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STRUCTURE AND SPECTROSCOPY OF DIAQUA(μ_3-ACETATO)(ACETATO-*O*)(ACETIC ACID-*O*)EUROPIUM(II), [Eu(OAc)$_2$(AcOH)(H$_2$O)$_2$]

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Abstract—The crystal structure and absorption spectrum of the title compound are presented. The crystals are isomorphic with those of the analogous strontium compound. The spectrum shows a shift of the *f–d* transitions towards longer wavelengths as compared with Eu$^{\text{II}}$ halogenide systems.

Contrary to considerable interest in the physical chemistry of divalent lanthanide compounds (ref. 1 and references therein), a paucity of structural data, especially of complexes with organic ligands, in this area may be noticed. In the particular case of europium, the reported structures include those of compounds with pentamethyl-cyclopentadienyl,[2,3] bis(trimethylsilyl)amine,[4,5] carbazol-9-yl,[6] t-butanolate,[7] 2,4-dicarbadodecaborane[8] and an acetate.[9] The present paper deals with another acetate, obtained in an acidic aqueous environment.

EXPERIMENTAL

Reagents

The title compound was obtained by electrolytic reduction of a europium(III) acetate aqueous solution acidified with acetic acid. The vessel used was an H-shaped electrolyser with sintered glass diaphragm, mercury cathode and platinum anode. A solution of potassium acetate in *ca* 50% acetic acid was utilized as the anolyte. The reduction was conducted with the cathode potential set at -1.5 V with respect to the saturated calomel electrode. A mild stream of N$_2$ was passed over the reduced solution of europium acetate; this was designed to accelerate water evaporation only, and no means to prevent air access were applied. After a few days of electrolysis small, plate-shaped lemon yellow crystals were formed, which were stable in air, enough to withstand a few days of X-ray data collection. Freshly obtained crystals did not show the characteristic brick red luminescence of Eu$^{\text{III}}$ under a UV lamp.

X-ray data collection

A crystal of approximate dimensions $0.4 \times 0.4 \times 0.2$ mm was cut from a larger one, and then mounted on a Kuma KM4 diffractometer with κ geometry. The structure was solved using Patterson methods with SHELXS-86[10] and then refined with SHELXL-93.[11] The positions of oxygen-bonded hydrogen atoms were found from difference Fourier synthesis, and the methyl ones were placed geometrically, taking into account the distribution of electron density around the relevant carbon atoms. The absorption corrections were calculated with locally modified ABSORB.[12] The structure was refined with all non-hydrogen atoms anisotropic and hydrogen atoms isotropic (methyl-bonded hydrogen atoms with common U factor) with restrained positional parameters. Other information pertinent to the data collection, solution and refinement is presented in Table 1.

Spectroscopy

Since the crystals were too small to perform a single-crystal measurement, the absorption of

Table 1. Crystal data and structure refinement details

Empirical formula	$C_6H_{14}O_8Eu$
Formula weight	366.13
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 7.021(3)$ Å $b = 7.144(3)$ Å $c = 12.454(4)$ Å $\alpha = 88.05(3)^\circ$ $\beta = 83.42(4)^\circ$ $\gamma = 71.84(4)^\circ$
Volume	589.6(4) Å^3
Z	2
Density (calculated)	2.062 Mg m^{-3}
Absorption coefficient	5.338 mm^{-1}
$F(000)$	354
Crystal size	0.4 × 0.4 × 0.2 mm
Theta range for data collection	2–30°
Index ranges	$0 \leqslant h \leqslant 9$, $-9 \leqslant k \leqslant 10$, $-17 \leqslant l \leqslant 17$
Reflections collected	3696
Reflections observed	$[I \geqslant 3\sigma(I)]$ 3338
Independent reflections	3096 ($R_{int} = 0.0599$)
Refinement	Full-matrix least-squares on F^2; 3093 reflections; 160 parameters, 12 restraints; weights: $w = 1/\sigma^2(F^2)$
Goodness-of-fit on F^2	3.207
Final R indices	$R(F) = 0.0285$, $R_w(F^2) = 0.0669$
Largest diff. peak and hole	2.089 and -2.196 e Å^{-3}

powder suspended in paraffin oil was recorded on a Cary 5 spectrophotometer at room temperature.

RESULTS AND DISCUSSION

Structure

The essence of the results obtained is presented in Table 2. The present compound is isomorphic with the previously reported diaqua(μ_3-acetato)(acetato-*O*)(acetic acid-*O*)strontium.[13] The europium cation is eight-coordinate. The Eu—O bond distances (average 2.617 Å) are similar to those in the strontium analogue (mean Sr—O distance 2.602 Å), and somewhat shorter than in potassium europium(II) acetate (2.678 Å).[9] On the other hand, the Eu^{II}—$O_{carboxylate}$ bond lengths are well within the range observed for the relevant bonds in europium(III) acetates,[14–16] [minimum 2.333 Å, maximum 2.782 Å, mean 2.496(112) Å], whereas the europium–water distances in the present compound are definitely larger than in Eu^{III} complexes [the relevant mean taken from 27 structures deposited in the Cambridge Structural Database[17] being 2.449(48) Å]. The coordination geometry around the metal ion may be described as intermediate between a dodecahedron [with O(1), O(2), O(5) and O(3) forming an elongated tetrahedron or A-type vertices,[18] and O(W1), O(W2), O(1^b) and O(2^a) spanning the flattened tetrahedron of B-type vertices] and a bicapped trigonal prism [O(1), O(W2), O(1^b) and O(W1), O(2^a), O(3) forming the bases, and O(2), O(5) being the caps]. The parameter Δ, defined as the average of squares of distances between the real atoms and corresponding vertices of the least-squares fitted ideal polyhedron,[18] $\Sigma d_i^2/8$, is 0.168 Å^2 for the former and 0.179 Å^2 for the latter. The structure is composed of polymeric europium–acetate chains running along the (010) direction, which, in turn, are connected with a network of hydrogen bonds, of which a more detailed description is given elsewhere,[13] and will not be repeated here for the sake of brevity. An ORTEP[19] view of europium, acetate and acetic acid coordination is given in Fig. 1, and the view of the unit cell is presented in Fig. 2.

Table 2. Selected bond lengths (Å) and angles (°)

Eu—O(2^a)	2.473(3)	O(1)—Eu^b	2.489(3)
Eu—O(1^b)	2.489(3)	O(2)—C(1)	1.256(5)
Eu—O(5)	2.601(3)	O(2)—Eu^a	2.473(3)
Eu—O(W2)	2.643(4)	O(3)—C(3)	1.237(6)
Eu—O(W1)	2.667(4)	O(4)—C(3)	1.303(6)
Eu—O(3)	2.669(4)	O(5)—C(5)	1.265(6)
Eu—O(1)	2.684(3)	O(6)—C(5)	1.229(6)
Eu—O(2)	2.710(3)	C(1)—C(2)	1.506(6)
Eu—Eu^b	4.238(2)	C(3)—C(4)	1.507(7)
Eu—Eu^a	4.267(2)	C(5)—C(6)	1.514(7)
O(1)—C(1)	1.272(5)		

O(2^a)—Eu—O(1^b)	170.3(2)	O(5)—Eu—O(3)	71.3(2)
O(2^a)—Eu—O(5)	82.9(2)	O(W2)—Eu—O(3)	142.6(2)
O(1^b)—Eu—O(5)	87.5(2)	O(W1)—Eu—O(3)	69.6(2)
O(2^a)—Eu—O(W2)	85.6(2)	O(2^a)—Eu—O(1)	117.5(2)
O(1^b)—Eu—O(W2)	90.3(2)	O(1^b)—Eu—O(1)	70.0(2)
O(5)—Eu—O(W2)	72.3(2)	O(5)—Eu—O(1)	142.3(2)
O(2^a)—Eu—O(W1)	76.5(2)	O(W2)—Eu—O(1)	77.8(2)
O(1^b)—Eu—O(W1)	111.2(2)	O(W1)—Eu—O(1)	85.1(2)
O(5)—Eu—O(W1)	132.2(2)	O(3)—Eu—O(1)	129.9(2)
O(W2)—Eu—O(W1)	145.9(2)	O(2^a)—Eu—O(2)	69.3(2)
O(2^a)—Eu—O(3)	98.1(2)	O(1^b)—Eu—O(2)	117.8(2)
O(1^b)—Eu—O(3)	79.9(2)	O(5)—Eu—O(2)	136.5(2)
O(W2)—Eu—O(2)	72.8(2)		
O(W1)—Eu—O(2)	73.9(2)		
O(3)—Eu—O(2)	143.2(2)		
O(1)—Eu—O(2)	48.2(2)		

Symmetry transformations used to generate equivalent atoms: $^a -x, -y+1, -z$; $^b -x, -y, -z$.

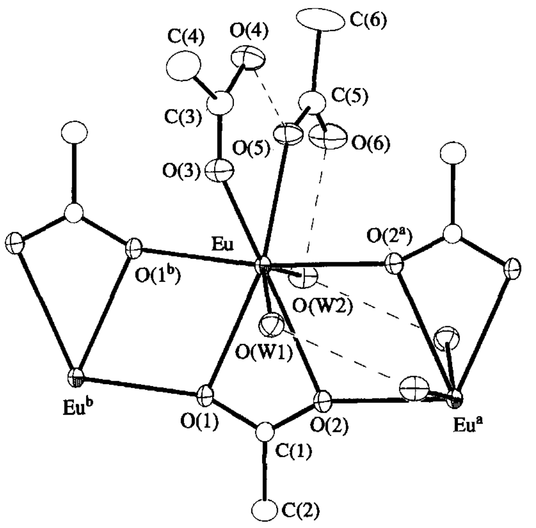

Fig. 1. Fragment of the polymeric chain, together with the atom numbering scheme. The symmetry codes have been adopted from Table 2, and the dashed lines show the hydrogen bonds.

Spectroscopy

The absorption spectrum of the powder suspended in paraffin oil is given in Fig. 3. The *f–d* absorption band, which starts at *ca* 450 nm, consists of a broad plateau with weakly developed structure, which was hardly susceptible to a reliable Gaussian decomposition. Four components, which are more or less discernible, are located at *ca* 422, 347, 305 and 260 nm (23,700, 28,800, 32,800 and 38,500 cm^{-1}, respectively). In terms of a $J\gamma$ coupling scheme,[20] they represent transitions between the $4f^7\,{}^8S_{7/2}$ ground state and the $4f^65d\,{}^7Fd$ state split due to interaction of the 5*d* electron with the crystal field. Because the metal ion environment is highly irregular, the origin of the $4f^65d$ state, E_{fd}, may be determined only approximately by taking the simple average of the positions of the observed crystal field components, which is 30,900 cm^{-1}. The maximum splitting of the ${}^7Fd$ state (Δ) is 14,800 cm^{-1}. It is interesting to compare these quantities, with all these reservations in mind, to some other reported systems. Thus, the E_{fd} energy is 37,700

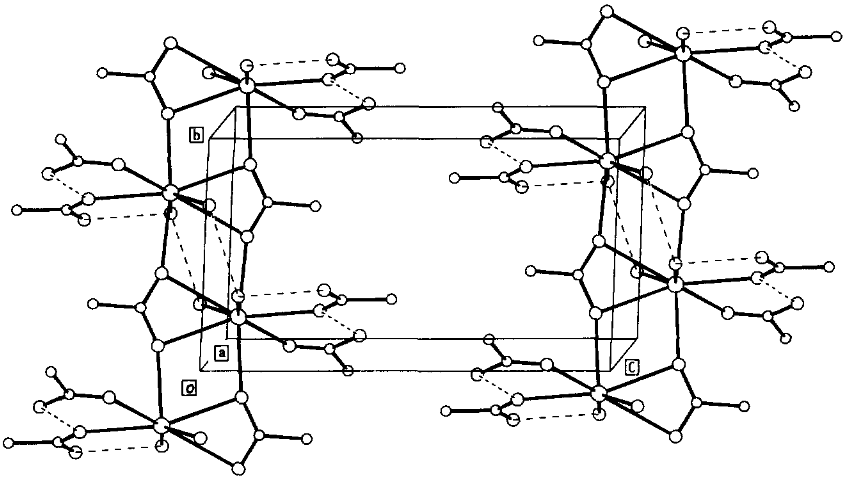

Fig. 2. Packing of the unit cell.

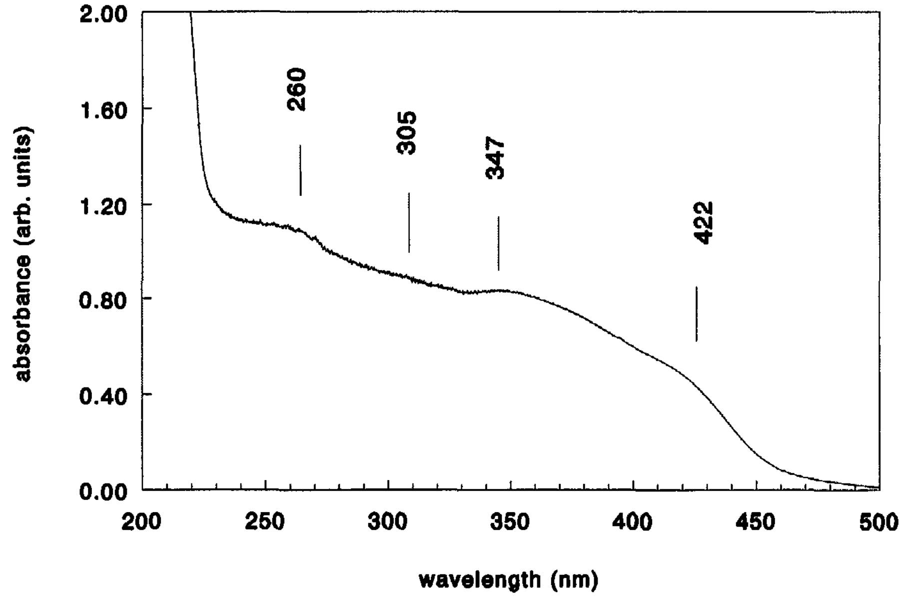

Fig. 3. The absorption spectrum of a powdered sample together with presumable crystal field components.

cm^{-1} for Eu^{2+} embedded in a CaF_2 matrix,[20,21] 35,900 cm^{-1} for $EuCl_2$ in water, 33,800 cm^{-1} for $EuCl_2$ in HMPA (hexamethylphosphoramide) and 34,900 cm^{-1} for EuI_2 in THF (tetrahydrofuran).[22,23] The crystal field splittings are 17,000, 9400, 8000 and 13,500 cm^{-1} for the reported systems, respectively. (The latter quantity was calculated as the difference between the first and the last levels of the ^7Fd state, which is why it differs from that given by the authors.) Accordingly, a nepheloauxetic effect brought about by the acetate anions may be observed. Also, the crystal field splitting, larger than that in the great majority of systems with europous halogenides, may indicate a larger contribution of covalency in the metal–ligand bonds. The E_{fd} and Δ parameters resemble most closely those for the EuI_2–THF system.

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