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Trinitrato-(O,O')(triethylene glycol)europium(III), Eu(NO₃)₃(C₆H₁₄O₄)*

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Abstract. $M_r = 488$, monoclinic, $P2_1/c$, $a = 12\cdot342$ (5), $b = 9\cdot305$ (4), $c = 14\cdot201$ (5) Å, $\beta = 110\cdot88$ (5)°, $V = 1524$ (1) Å³, $Z = 4$, D_m(flotation) = $2\cdot12$ (1), $D_x = 2\cdot13$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 4\cdot55$ mm⁻¹, $F(000) = 952$, room temperature, $R = 3\cdot16\%$ for 2286 observed reflections. The Eu atom is ten-coordinated being directly bonded to the oxygen atoms of the glycol and of three bidentate nitrates. The glycol molecule forms a ring-like structure around the metal together with a nitrate ion; two other nitrates are axial above and below the ring plane. Eu–O bond distances are in the range $2\cdot433$ (4)–$2\cdot508$ (4) Å for the glycol and $2\cdot488$ (5)–$2\cdot522$ (5) Å for the nitrato oxygen atoms.

Introduction. Coordination compounds of rare earths with macrocyclic ligands such as crown ethers and cryptands have been increasingly studied in recent years, whereas relatively little attention has been devoted to the coordination behaviour of lanthanoids towards acyclic polyethers and their derivatives with various chain lengths. Recently, structural investigations on complexes of lanthanoid ions with some polyethylene glycols have shown that the etheric chain wraps the metal ion achieving a ring-like structure,

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* Triethylene glycol is 2,2'-(ethylenedioxy)diethanol.

similar to those of the crown ethers, and the possibility of separation of lanthanoids by fractional crystallization by using polyoxyethylene derivatives has been suggested (Hirashima & Shiokawa, 1979; Hirashima, Tsutsui & Shiokawa, 1980), as a consequence of the decreasing stability of the complexes with the decrease of the cationic radius. These properties, together with the high flexibility of the etheric chain, make the polyoxyethylene derivatives attractive ligands for cations with different ionic radii such as the lanthanoids. We report here the crystal and molecular structure of the complex of europium nitrate with triethylene glycol.

Experimental. Very stable crystals obtained by adding a solution of Eu(NO₃)₃.5H₂O in methyl cyanide to an equimolecular solution of the ligand in the same solvent; the mixture was refluxed for 1–2 h, crystals were obtained after addition of CH₂Cl₂. Crystal $0\cdot12 \times 0\cdot16 \times 0\cdot18$ mm, Philips PW 1100 four-circle diffractometer; lattice parameters by least-squares refinement of 25 medium-angle settings; integrated intensities up to $\theta = 25°$, $h_{max} = \pm13$, $k_{max} = 10$, $l_{max} = 14$, $\theta/2\theta$ scan, graphite-monochromated Mo $K\alpha$ radiation; 2 standard reflections: no variation; 2686 unique reflections measured, 2286 with $I > 3\sigma(I)$ used; intensities corrected for Lorentz, polarization and for

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{eq}(\text{Å}^2)$
Eu	0·27469 (3)	0·20736 (3)	0·22542 (2)	0·0408 (2)
O(1)	0·4360 (4)	0·2859 (5)	0·1777 (4)	0·062 (3)
O(2)	0·3295 (5)	0·0397 (5)	0·1115 (4)	0·074 (3)
O(3)	0·1677 (5)	−0·0251 (6)	0·1813 (4)	0·074 (3)
O(4)	0·2004 (5)	0·1098 (5)	0·3525 (4)	0·076 (4)
O(5)	0·0700 (5)	0·2722 (7)	0·1228 (5)	0·086 (4)
O(6)	0·1858 (5)	0·2906 (8)	0·0451 (4)	0·087 (4)
O(7)	0·0093 (6)	0·3490 (8)	−0·0307 (5)	0·094 (5)
O(8)	0·4342 (4)	0·0372 (5)	0·3212 (3)	0·056 (3)
O(9)	0·4422 (4)	0·2487 (5)	0·3843 (4)	0·059 (3)
O(10)	0·5820 (5)	0·0945 (7)	0·4541 (4)	0·075 (4)
O(11)	0·2895 (5)	0·4745 (5)	0·2269 (5)	0·088 (4)
O(12)	0·2068 (6)	0·3895 (6)	0·3217 (5)	0·094 (4)
O(13)	0·2233 (7)	0·6178 (6)	0·3145 (5)	0·107 (5)
N(1)	0·0866 (6)	0·3035 (7)	0·0425 (5)	0·062 (4)
N(2)	0·4900 (5)	0·1263 (7)	0·3895 (4)	0·056 (4)
N(3)	0·2394 (6)	0·4963 (6)	0·2890 (5)	0·063 (4)
C(1)	0·4794 (9)	0·2006 (12)	0·1214 (8)	0·128 (9)
C(2)	0·4123 (8)	0·0837 (8)	0·0716 (7)	0·079 (6)
C(3)	0·2669 (8)	−0·0842 (9)	0·0736 (6)	0·076 (5)
C(4)	0·1977 (11)	−0·1271 (11)	0·1273 (9)	0·130 (9)
C(5)	0·0940 (7)	−0·0631 (9)	0·2359 (6)	0·074 (5)
C(6)	0·1580 (8)	−0·0362 (9)	0·3443 (7)	0·084 (6)

Table 2. *Interatomic distances (Å) and selected angles (°)*

Coordination

Eu—O(1)	2·433 (4)	Eu—O(6)	2·522 (5)
Eu—O(2)	2·508 (4)	Eu—O(8)	2·515 (5)
Eu—O(3)	2·495 (5)	Eu—O(9)	2·488 (5)
Eu—O(4)	2·469 (4)	Eu—O(11)	2·492 (5)
Eu—O(5)	2·498 (5)	Eu—O(12)	2·502 (5)
O(1)—Eu—O(2)	64·6 (2)	O(4)—Eu—O(12)	64·3 (2)
O(2)—Eu—O(3)	62·5 (2)	O(11)—Eu—O(12)	50·1 (2)
O(1)—Eu—O(11)	68·8 (2)	O(8)—Eu—O(9)	50·9 (2)
O(3)—Eu—O(4)	64·2 (2)	O(5)—Eu—O(6)	49·5 (2)

Nitrates

N(1)—O(5)	1·262 (8)	N(2)—O(10)	1·214 (7)
N(1)—O(6)	1·217 (8)	N(3)—O(11)	1·262 (7)
N(1)—O(7)	1·210 (8)	N(3)—O(12)	1·225 (7)
N(2)—O(8)	1·276 (7)	N(3)—O(13)	1·225 (7)
N(2)—O(9)	1·273 (7)		
Eu—O(5)—N(1)	97·3 (4)	Eu—O(8)—N(2)	96·2 (4)
Eu—O(6)—N(1)	97·4 (4)	Eu—O(9)—N(2)	97·6 (4)
O(5)—N(1)—O(6)	115·8 (6)	O(8)—N(2)—O(9)	115·1 (6)
O(5)—N(1)—O(7)	121·7 (7)	O(8)—N(2)—O(10)	121·5 (7)
O(6)—N(1)—O(7)	122·4 (8)	O(9)—N(2)—O(10)	123·4 (7)
Eu—O(11)—N(3)	96·5 (4)	O(11)—N(3)—O(13)	121·8 (7)
Eu—O(12)—N(3)	97·1 (4)	O(12)—N(3)—O(13)	121·8 (6)
O(11)—N(3)—O(12)	116·4 (6)		

Glycol

O(1)—C(1)	1·36 (1)	O(3)—C(4)	1·35 (1)
C(1)—C(2)	1·40 (1)	O(3)—C(5)	1·43 (1)
O(2)—C(2)	1·40 (1)	C(5)—C(6)	1·48 (1)
O(2)—C(3)	1·39 (1)	O(4)—C(6)	1·45 (1)
C(3)—C(4)	1·39 (1)		
Eu—O(1)—C(1)	121·3 (5)	Eu—O(4)—C(6)	120·3 (4)
Eu—O(2)—C(2)	119·0 (4)	Eu—O(3)—C(4)	121·6 (5)
Eu—O(2)—C(3)	121·8 (4)	Eu—O(3)—C(5)	117·3 (4)
C(2)—O(2)—C(3)	118·3 (6)	C(4)—O(3)—C(5)	119·2 (6)
O(1)···O(11)	2·78 (1)	O(4)···O(12)	2·64 (1)
O(1)···O(2)	2·64 (1)	O(1)···O(8ⁱ)	2·83 (1)
O(2)···O(3)	2·60 (1)	O(4)···O(6ⁱⁱ)	2·95 (1)
O(3)···O(4)	2·64 (1)		

Symmetry code: (i) $1 - x, \tfrac{1}{2} + y, \tfrac{1}{2} - z$; (ii) $x, \tfrac{1}{2} - y, \tfrac{1}{2} + z$.

absorption (North, Phillips & Mathews, 1968), 0·27 < μR < 0·41; diffraction effects are dominated by heavy-atom contributions and the structure was solved by Patterson and Fourier methods; full-matrix least-squares anisotropic refinement, $R = 3.16\%$, $R_w = 3.16\%$; $\Sigma w(k|F_o| - |F_c|)^2$ minimized, $w = 1$; (carbon) H atoms introduced in calculated positions ($U_{iso} = 0.06 \text{ Å}^2$), max. $\Delta/\sigma = 0.2$; max. and min. heights in final difference synthesis 1·0 and −0·7 e Å⁻³; no correction for secondary extinction; scattering factors from *International Tables for X-ray Crystallography* (1974) for Eu, with corrections for anomalous dispersion (Cromer & Liberman, 1970), and from *SHELX* (Sheldrick, 1976) for the other atoms; calculations performed using *SHELX* and *XRAY72* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).*

Discussion. Final coordinates are given in Table 1. Interatomic distances and angles are reported in Table 2.

As shown in Fig. 1, the europium ion is ten-coordinated, being directly bonded to the four oxygen atoms of the triethylene glycol (EO3) and to three bidentate nitrates. The glycol molecule and one nitrate form a ring-like structure around Eu, two other nitrates being axial, in bisphenoidal positions, above and below the plane of the equatorial ligands. The six base oxygens are not coplanar, the shift of each oxygen from the mean plane being between +1·036 (9) and −1·222 (9) Å. The nitrates, which are nearly perpendicular to one another, are planar within 0·01 Å.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Divison as Supplementary Publication No. SUP 39202 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
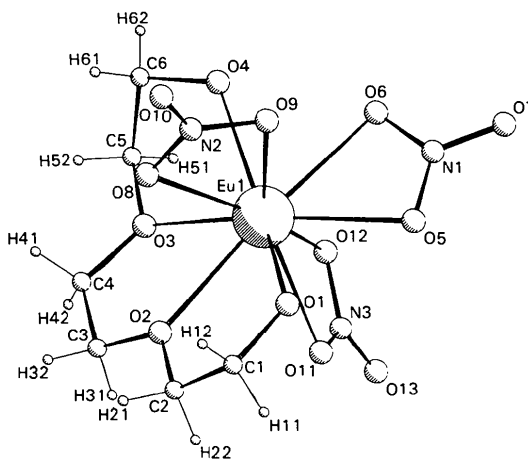

Fig. 1. Crystal structure of trinitrato(triethylene glycol)-europium(III).

Bond angles subtended at Eu by the nitrates [mean 50·2 (2)°] are fully comparable; the other O—Eu—O angles are spread over a range of larger values 62·5 (2)–68·8 (2)°. The angles at the oxygen atoms of the glycol are all very near to 120°. As already observed in coordinated bidentate nitrates, the terminal N—O bonds are shorter [mean 1·216 (7) Å] than the N—O bonds involving the chelating oxygens [mean 1·253 (8) Å] and the O—N—O bond angles involving the chelating oxygens are smaller than 120° [mean 115·8 (6)°] whereas the other two angles are correspondingly larger [mean 122·1 (8)°], indicating a tendency of the NO_3^- groups to assume a local C_{2v} symmetry. The six Eu—O (nitrate) distances [2·488 (5)–2·522 (5) Å] compare well with the two Eu—O (ether) lengths [mean 2·501 (5) Å], whereas the Eu—O (alcohol) ones are shorter [mean 2·451 (4) Å]. No significant difference in bond lengths or angles is observed between the equatorial and the axial nitrates. The O(1)···O(11) and O(4)···O(12) contact distances strongly suggest the presence of intramolecular hydrogen bonds between the glycol and the equatorial nitrate.

Apart from the difference in the chemical stoichiometry and in several other details, the molecular structure of [Eu(NO₃)₃(EO3)] is basically similar to that of [Nd(NO₃)₃(EO3)] (Hirashima, Tsutsui & Shiokawa, 1982), [Nd(NO₃)₃(EO4)] (Hirashima, Tsutsui & Shiokawa, 1981), [Nd(NO₃)₃(EO5)] (Hirashima, Kanetsuki, Shiokawa & Tanaka, 1981) and [La(NO₃)₃-(EO4)] (Casellato, Tomat, Di Bernardo & Graziani, 1982).

In all these complexes the noncyclic polyether acts as a multidentate ligand forming ring-like structures, possibly with the aid of the oxygen atoms of a nitrate group, two other nitrates being axial.

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Structures du Tris(nitroso-1 éthanal oximato-N,O')ferrate(II) de Tétraphénylphosphonium, [P(C₆H₅)₄][Fe(C₂H₃N₂O₂)₃], et du Tris(nitroso-1 éthanal oximato-N,O')ferrate(II) de Tétraphénylarsonium, [As(C₆H₅)₄][Fe(C₂H₃N₂O₂)₃]: Deux Exemples de Dédoublement Spontané des Isomères Optiques lors de la Cristallisation

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Abstract. [P(C₆H₅)₄][Fe(C₂H₃N₂O₂)₃]: $M_r = 656\cdot4$, monoclinic, $P2_1$, $a = 11\cdot663$ (5), $b = 12\cdot974$ (5), $c = 10\cdot272$ (5) Å, $\beta = 102\cdot9$ (1)°, $V = 1515$ (2) Å³, $Z = 2$, $D_x = 1\cdot44$ Mg m⁻³, Mo Kα, $\lambda = 0\cdot71069$ Å, $\mu = 0\cdot62$ mm⁻¹, $F(000) = 680$, room temperature, final $R = 0\cdot070$ for 1330 reflexions. [As-(C₆H₅)₄][Fe(C₂H₃N₂O₂)₃]: $M_r = 700\cdot4$, monoclinic, $P2_1$, $a = 11\cdot719$ (3), $b = 13\cdot038$ (4), $c = 10\cdot342$ (3) Å, $\beta = 103\cdot2$ (1)°, $V = 1538$ (2) Å³, $Z = 2$, $D_x = 1\cdot51$ Mg m⁻³, Mo Kα, $\lambda = 0\cdot71069$ Å, $\mu = 1\cdot69$ mm⁻¹, $F(000) = 716$, room temperature, final $R = 0\cdot056$ for 2041 reflexions. The compounds are isomorphous. The iron atom is chelated by three

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