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# Synthesis and structure of bis(triethanolamine)europium(II) diperchlorate

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## Abstract

The crystal structure of the title compound was determined at 293 and 100 K. The structure contains bis(triethanolamine)europium(II) cations, and perchlorate anions. The metal ion coordination environment is composed of two N and six O atoms. At room temperature, all triethanolamine molecules are partially disordered. On going to 100 K, the disorder partially disappears, giving rise to a commensurate modulation of the structure. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Europium; Divalent; Lanthanide; Crystal structure; Triethanolamine

## 1. Introduction

This work is a continuation of our studies on Eu(II) complexes with O- and N-donor ligands. Previously, we published crystal structures of a few Eu(II) carboxylates ([1–3], and references therein). The present work reports an attempt to prepare a complex with a ligand of somewhat different chemical nature, which could impose a higher symmetry around the metal cation.

## 2. Experimental

Eu<sub>2</sub>O<sub>3</sub> (2 g, 99.99%, Stanford Materials) was dissolved in a few ml of 60% HClO<sub>4</sub> (analytical grade) and then was concentrated by cautious heating until the first crystals appeared. The slurry was placed in the cathode compartment of an H-shaped electrolyzer with a sintered glass diaphragm and with a mercury cathode. Then, 4.1 g of triethanolamine (pure for syntheses) was added, and the whole was diluted with a few ml of a methanol–water (2:1, v/v) mixture. The anode compartment was filled with perchloric acid diluted with the same methanol–water solvent. The electrolysis, performed with the cathode potential set at –1.5 V with respect to the saturated calomel electrode, and with a gentle stream of N<sub>2</sub> passing over the surface of the solution, lasted a few days, and yielded yellow crystals. X-ray data collection was performed at 293 and 100 K on a Kuma KM4 diffractometer

equipped with a CCD counter and an Oxford Cryosystem appliance. Both structures were solved in a routine way, using the SHELXS-97 program [4], and were refined with SHELXL-97 [5] (see Table 1 for the details). It should be noted, however, that although the low-temperature data were finally solved with the parameters given in Table 1, inspection of the reciprocal space and the final atom positions allows one to interpret the structure as a commensurately modulated one, with the basic cell spanned by  $\frac{1}{3}\mathbf{a}_{LT}$ ,  $\mathbf{b}_{LT}$ , and  $\mathbf{c}_{LT}$  (the index LT indicates the low-temperature phase; the vectors refer to the relevant cells, as presented in Table 1), the modulation vector  $\mathbf{q}_{LT} = \frac{1}{3}\mathbf{a}_{LT}^*$ , and the superspace group  $P2_1/c(\frac{1}{3}, 0, 0)$ . Indeed, the Eu and Cl positions were found in the above-mentioned basic cell, and then transformed to the final cell, given in Table 1. The relation between the room-temperature cell (RT) and the low-temperature one is as follows:  $\mathbf{a}_{LT} \approx -3\mathbf{c}_{RT}$ ;  $\mathbf{b}_{LT} \approx \mathbf{b}_{RT}$ ;  $\mathbf{c}_{LT} \approx \mathbf{a}_{RT} + 2\mathbf{c}_{RT}$ . A possible orthorhombic cell for the low-temperature phase gave too high a value of  $R_{int}$  (0.277) to be considered. The refinement was full-matrix with all ordered non-H atoms anisotropic.

## 3. Results

The atomic parameters are given in Table 2, and the Eu–O and Eu–N distances are given in Table 3. The crystals are built of complex bis-(triethanolamine)europium(II) cations and perchlorate anions. In the room-temperature phase, the unit cell contains two Eu cations located on positions with site symmetry

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Table 1  
Crystal data and structure-refinement details

Empirical formula	$C_{12}H_{30}Cl_2EuN_2O_{14}$	
Formula weight	649.24	
Wavelength	0.71073 Å	
Temperature	293(2) K	100(2) K
Crystal system, space group	monoclinic, $C2/m$	monoclinic, $P2_1/c$
Unit cell dimensions	$a = 18.458(4)$ Å $b = 8.873(2)$ Å $c = 7.341(2)$ Å $\beta = 105.12(3)^\circ$	21.422(12) Å 8.859(4) Å 20.125(12) Å 118.19(6)°
Volume	1160.7(4) Å <sup>3</sup>	3366(3) Å <sup>3</sup>
Z, Calculated density	2, 1.858 Mg/m <sup>3</sup>	6, 1.922 Mg/m <sup>3</sup>
Absorption coefficient	3.00 mm <sup>-1</sup>	3.10 mm <sup>-1</sup>
$F(000)$	650	1950
Crystal size	0.4 × 0.2 × 0.1 mm	0.5 × 0.4 × 0.2 mm
Theta range	3.6 to 28.8°	3.7 to 28.8°
Index ranges	$-17 \leq h \leq 24$ , $-11 \leq k \leq 11$ , $-9 \leq l \leq 8$	$-19 \leq h \leq 28$ , $-11 \leq k \leq 11$ , $-26 \leq l \leq 26$
Reflections collected/unique	3712/1466 ( $R_{int} = 0.0540$ )	19368/7987 ( $R_{int} = 0.0274$ )
Completeness of the set	45.7%	85.9%
	refinement of $ F_c^2  -  F_o^2 $	
Absorption correction		
Max. and min. transmission	1.261 and 0.616	1.274 and 0.742
Data/restraints/parameters	1466/0/80	7987/3/415
Goodness-of-fit on $F^2$	2.645	1.456
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R(F) = 0.0439$ , $R_w(F^2) = 0.0944$	$R(F) = 0.0363$ , $R_w(F^2) = 0.1009$
Largest diff. peak and hole	0.956 and $-1.321$ eÅ <sup>-3</sup>	1.092 and $-1.456$ eÅ <sup>-3</sup>

$2/m$  (Wyckoff position  $a$ ), four disordered triethanolamine (tea) ligand molecules with the local symmetry  $m$ , and four perchlorate anions also with the  $m$  symmetry. The tea molecules are bisected by a mirror plane,  $m$ , which results in the following disorder. All three carbon atoms connected with the nitrogen atom are disordered over two sites each [C(2) and C(2'), C(4) and C(6), C(4') and C(6')], the prime stands for the symmetry operation  $x, -y, z$ , giving rise to clockwise and anti-clockwise twisted tea molecules. Two symmetry-related carbon atoms, C(3) [bonded to C(4)/C(6)] and C(3') [bonded to C(4')/C(6')], and two symmetry related oxygen atoms, O(2) and O(2'), are ordered. The disordered C(2) and C(2') atoms are bonded to the ordered C(1) atom, which, in turn, is bonded to an oxygen atom that is disordered between two sites, O(1) and O(1'). In this way, two settings of a disordered tea molecule can be postulated: (a) N, C(2), C(4), C(6'), C(1), C(3), C(3'), O(1), O(2) and O(2'); the parts that belong to the disordered fragments are rendered by empty bonds in Fig. 1; (b) N, C(2'), C(4'), C(6), C(1), C(3), C(3'), O(1'), O(2) and O(2'); analogously, its fragments in the disordered regions are marked with dashed bonds. It must be said that disordering of tea molecules (or its deprotonated anions) is not an uncommon phenomenon. It was detected in various variants, e.g. in tris(1-methylstannatrate) hexahydrate [6], chloro-(triethanolaminate)-copper(II) [7], bis(triethanolamine)-bis(2,4,6-trinitrophenolato- $O$ )barium(II) [8], di-isothiocyanato-(triethanolamine)-nickel(II) [9], hexafluoroacetylacetonato-triethanolamine-copper methanol solvate [10], chloro-(triethanolaminate)-cobalt(II) [11] and in disodium (triethanolaminate)-nitrosyl-vanadium(i) iodide pentahydrate [12]. The present case is similar to those described for the copper [7] or cobalt [11] complexes.

In the 100 K phase, partial ordering of the tea molecules occurs, resulting in formation of two crystallographically independent Eu sites. One of them remains on the inversion centre and both tea molecules surrounding it are now ordered. The other Eu cation is located on a general position with one tea molecule ordered and the other disordered, in a manner similar to that described for the

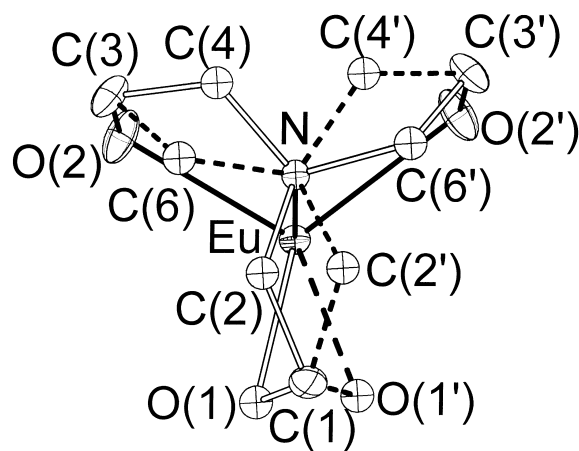


Fig. 1. View of one half of the complex cation at room temperature together with the atom labels (the prime denotes the position obtained by the symmetry operation  $x, -y, z$ ). The mirror plane passes through Eu, N and C(1). The alternative disordered fragments are shown with dashed or empty lines (see text). The other tea ligand, generated by inversion, has been omitted for the sake of clarity.

Table 2

Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	x	y	z	$U_{\text{eq}}$
<i>T</i> = 293 K				
Eu	0	0	0	0.04959(19)
Cl	0.13046(8)	−0.5	0.2822(2)	0.0510(3)
O(1) <sup>a</sup>	0.1188(4)	0.0677(8)	0.2630(9)	0.0648(16)
O(2)	0.0237(2)	0.2253(5)	−0.1923(7)	0.1040(16)
O(11)	0.1646(3)	−0.6297(6)	0.3714(9)	0.1246(19)
O(12)	0.0559(4)	−0.5	0.2867(16)	0.131(3)
O(13)	0.1342(10)	−0.5	0.0995(14)	0.201(6)
N	0.1340(3)	0	−0.1131(7)	0.0462(10)
C(1)	0.1872(5)	0	0.2327(11)	0.083(3)
C(2) <sup>a</sup>	0.1951(5)	0.0538(11)	0.0459(12)	0.062(2)
C(3)	0.0869(4)	0.2402(8)	−0.2627(9)	0.0882(18)
C(4) <sup>a</sup>	0.1269(6)	0.0982(12)	−0.2749(14)	0.061(2)
C(6) <sup>a</sup>	0.1513(6)	0.1545(13)	−0.1542(15)	0.064(2)
<i>T</i> = 100 K				
Eu(1)	0.0000	0.0000	0.0000	0.01803(9)
Eu(2)	0.334350(12)	−0.02807(2)	0.000898(13)	0.01560(8)
Cl(1)	−0.00715(5)	0.50428(14)	0.12707(6)	0.0183(2)
Cl(2)	0.32799(5)	0.47315(10)	0.13085(6)	0.0176(2)
Cl(3)	0.66187(5)	0.52148(11)	0.13000(6)	0.0187(2)
O(11)	−0.03090(17)	0.6254(4)	0.15729(18)	0.0288(7)
O(12)	−0.00397(17)	0.3656(4)	0.16530(18)	0.0273(7)
O(13)	−0.0577(2)	0.4848(4)	0.04750(18)	0.0344(9)
O(14)	0.05959(18)	0.5442(4)	0.1333(2)	0.0432(10)
O(21)	0.33597(19)	0.6141(4)	0.16736(19)	0.0364(9)
O(22)	0.27178(19)	0.4864(4)	0.0537(2)	0.0358(9)
O(23)	0.3111(2)	0.3556(4)	0.1687(2)	0.0360(9)
O(24)	0.39171(19)	0.4348(5)	0.1298(2)	0.0484(10)
O(31)	0.61112(19)	0.5344(4)	0.0508(2)	0.0374(10)
O(32)	0.6593(2)	0.6544(4)	0.1680(2)	0.0421(10)
O(33)	0.6434(2)	0.3910(4)	0.1601(2)	0.0423(10)
O(34)	0.73052(19)	0.5016(5)	0.1376(3)	0.0505(11)
O(1)	−0.01451(14)	−0.0760(3)	0.11510(16)	0.0207(6)
O(2)	0.06698(15)	0.2522(3)	0.03617(16)	0.0257(7)
O(3)	0.09440(15)	−0.1975(4)	0.02060(16)	0.0269(7)
N(1)	0.12577(17)	0.0144(4)	0.13905(19)	0.0159(7)
C(1)	0.0395(2)	−0.0187(5)	0.1869(2)	0.0220(9)
C(2)	0.1119(2)	−0.0563(5)	0.1971(2)	0.0218(9)
C(3)	0.1409(2)	0.2636(5)	0.0935(2)	0.0233(9)
C(4)	0.1491(2)	0.1719(5)	0.1598(2)	0.0223(8)
C(5)	0.1560(2)	−0.2194(5)	0.0913(2)	0.0246(9)
C(6)	0.18107(19)	−0.0697(5)	0.1302(2)	0.0241(9)
O(4)	0.40952(17)	−0.2702(3)	0.03401(17)	0.0343(8)
O(5)	0.42168(18)	0.1771(4)	0.01392(18)	0.0382(9)
N(2)	0.46409(19)	−0.0270(4)	0.1357(2)	0.0202(8)
C(7)	0.4783(2)	−0.2864(5)	0.0967(3)	0.0243(9)
O(6) <sup>a</sup>	0.3289(4)	−0.0783(9)	0.1229(4)	0.0457(18)
C(11) <sup>a</sup>	0.3845(4)	−0.006(3)	0.1892(6)	0.0266(11)
C(12) <sup>a</sup>	0.4540(4)	−0.0566(11)	0.1984(5)	0.0259(18)
C(8) <sup>a</sup>	0.5146(4)	−0.1263(9)	0.1272(5)	0.0237(17)
C(10) <sup>a</sup>	0.4948(4)	0.1338(10)	0.1424(5)	0.0244(18)
O(61) <sup>a</sup>	0.3242(2)	0.0579(6)	0.1197(3)	0.0131(10)
C(81) <sup>a</sup>	0.4846(4)	−0.1942(9)	0.1606(4)	0.0191(16)
C(101) <sup>a</sup>	0.5154(4)	0.0477(9)	0.1261(5)	0.0193(16)
C(111) <sup>a</sup>	0.3795(4)	0.000(3)	0.1898(6)	0.0266(11)
C(121) <sup>a</sup>	0.4498(4)	0.0373(10)	0.1970(5)	0.0231(19)
C(9)	0.4883(2)	0.1972(6)	0.0790(3)	0.0357(12)
O(7)	0.34184(14)	−0.0955(3)	−0.11960(16)	0.0226(6)
O(8)	0.24462(15)	−0.2344(3)	−0.02097(18)	0.0298(8)
O(9)	0.26561(18)	0.2200(4)	−0.0274(2)	0.0463(11)
N(3)	0.20475(18)	−0.0149(4)	−0.1352(2)	0.0180(7)
C(13)	0.2881(3)	−0.0332(6)	−0.1868(3)	0.0337(13)
C(14)	0.2154(2)	−0.0724(5)	−0.1976(2)	0.0260(9)
C(15)	0.1804(2)	−0.2569(5)	−0.0905(2)	0.0202(9)
C(16)	0.1522(2)	−0.1066(5)	−0.1256(2)	0.0232(9)
C(17)	0.1921(2)	0.2284(6)	−0.0818(3)	0.0408(14)
C(18)	0.1806(2)	0.1439(5)	−0.1515(2)	0.0280(10)

<sup>a</sup> Atoms with site occupancy 0.5.

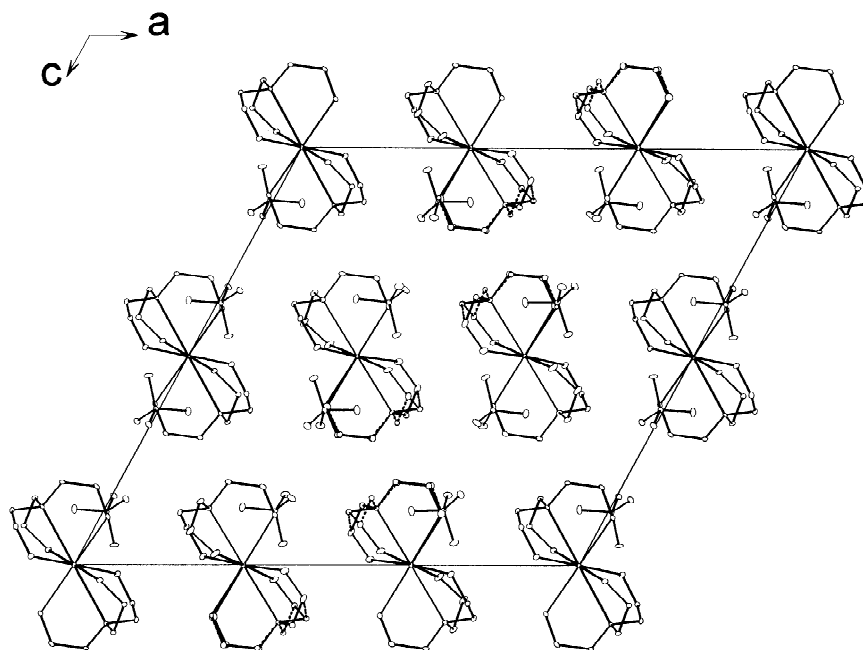


Fig. 2. View of the unit cell of the low-temperature phase along the *b* axis.

room-temperature phase (all N-bonded carbon atoms and one ethanol arm disordered). Taking all of the above into account, as well as the fact that Eu(2) is shifted practically  $\frac{1}{3}\mathbf{a}$  from Eu(1), and the space group symmetry, one obtains a picture of an ordering/disordering modulation wave running along the *a* direction, which could be described in the following way: . . . — ordered — lower half disordered — upper half disordered — ordered — . . . , and which is accompanied by small shifts and rotations of the perchlorate anions.

The metal ion is eight-coordinated, with six bonds formed with hydroxyl oxygen atoms and two with nitrogen atoms. The coordination pattern resembles that displayed by  $\text{Sr}^{2+}$  cations in bis(triethanolamine)strontium nitrate [13], bis(triethanolamine)strontium bis(2,4-dinitrophenolate) [14] and aqua-bis(triethanolamine)strontium bis-

(triethanolamine)strontium dichloride [15], although in the latter case, a part of  $\text{Sr}^{2+}$  cations accept a water molecule as the ninth ligand. The Eu–O and Eu–N distances are comparable to the Sr–O and Sr–N ones, which, for the quoted structures, are in the range 2.517–2.625 and 2.753–2.845 Å, respectively; this is brought about by close proximity of the crystal radii of both elements (1.39 Å for  $\text{Eu}^{2+}$  and 1.40 Å for  $\text{Sr}^{2+}$ ; both quantities for eight-coordinated ions [16]). It must be noted that lowering of the temperature does not bring about significant Eu–O and Eu–N bond length changes. It is also interesting to compare these data with those for Ln(III)–tea complexes. Thus, two analogous compounds of trivalent lanthanides, bis(triethanolamine)–(tetrahydrofuran)–praseodymium and ytterbium trifluoromethanesulfonates tetrahydrofuran solvates [17], are nine-coordinated, whereas a La complex, dodecakis(isopropoxy)-bis(triethanolaminato)-lanthanum-triniobium [18], is eight-coordinated. In all three of these structures, the relevant bonds are 0.1–0.2 Å shorter than those in the present compound.

The structures are held together by a moderate network of hydrogen bonds between the hydroxyl and perchlorate oxygen atoms. DIAMOND2 [19] views of a half of the complex cation in the room-temperature phase and of the crystal cell for the low-temperature phase are presented in Fig. 1 and Fig. 2, respectively.

Table 3

Eu–O and Eu–N bond lengths (Å)

<i>T</i> = 293 K			
Eu–O(1)	2.586(7)		
Eu–O(2)	2.550(4)		
Eu–N	2.806(4)		
<i>T</i> = 100 K			
Eu(1)–O(3)	2.556(3)	Eu(2)–O(5)	2.532(3)
Eu(1)–O(2)	2.568(3)	Eu(2)–O(8)	2.536(3)
Eu(1)–O(1)	2.568(3)	Eu(2)–O(6)	2.552(8)
Eu(1)–N(1)	2.825(4)	Eu(2)–O(9)	2.556(3)
		Eu(2)–O(4)	2.574(3)
		Eu(2)–O(7)	2.575(3)
		Eu(2)–O(61)	2.616(6)
		Eu(2)–N(2)	2.821(4)
		Eu(2)–N(3)	2.835(4)

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