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Crystal structure of europium(II) bis(hydroxyacetate)

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Abstract

The crystals of the title compound are composed of polymeric network built up from europium(II) cations and hydroxyacetate anions. The coordination environment of the metal is composed of six carboxylate oxygen atoms, and two hydroxyl oxygen atoms. The distances Eu–O are generally longer than those observed in Eu(III) carboxylates. © 1998 Published by Elsevier Science S.A.

Keywords: Crystal structure; Hydroxyacetate; Divalent europium; Lanthanide

1. Introduction

In previous works we have published the structures of europium(II) hydrogen acetate [1], and oxydiacetates [2,3]. Now, as a continuation of our studies on synthesis, structure and spectroscopy of compounds of divalent europium, the structure of europium(II) bis(hydroxyacetate) is presented.

2. Experimental

The crystals were obtained by electrolytical reduction of stock solution, prepared by dissolving europium oxide in hydrochloric acid, and then adding hydroxyacetic acid, and partially neutralizing the mixture with NaOH. The electrolysis was performed in an H-shaped electrolyzer with a sintered glass diaphragm at the cathode potential −1.5 V with respect to the saturated calomel electrode. A mild stream of N_2 was passed over the reduced solution in order to speed up water evaporation. After a few days yellow crystals were formed. A crystal suitable for X-ray measurement was selected, bathed in a paraffin oil, and mounted on a Kuma KM4 diffractometer. No precautions were taken against the access of air, since the dry compound is sufficiently stable. The data collection and refinement were performed with settings and parameters given in Table 1. The data were corrected for polarization and Lorentz factors, but not for absorption. The structure was solved using SHELXS-86 [4]. The europium site was found from a Patterson synthesis, the non-H atoms from a difference Fourier synthesis, the C-bonded hydrogen atoms were placed geometrically, and two hydroxyl H atoms were located on a difference map. The refinement was performed with SHELXL93 [5], with all non H atoms anisotropic and hydrogen atoms isotropic with common temperature factors separately for C- and O-bonded atoms. Constraints and restraints were applied to the C–H and O–H distances during the refinement.

Table 1
Crystal data and structure refinement details

Empirical formula	$Eu(C_2H_3O_3)_2$
Formula weight	302.1
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	Pbca
Unit cell dimensions	a=9.428(2) Å
	b=9.702(2) Å
	c=15.916(3) Å
Volume	1455.8(5) $Å^3$
Z	8
Density (calculated)	2.756(1) Mg m^{-3}
Absorption coefficient	8.597 mm^{-1}
F(000)	1128
Crystal size	0.4×0.3×0.2 mm
Theta range for data collection	2. to 30 deg.
Index ranges	$0 \le h \le 13$, $0 \le k \le 13$, $-22 \le l \le 22$
Reflections collected	4551
Reflections observed ($I \ge 3\sigma(I)$)	3343
Independent observed reflections	1768 [R(int)=0.0253]
Refinement method	Full-matrix least-squares on F^2
Weighting scheme	$w=1/\sigma^2(F^2)$
Data/restraints/parameters	1768/3/109
Goodness-of-fit on F^2	3.693
Final R indices ($I \ge 3\sigma(I)$)	$R(F)$=0.0289, $wR(F^2)$=0.0625
Extinction coefficient	0.0065(2)
Maximum shift/e.s.d.	0.012
Largest diff. peak and hole	1.307 and −2.247 e $Å^{-3}$

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Table 2
Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$)

Atom	x	y	z	U_{eq}
Eu	0.15972(2)	0.02633(2)	0.09040(2)	0.01833(11)
O(1)	−0.0517(4)	−0.0334(4)	0.1807(3)	0.0335(9)
O(2)	−0.1506(4)	−0.0404(4)	0.3061(3)	0.0346(10)
O(3)	0.1070(5)	0.1812(4)	0.2183(3)	0.0384(10)
O(4)	0.2921(4)	0.2491(4)	0.0573(3)	0.0290(8)
O(5)	0.4631(4)	0.3547(4)	−0.0129(3)	0.0287(8)
O(6)	0.2705(4)	0.0478(4)	−0.0608(3)	0.0343(9)
C(1)	−0.0712(5)	0.0139(6)	0.2531(3)	0.0259(11)
C(2)	0.0076(6)	0.1426(6)	0.2791(4)	0.0364(13)
C(3)	0.3739(5)	0.2593(5)	−0.0050(3)	0.0227(9)
C(4)	0.3649(7)	0.1591(7)	−0.0768(5)	0.045(2)

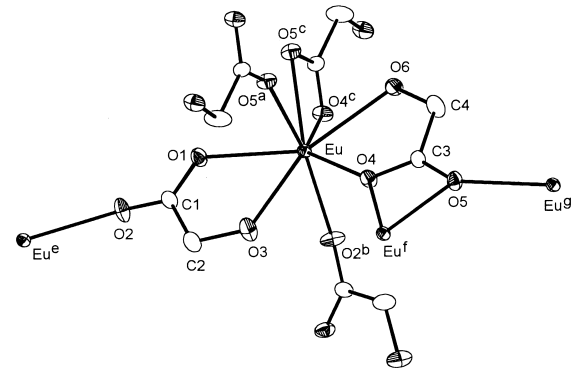

Fig. 1. Coordination of Eu cation and hydroxyacetate anions, together with atom numbering scheme. The symmetry operations are those from Table 3, and apart from that: [e] $x-1/2,y,-z+1/2$; [f] $-x+1/2,y+1/2,z$; [g] $x+1/2,-y+1/2,-z$.

3. Results

The atomic coordinates are given in Table 2, and the distances and angles around europium atom are presented in Table 3. The crystal is composed of europium(II) cations and hydroxyacetate anions. It is noteworthy, that in spite of the compound preparation method from a water solution, there are no water molecules in the structure. The same was, however observed in two lanthanide(III) hydroxyacetates [6,7]. The metal ion is surrounded by eight oxygen atoms, namely six carboxyl ones and two hydroxyl ones, which together form a rather irregular coordination polyhedron. The Eu–O distances are slightly longer (2.509(3)–2.778(4) Å, mean 2.59 Å) than those reported for europium(III) hydroxyacetate [6] (2.40(2)–2.70(2) Å, mean 2.51 Å), although the differences are not large; the largest ones may be observed for the shortest bonds of each compound. On the other hand, the Eu–O distances fall within the range of bond lengths observed for other Eu(II) carboxylates [1–3,8]. Each of the hydroxyacetate anions forms a five-membered chelate ring with europium, involving one of its carboxyl oxygen atoms and the hydroxyl one. Apart from that the hydroxyacetate anion (O1, O2, O3) is bonded to another neighbouring europium ion (Eu^e; see Fig. 1 for the meaning of the symmetry operation indices). The anion (O4, O5, O6) is involved through its O4 and O5 atoms in an additional four-membered chelate ring with the Eu^f site, and apart from that O5 forms a bond with Eu^g; thus the carboxyl group (O4, O5) is linked with three different europium sites. Such a rather complicated system of carboxyl bridges gives rise to formation of a three-dimensional polymeric network. The details of europium and hydroxyacetate coordination are shown in Fig. 1, while the crystal cell packing is given in Fig. 2.

Table 3
Selected bond lengths (Å) and angles (deg)

Eu–O(5)[a]	2.509(3)		
Eu–O(2)[b]	2.516(4)		
Eu–O(1)	2.525(4)		
Eu–O(4)	2.551(4)		
Eu–O(3)	2.579(4)		
Eu–O(5)[c]	2.611(4)		
Eu–O(6)	2.631(4)		
Eu–O(4)[c]	2.778(4)		
Eu–Eu[d]	4.1965(7)		
O(5)[a]–Eu–O(2)[b]	165.0(2)	O(3)–Eu–O(5)[c]	141.6(2)
O(5)[a]–Eu–O(1)	78.6(2)	O(5)[a]–Eu–O(6)	78.9(2)
O(2)[b]–Eu–O(1)	97.4(2)	O(2)[b]–Eu–O(6)	109.7(2)
O(5)[a]–Eu–O(4)	82.5(2)	O(1)–Eu–O(6)	148.4(2)
O(2)[b]–Eu–O(4)	90.3(2)	O(4)–Eu–O(6)	63.3(2)
O(1)–Eu–O(4)	134.3(2)	O(3)–Eu–O(6)	138.8(2)
O(5)[a]–Eu–O(3)	88.7(2)	O(5)[c]–Eu–O(6)	69.6(2)
O(2)[b]–Eu–O(3)	76.7(2)	O(5)[a]–Eu–O(4)[c]	118.3(2)
O(1)–Eu–O(3)	62.1(2)	O(2)[b]–Eu–O(4)[c]	76.0(2)
O(4)–Eu–O(3)	76.3(2)	O(1)–Eu–O(4)[c]	90.8(2)
O(5)[a]–Eu–O(5)[c]	69.9(2)	O(4)–Eu–O(4)[c]	134.5(2)
O(2)[b]–Eu–O(5)[c]	124.3(2)	O(3)–Eu–O(4)[c]	138.2(2)
O(1)–Eu–O(5)[c]	82.1(2)	O(5)[c]–Eu–O(4)[c]	48.4(2)
O(4)–Eu–O(5)[c]	128.9(2)	O(6)–Eu–O(4)[c]	80.7(2)

Symmetry transformations used to generate equivalent atoms: [a] $x-1/2,-y+1/2,-z$; [b] $x+1/2,y,-z+1/2$; [c] $-x+1/2,y-1/2,z$; [d] $-x,-y,-z$.

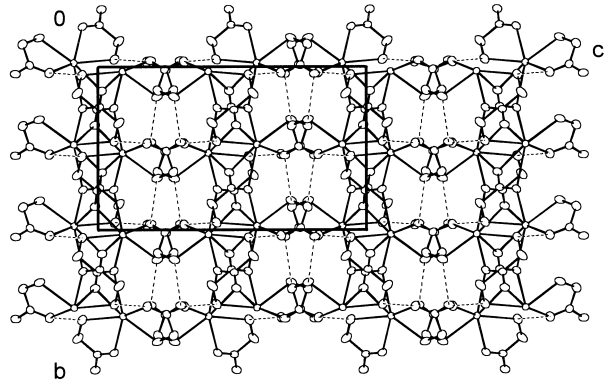

Fig. 2. Crystal cell packing. The dashed lines represent the hydrogen bonds.

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