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Journal of Alloys and Compounds 224 (1995) 217–219

Journal of ALLOYS AND COMPOUNDS

Crystal structure of triaquadihydrogen triaquatris(oxydiacetato)dieuropate(II)

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Received 16 December 1994; in final form 18 January 1995

Abstract

The crystal structure of the title compound has been determined by X-ray analysis. The crystals are hexagonal and there are two different metal sites. One of the europium ions is surrounded by nine oxygen atoms belonging to three oxydiacetate moieties, whereas the environment of the other is composed of six carboxylate oxygen atoms and three water molecules. The crystal as a whole is built up from a three-dimensional complex polymeric network.

Keywords: Europium; Lanthanides; Oxydiacetate; Crystal structure

1. Introduction

In a preceding paper [1] the crystal structure of monoclinic europium(II) oxydiacetate, together with a short survey of the structures of other Eu(II) complexes with organic ligands, have been presented. In the present paper another Eu(II) compound with an oxydiacetate ligand will be described.

2. Experimental

When performing the electrolysis, as described in [1], apart from the monoclinic crystals, more intensely coloured, yellow crystals with hexagonal habit were also occasionally obtained. They were stable in air for a few weeks, reduced iodine–starch papers, and the fresh samples did not show the characteristic brick-red luminescence of Eu(III). For a structural investigation a specimen was cut from a larger crystal, placed in a nitrogenated Lindemann glass capillary (which, as it proved later, was an excessive precaution), and mounted on a Kuma KM4 diffractometer. The structure was solved and refined with SHELXS-86 [2] and SHELXL93 [3] respectively. The Eu sites were found from a Patterson map, the non-H atoms from a difference map, and the C-bonded hydrogen atoms were placed geometrically. The O-bonded hydrogen atoms could not be located. The structure was set with respect to the absolute axes to choose the better *R* value. The refinement was performed with all non-H atoms anisotropic and the C–H distances constrained, and a common hydrogen thermal displacement factor. The other details of data collection and refinement are presented in Table 1.

3. Results

The atomic coordinates and equivalent thermal displacement factors are presented in Table 2, and the main distances and angles in Table 3. The Eu–$O_{carboxylate}$ bond distances are shorter than those in [1], and are comparable to those in relevant Eu(III) complexes [4,5]. The Eu1 cation has the 32 (D_3) site symmetry, and is surrounded by three oxydiacetate moieties. The coordination figure may be described as a distorted tricapped trigonal prism (TCTP). The geometry of the ligand imposes a twist of one base (O2, $O2^a$, $O2^b$) with respect to the other ($O2^c$, $O2^d$, $O2^e$), which, measured as the torsion angle defined by O2–center of the first base–center of the other–$O2^d$ (which belongs to the same oxydiacetate moiety as O2), is $-104.5°$. This may be compared with the value of $-120°$ for an ideal tricapped trigonal prism (which is here thought of as a figure with perfect D_{3h} or $\bar{6}2m$ symmetry). The environment of Eu2 has the site symmetry $\bar{6}$ (C_{3h}) and forms a slightly distorted TCTP. The distortion in this case consists in small twisting of the triangle spanned by equatorial water molecules (OW1 and symmetry related) with respect to the bases (formed by O1, $O1^h$, $O1^i$ and $O1^f$, $O1^g$, $O1^j$ respectively). The twist angle

0925-8388/95/$09.50
SSDI 0925-8388(95)01554-X

Table 1
Crystal data and structural refinement details

Empirical formula	$(H_8O_3)^{2+}[Eu_2(C_4H_4O_5)_3(H_2O)_3]^{2-}$
Formula weight	810.2
Temperature	301(2) K
Wavelength	0.710 69 Å
Crystal system	Hexagonal
Space group	$P\bar{6}2c$
Reflections for unit cell determination	25, $18° \leqslant 2\theta \leqslant 22$
Unit cell dimensions	$a = 9.318(8)$ Å $c = 17.427(9)$ Å
Volume	1310(2) $Å^3$
Z	2
Density calculated	2.053(3) Mg m^{-3}
Density measured	2.05 Mg m^{-3} in $C_2H_4Br_2/CCl_4$
Absorption coefficient	4.87 mm^{-1}
$F(000)$	784
Crystal size	$0.4 \times 0.3 \times 0.2$ mm
Theta range for data collection	2–30°
Index ranges	$-13 \leqslant h \leqslant 12$, $-12 \leqslant k \leqslant 12$, $-20 \leqslant l \leqslant 24$
Standards 3 per 100 reflections, mean $\sigma(I)/\langle I \rangle$	2.4%
Reflections measured	5352
Reflections observed ($I \geqslant 3\sigma(I)$)	3801
Independent reflections	1041 [$R(\text{int}) = 0.0512$]
Absorption corrections	Between 0.8120 and 1.2988, calculated with locally modified ABSORB [7]
Refinement method	Full-matrix least-squares on F^2
Weights	$1/\sigma^2(F^2)$
Data/restraints/parameters	1036/1/59
Goodness-of-fit on F^2	2.474
Final R indices [$I \geqslant 3\sigma(I)$]	$R(F) = 0.0306$, $wR(F^2) = 0.0592$
Maximum shift/e.s.d.	< 0.001
Largest diff. peak and hole	0.804 and -0.854 e $Å^{-3}$

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

Atom	x	y	z	U_{eq}
Eu1	0.0	0.0	0.5	0.02903(11)
Eu2	0.3333	−0.3333	0.75	0.03708(13)
OW1	−0.011(2)	−0.566(2)	0.75	0.129(5)
OW2	0.879(2)	0.084(2)	0.75	0.114(4)
O1	0.1663(7)	−0.2673(7)	0.6572(3)	0.074(2)
O2	0.0291(5)	−0.1705(6)	0.5937(2)	0.0507(10)
O3	0.2650(6)	0.0	0.5	0.0452(14)
C1	0.1556(14)	−0.183(2)	0.6053(2)	0.049(2)
C2	0.3027(10)	−0.0900(11)	0.5529(4)	0.064(2)

is 2.6°, which is the complement of the torsion angle, say, OW1–Eu2–center of the O1, $O1^h$, $O1^i$ base–$O1^h$, 177.4°, to 180° required for the ideal figure. Oxydiacetate moieties are bonded to three different metal cations each, thus giving rise to a complex three-dimensional polymeric network, the holes of which are filled with OW2 molecules. The fivefold coordination of OW2 (with respect to H-bonding) merits some attention. The nearest environment of OW2 consists of two other, symmetry-generated, OW2 atoms (at the distance of 2.88(2) Å), thus forming a triangular $(OW2)_3$ complex,

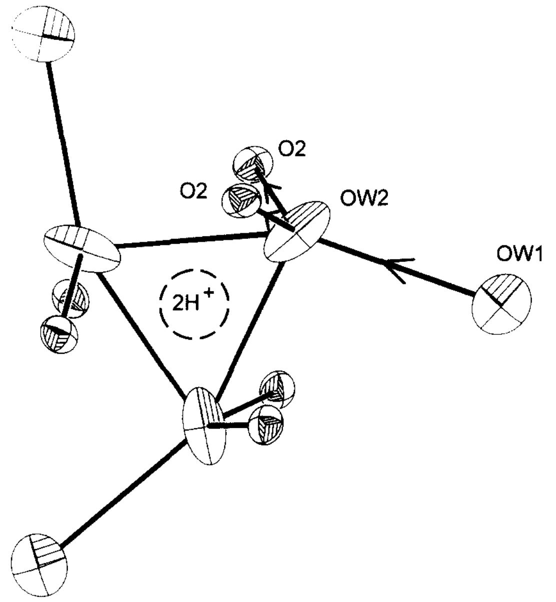

Fig. 1. The scheme of hydrogen bonds around the OW2 water molecules and the possible site for two additional protons. The arrows show the donor-to-acceptor direction. The symmetry indices are not shown for the sake of simplicity.

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

Eu1-O2,O2^{a},O2^{b},O2^{c},O2^{d},O2^{e}			2.386(4)
Eu1-O3,O3^{a},O3^{e}			2.469(6)
Eu2-O1,O1^{f},O1^{g},O1^{h},O1^{i},O1^{j}			2.525(4)
Eu2-OW1,OW1^{h},OW1^{i}			2.83(2)
O2^{a}-Eu1-O2	78.4(2)	O2-Eu1-O3^{a}	136.3(2)
O2^{b}-Eu1-O2	87.4(2)	O3-Eu2-O1^{f}	120.0
O2^{c}-Eu1-O2	147.9(2)	O1-Eu2-O1^{f}	79.7(3)
O2^{d}-Eu1-O2	126.9(2)	O1-Eu2-O1^{g}	134.85(9)
O2^{e}-Eu1-O2	78.4(2)	O1-Eu2-O1^{h}	83.3(2)
O2-Eu1-O3^{e}	74.0(2)	O1-Eu2-O1^{i}	83.3(3)
O2^{a}-Eu1-O3	74.0(2)	O1-Eu2-O1^{j}	134.85(9)
O2^{b}-Eu1-O3	74.9(2)	O1-Eu2-OW1^{h}	69.3(32)
O2^{c}-Eu1-O3	136.3(2)	O1-Eu2-OW1	56.6(2)
O2^{d}-Eu1-O3	63.5(2)	O1^{f}-Eu2-OW1	65.6(2)
O2^{e}Eu1-O3	136.3(2)	O1^{g}-Eu2-OW1	140.1(2)
O2-Eu1-O3	63.5(2)	O1^{h}-Eu2-OW1	140.1(2)
O3^{e}-Eu1-O3	120.0	O1^{i}-Eu2-OW1	69.3(2)
O2^{a}-Eu1-O3^{a}	63.5(2)	O1^{j}-Eu2-OW1	69.3(2)
O2^{b}-Eu1-O3^{a}	136.3(2)	OW1^{h}-Eu2-OW1	120.0
O2^{c}Eu1-O3^{a}	63.5(2)	O1-Eu2-OW1^{i}	140.1(2)
O2^{d}-Eu1-O3^{a}	74.0(2)	OW1-Eu2-OW1^{i}	120.0
O2^{e}-Eu1-O3^{a}	74.0(2)		

Symmetry transformations used to generate equivalent atoms: $^{a}-y,\ x-y,\ z$ $^{b}-x,\ -x+y,\ -z+1$ $^{c}y,\ x,\ -z+1$ $^{d}x-y,\ -y,\ -z+1$ $^{e}-x+y,\ -x,\ z$ $^{f}x,\ y,\ -z+3/2$ $^{g}-x+y+1,\ -x,\ ,-z+3/2$ $^{h}-x+y+1,\ -x,\ z$ $^{i}-y,\ x-y-1,\ z$ $^{j}-y,\ x-y-1,\ -z+3/2$.

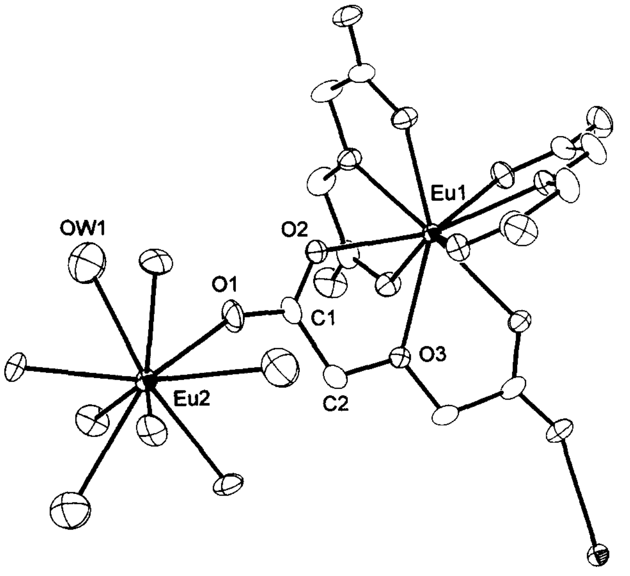

Fig. 2. Coordination of Eu cations, and the oxydiacetate anion, together with labels of symmetry-independent atoms.

two symmetry-generated O2 atoms (2.880(6) Å) and a symmetry-generated OW1 molecule (2.89(2) Å). These bonds cannot be served by water hydrogen atoms only. Therefore it seems probable that each $(OW2)_3$ complex is held together by the two additional protons necessary for electric neutrality of the structure, and in this way the complex $(H_8O_3)^{2+}$ cation is formed. The scheme of the hydrogen bonding around the OW2 atoms, together with donor–acceptor directions, is shown in Fig. 1. The coordination of both metal ions and the oxydiacetate ligand is presented in Fig. 2, and the crystal cell packing is shown in Fig. 3 [6].

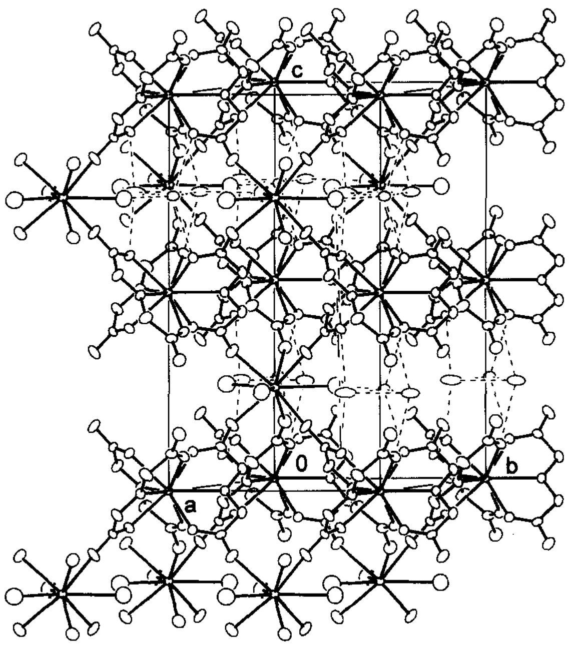

Fig. 3. Crystal cell packing. The dashed lines represent the hydrogen bonds.

Acknowledgements

The author would like to thank Prof. K. Bukietyńska for discussion, Dr. S. Krzewska for valuable suggestions, and Prof. T. Głowiak for help in X-ray measurements. This work was supported by Komitet Badań Naukowych (grant 4133/PB/ICH/92).

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