, 2426w, 2396w, 1763m, 1688s, 1641s, 1617s, 1575s, 1463m, 1407s, 1384s, 1249m, 1213w, 1182m, 1149m, 1076w, 1067m, 992w, 884m, 872m, 825s, 788s, 686s, 667s, 631m, 566m.

Crystal Structure Determination

Information concerning crystallographic data and structure refinement of the title complex is summarized in Table I. Data collection was performed

TABLE I Summary of data collection, cell parameters and structural refinement

Formula	$C_{15}H_{27}N_5O_{19.5}Eu$
Formula weight	741.38
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
Cell dimension	
a/Å	10.509(3)
b/Å	11.438(2)
c/Å	12.628(2)
α/°	69.77(1)
β/°	71.27(2)
γ/°	89.80(2)
Cell volume U/Å^3	1338.9(6)
Z	2
D_{calc}/g cm^{-3}	1.839
μ/mm^{-1}	2.438
F(000)	742
Crystal size/mm	0.28 × 0.34 × 0.38
Collect range, $2\theta_{max}$	h, $\pm k$, $\pm l$, 52°
Data collected	6054
Unique data	5149 ($R_{int} = 3.86\%$)
Observed data ($I > 2\sigma(I)$), n	4273
No. of variables, p	365
Final R (for data with $I > 2\sigma(I)$)	$R1 = 4.84\%$, $wR2 = 11.00\%$
Final R (for all data)	$R1 = 6.53\%$, $wR2 = 12.01\%$
S (goodness-of-fit)	1.026
Largest difference peak and hole/e Å^{-3}	0.962, −0.925

$R1 = \sum\Delta/\sum|Fo|$, $wR2 = \{\sum w[(Fo)^2 - (Fc)^2]^2/\sum w[(Fo)^2]^2\}^{1/2}$ and $S = [\sum w\Delta^2/(n-p)]^{1/2}$, $\Delta = ||Fo| - |Fc||$; $w = 1/[\sum(|Fo|^2)^2 + (0.059P)^2 + 1.1P]$ where $P = [\mathrm{Max}\,(|Fo|^2, 0) + 2(Fc)^2]/3$.

on a Siemens R3m/V diffractometer in the variable ω-scan mode[9] using MoKα radiation (λ = 0.71073 Å) at 294 K. Unit cell parameters were calculated from least-squares fitting of 2θ angles for 25 reflections. Crystal stability was monitored by recording three check reflections at intervals of 197

TABLE II Atomic coordinates ($\times 10^5$ for Eu(III) atom; $\times 10^4$ for other atoms) and equivalent isotropic displacement parameters (Å$^2 \times 10^4$ for Eu(III) atom; $\times 10^3$ for other atoms) for the title complex

Atom	*x/a*	*y/b*	*z/c*	*U(eq)*
Eu(1)	10466(1)	6383(1)	12533(1)	240(1)
O(1)	−1458(5)	153(5)	2062(4)	34(1)
O(2)	−668(5)	1671(5)	2459(4)	34(1)
O(3)	277(5)	2256(5)	−99(4)	38(1)
O(4)	−519(5)	1193(4)	−979(4)	36(1)
N(1)	−5666(6)	1613(5)	4110(5)	28(1)
N(2)	−930(6)	5607(5)	−3208(5)	31(1)
C(1)	−1634(7)	998(7)	2497(6)	28(2)
C(2)	−3048(7)	1203(6)	3085(6)	27(1)
C(3)	−3328(7)	2096(7)	3630(7)	36(2)
C(4)	−4638(8)	2300(7)	4119(6)	37(2)
C(5)	−4145(7)	508(7)	3123(7)	37(2)
C(6)	−5451(7)	718(7)	3630(6)	34(2)
C(7)	−7070(7)	1906(7)	4593(6)	32(2)
C(8)	−7334(7)	3030(7)	3634(7)	37(2)
C(9)	−1176(7)	6782(7)	−4033(7)	38(2)
C(10)	−467(8)	5612(7)	−2330(7)	39(2)
C(11)	−246(8)	4508(7)	−1557(7)	37(2)
C(12)	−1170(9)	4534(7)	−3345(7)	43(2)
C(13)	−980(8)	3407(7)	−2581(6)	38(2)
C(14)	−494(7)	3383(6)	−1681(6)	28(2)
C(15)	−224(7)	2175(6)	−849(5)	28(2)
O(1w)	3068(6)	−419(6)	1337(5)	51(2)
O(2w)	2513(5)	852(5)	−773(4)	40(1)
O(3w)	2537(6)	2533(5)	655(5)	45(1)
O(4w)	7418(11)	4986(8)	930(7)	108(3)
O(5w)	4355(9)	2986(8)	7691(8)	114(3)
O(6w)	6312(8)	1884(7)	6660(6)	76(2)
O(7w)	4610(33)	5489(32)	1370(31)	242(16)
N(3)	1108(6)	−346(5)	3739(5)	30(1)
O(31)	384(5)	−915(5)	3403(4)	36(1)
O(32)	1763(5)	696(5)	2984(4)	36(1)
O(33)	1211(6)	−768(5)	4740(4)	48(2)
N(4)	5834(11)	2500(14)	476(11)	107(4)
O(41)	5532(12)	1827(16)	59(15)	202(8)
O(42)	6990(9)	2749(12)	458(9)	134(4)
O(43)	4939(11)	2947(12)	1086(9)	135(4)
N(5)	7224(11)	5028(10)	4168(9)	78(3)
O(51)	7297(15)	5976(11)	4298(12)	167(5)
O(52)	6736(11)	4979(9)	3390(10)	115(3)
O(53)	7813(9)	4115(9)	4618(7)	90(3)

Equivalent isotropic *U* defined as one third of the trace of the orthogonalized *Uij* tensor. Atom O(7w) has a site occupancy factor of $\frac{1}{2}$.

data measurements, and no significant variation was detected. The raw data were processed with a learnt-profile procedure[10] and empirical absorption corrections based on ψ-scan data were also applied.

All calculations were performed on a PC 486 computer with the SHELXTL-PC program package[11] and SHELXL-93 program package which refines the structure based on F^2.[12] The crystal structure was solved by Patterson method. Non-hydrogen atoms were refined anisotropically. The lattice water molecule (O(7w)) was given a site occupancy factors of $\frac{1}{2}$ according to the occupancy refinement. All hydrogen atoms were generated geometrically, assigned fixed isotropic thermal parameters and included in the structure factor calculations. Analytical expressions of neutral atom scattering factors were employed,[13] and anomalous dispersion corrections were incorporated. Final atomic coordinates are listed in Table II.

RESULTS AND DISCUSSION

Crystal Structure of $\{[Eu(L^1)(NO_3)(H_2O)_3](NO_3)_2 \cdot 3.5H_2O\}_n$

The crystal structure of the complex comprises a metal carboxylate chain built from two *syn–anti* carboxylato-*O,O′* bridged dimeric units, discrete nitrate anions and lattice water molecules. As illustrated in Figure 1, the europium(III) atom is nine-coordinated by four oxygen atoms from three separate L^1 ligands, two oxygen atoms from a bidentate nitrate anion and three aqua ligands. Mean Eu–O (carboxylate), Eu–O (nitrate) and Eu–O (aqua) bond lengths are 2.435(5), 2.547(5) and 2.442(5) Å, respectively. The carboxylate groups of the ligand are involved in two kinds of coordination modes, bidentate chelating mode (O(1)–C(1)–Eu(1) 60.1(4)° and O(2)–C(1)–Eu(1) 62.5(3)°) and *syn–anti* bidentate bridging mode (C(14)–C(15)–O(3)–Eu(1) −174.0° and C(14)–C(15)–O(4)–Eu(1a) 63.9°). The distance between the two metal ions in the dimeric unit is 4.968(1) Å.

Each pair of dimeric units is connected by a pair of L^1 ligands to form infinite double chains in the *b* direction (Figure 1). The linkage of L^1 ligands with the europium(III) ions results in the formation of the large and small voids which are alternate along the double chains. The small void is formed by two metal ions and a pair of bidentate bridging carboxylate groups, whereas the large cavity is created by four europium(III) atoms and a pair of L^1 ligands. Adjacent such chains are further cross-linked by hydrogen bonds among both coordinated and discrete nitrate anions, and both aqua ligands and lattice water molecules to form a three-dimensional network (Figure 2 and Table III).

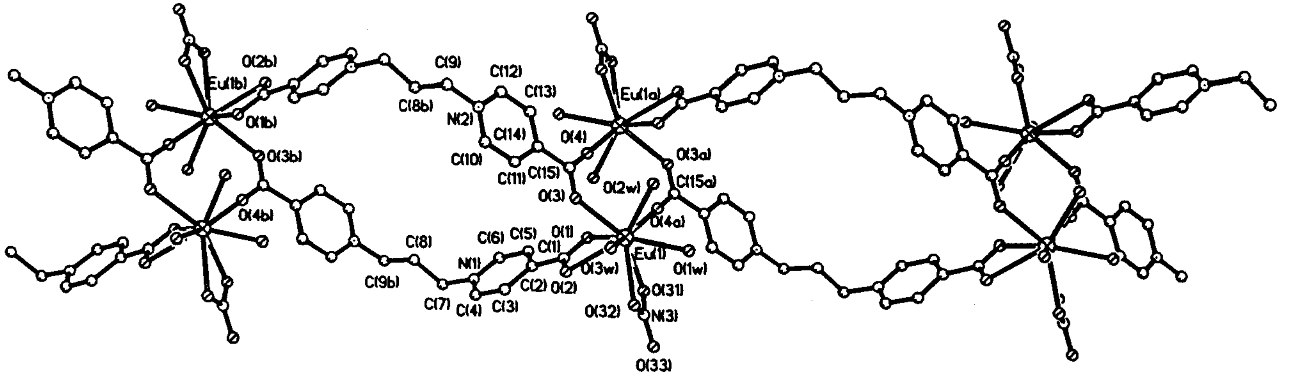


FIGURE 1 Perspective view showing the metal carboxylate double chains of complex **1** along the *b* direction with the atom labelling scheme (the lattice water molecules and uncoordinated nitrate anions have been omitted for clarity).

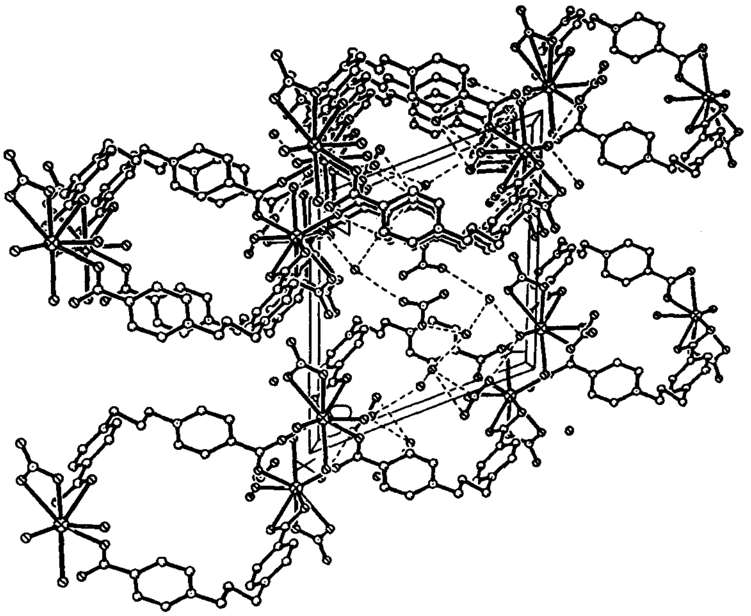


FIGURE 2 Packing drawing showing the linkage of metal carboxylate chains through hydrogen bonds among both coordinated and discrete nitrate anions, aqua ligands and lattice water molecules.

The coordination geometry of the europium(III) atom is best described as a distorted mono-capped square antiprism. The least-squares plane fitted to atoms O(31), O(32), O(1) and O(2) has a mean deviation of 0.246 Å, whereas another face defined by O(1w), O(3w), O(3) and O(4a) has a mean deviation of 0.091 Å with the capping atom (O(2w)) displaced 1.780 Å above. The dihedral angle between these two least-squares planes is ca 2.3°. The europium(III) atom resides 1.754 and 0.671 Å, respectively, from the above two faces (Figure 3).

Luminescent Properties of $\{[Eu(L^1)(NO_3)(H_2O)_3](NO_3)_2 \cdot 3.5H_2O\}_n$

The excitation spectrum of the title complex ($\lambda_{em} = 614\,nm$) exhibits a very strong ligand absorption band at 320 nm and the characteristic absorption bands of the europium(III) ion (362, 367, 376, 381, 386, 395(max), 417, 465 and 474 and 490 (nm)). Excitation at 320 nm for L^1 ligand and 395 nm for the europium(III) ion results in two similar emission spectra. The intensities of each transition in these two spectra are almost equal. This indicates that ligand L^1, which possesses conjugated pyridinio and carboxylato groups,

TABLE III Bond lengths (Å) and angles (°) for the complex

Eu(1)–O(4a)	2.335(5)	Eu(1)–O(3)	2.384(5)	Eu(1)–O(3w)	2.419(5)
Eu(1)–O(2w)	2.453(5)	Eu(1)–O(1w)	2.454(5)	Eu(1)–O(1)	2.484(5)
Eu(1)–O(2)	2.536(5)	Eu(1)–O(31)	2.544(5)	Eu(1)–O(32)	2.550(5)
O(4)–Eu(1a)	2.335(5)	C(8)–C(9b)	1.522(10)	C(9)–C(8b)	1.522(10)
Eu(1)···Eu(1a)	4.968(1)				
Hydrogen bonding					
O(1w)···O(2w)	2.804	O(5w)···O(6w)	2.629	O(53)···O(6w)	2.917
O(4w)···O(7w)	2.916	O(42)···O(4w)	2.886	O(52)···O(4w)	2.954
O(32)···O(1w)	2.796	O(32)···O(3w)	2.815	O(43)···O(3w)	2.822
O(41)···O(1wc)	2.856	O(3w)···O(4wc)	2.842	O(52)···O(5wd)	2.718
O(5w)···O(7wd)	2.812	O(1w)···O(6we)	2.784	O(2w)···O(5wf)	2.795

O(4a)–Eu(1)–O(3)	104.8(2)	O(4a)–Eu(1)–O(3w)	150.5(2)
O(3)–Eu(1)–O(3w)	73.8(2)	O(4a)–Eu(1)–O(2w)	73.6(2)
O(3)–Eu(1)–O(2w)	73.9(2)	O(3w)–Eu(1)–O(2w)	77.9(2)
O(4a)–Eu(1)–O(1w)	78.8(2)	O(3)–Eu(1)–O(1w)	140.7(2)
O(3w)–Eu(1)–O(1w)	84.5(2)	O(2w)–Eu(1)–O(1w)	69.7(2)
O(4a)–Eu(1)–O(1)	72.7(2)	O(3)–Eu(1)–O(1)	75.3(2)
O(3w)–Eu(1)–O(1)	132.5(2)	O(2w)–Eu(1)–O(1)	125.8(2)
O(1w)–Eu(1)–O(1)	139.6(2)	O(4a)–Eu(1)–O(2)	124.0(2)
O(3)–Eu(1)–O(2)	71.7(2)	O(3w)–Eu(1)–O(2)	84.2(2)
O(2w)–Eu(1)–O(2)	144.5(2)	O(1w)–Eu(1)–O(2)	139.0(2)
O(1)–Eu(1)–O(2)	52.0(2)	O(4a)–Eu(1)–O(31)	80.1(2)
O(3)–Eu(1)–O(31)	143.9(2)	O(3w)–Eu(1)–O(31)	118.9(2)
O(2w)–Eu(1)–O(31)	139.5(2)	O(1w)–Eu(1)–O(31)	75.4(2)
O(1)–Eu(1)–O(31)	72.1(2)	O(2)–Eu(1)–O(31)	76.0(2)
O(4a)–Eu(1)–O(32)	124.6(2)	O(3)–Eu(1)–O(32)	129.1(2)
O(3w)–Eu(1)–O(32)	69.0(2)	O(2w)–Eu(1)–O(32)	127.7(2)
O(1w)–Eu(1)–O(32)	67.9(2)	O(1)–Eu(1)–O(32)	106.4(2)
O(2)–Eu(1)–O(32)	71.2(2)	O(31)–Eu(1)–O(32)	50.0(2)
C(1)–O(1)–Eu(1)	94.0(4)	C(1)–O(2)–Eu(1)	91.5(4)
C(15)–O(3)–Eu(1)	128.4(4)	C(15)–O(4)–Eu(1a)	179.1(5)

Symmetry codes: a: $-x, -y, -z$; b: $-x-1, -y+1, -z$; c: $-x+1, -y+1, -z$; d: $-x+1, -y+1, -z+1$; e: $-x+1, -y, -z+1$; f: $x, y, z-1$.

can transfer its energy efficiently to the europium(III) ion. The excitation spectrum and emission spectrum for ligand excitation are exhibited in Figure 4. Luminescence data are summarized in Table IV.[14,15] From the emission spectrum, it is noticed that the bands originating from the $^5D_0 \rightarrow {}^7F_3$ transition are very weak and the transitions to the $^7F_1$ and $^7F_2$ levels comprise one and two bands. The weak $^5D_0 \rightarrow {}^7F_0$ transition is also observed. Therefore the symmetry of the europium(III) ion in the title complex is C_n or C_{nv}.[14,15] From structural analysis its site symmetry is close to C_{4v} (See Figure 4). The europium ($^5D_0$) lifetime of the complex is 3.763 ms for $\lambda_{ex,em} = 320$, 614 nm, being much longer than those (in the range 2.12–2.36 ms at 77 K and 0.45–1.62 ms at 295 K) recently reported for several solvated dinuclear europium(III) triple-helical complexes of benzimidazolyl ligands.[14]

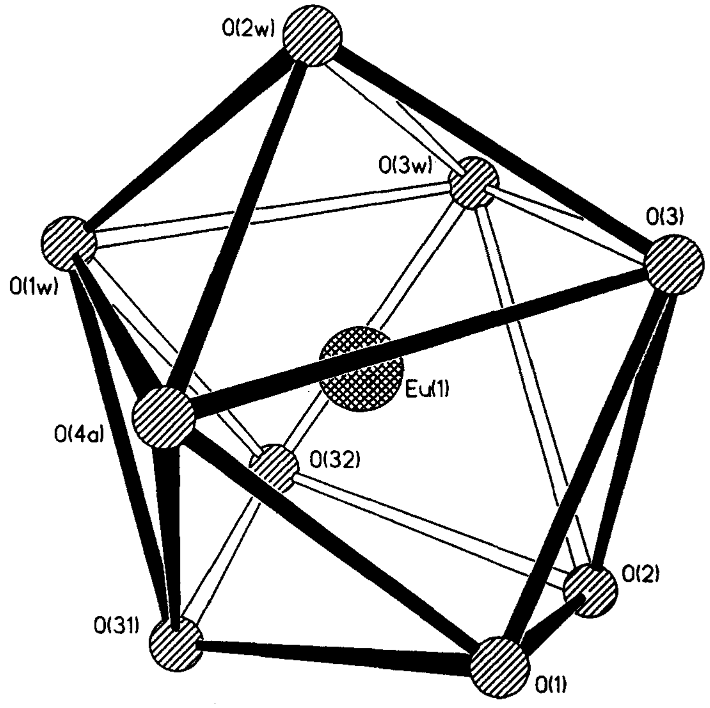


FIGURE 3 The coordination polyhedron of the europium(III) atom in the title complex.

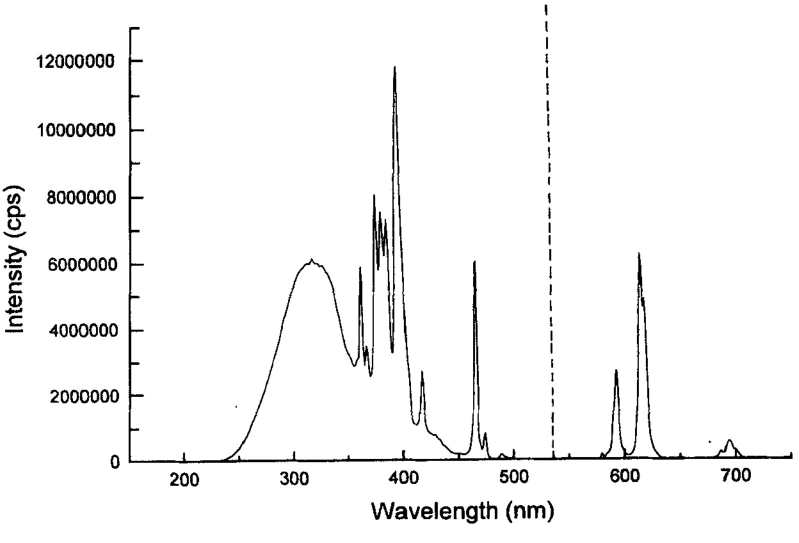


FIGURE 4 Excitation ($\lambda_{em} = 614\,nm$; left) and emission spectra at ligand excitation ($\lambda_{ex} = 320\,nm$; right).

TABLE IV Luminescence data for the title complex

E (cm^{-1})*	λ (nm)	E_0 (cm^{-1})*	*Assignment*
17271	579	0	$^5D_0 \rightarrow {}^7F_0$
16892	592	379	$^5D_0 \rightarrow {}^7F_1$
16287	614	954	$^5D_0 \rightarrow {}^7F_2$
16181	618	1090	$^5D_0 \rightarrow {}^7F_2$
15385	650	1886	$^5D_0 \rightarrow {}^7F_3$
14556	687	2715	$^5D_0 \rightarrow {}^7F_4$
14388	695	2883	$^5D_0 \rightarrow {}^7F_4$

*E represents the energy of each transition calculated from its wave lengths and E_0 is the relative energy of each transition to that of $^5D_0 \rightarrow {}^7F_0$ transition.

Supplementary Material

Atomic coordinates, anisotropic thermal parameters, full list of bond lengths and angles, observed and calculated structure factors are available from the authors on request.

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