Crystal structure of tetraaquabis(μ_4-fumarato)-μ_2-oxalato-diyttrium(III) hydrate, $Y_2(H_2O)_4(C_2O_4)(C_4H_2O_4)_2 \cdot H_2O$

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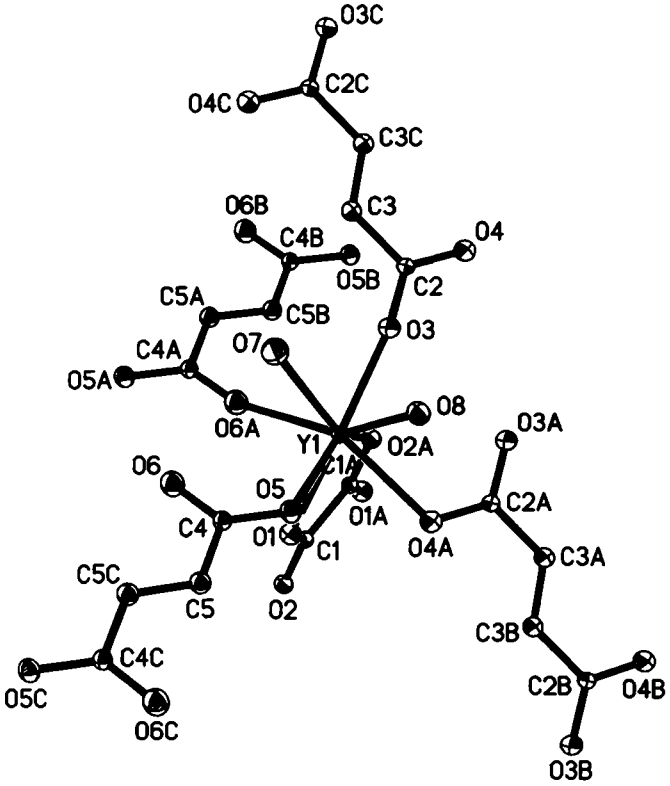
Received January 31, 2005, accepted and available on-line April 5, 2005; CCDC no. 1267/1475



Abstract

$C_5H_7O_{8.50}Y$, triclinic, $P\bar{1}$ (no. 2), $a = 7.859(3)$ Å, $b = 7.902(3)$ Å, $c = 7.993(3)$ Å, $\alpha = 106.786(6)°$, $\beta = 95.475(5)°$, $\gamma = 113.452(5)°$, $V = 423.3$ Å^3, $Z = 2$, $R_{gt}(F) = 0.047$, $wR_{ref}(F^2) = 0.130$, $T = 293$ K.

Source of material

1.2 mmol Fumaric acid, 0.4 mmol 1,10-phenanthroline and 0.4 mmol $Y(NO_3)_3 \cdot 6H_2O$ were dissolved in 12 ml water and its pH was controlled in a range 5-6 with 2 M NaOH solution. The mixture was placed in a Teflon-lined stainless-steel vessel (25 ml) and heated at 150 °C for 24 h, then the mixture was cooled to room temperature. Colorless crystals were obtained.
Elemental analysis: found – C, 20.70 %; H, 2.50 %; calc. for $C_{10}H_{14}O_{17}Y_2$ – C, 20.57%; H, 2.40%.

Discussion

The obtained yttrium(III) complex $[Y_2(C_4H_2O_4)_2(C_2O_4)(H_2O)_4] \cdot H_2O$ is different from eight-coordinated complex $[Y_2fum_3 \cdot 12H_2O]_n$ (fum = fumarate), which has been synthesized by conventional solution reaction [1]. The two complexes show isomorphism in spite of the different composition. Hydrothermal preparation may lead to an unexpected composition of the complex.
In the title complex, the Y(III) ion is eight-coordinated by four oxygen atoms (O3, O5, O4A and O6A) from four fumarate anions, two oxygen atoms (O1 and O2A) from oxalate anions and two oxygen atoms (O7 and O8) from two water molecules. The two carboxylate groups of each fumarato ligand coordinate four different Y(III) ions through their four oxygen atoms to form a tetradentate bridging. So, Y(III) ions are connected into a framework structure by the oxygen atoms of the fumarato ligands. Both carboxylate groups of an oxalate adopt bidentate chelating mode, in which four oxygen (O1, O2, O1A and O2A) atoms coordinate two different yttrium(III) ions (Y1 and Y1A). The Y—$O_{carboxyl}$ distances from 2.280(5) Å to 2.367(5) Å with an average distance of 2.3145 Å agree with corresponding Y—O distances in complex (II). The O–Y–$O_{carboxyl}$ bond angles fall in the region 82.3(2)° – 147.6(2)°. The bond lengths between oxygen atoms of oxalate anions and Y(III) ions are 2.421(4) Å and 2.442(5) Å.
There are two bonded water molecules (O7 and O8) at distances of 2.439(5) Å and 2.435(5) Å to the Y(III) ion, respectively. Extensive hydrogen bonds exist in the crystal. The uncoordinated water molecule forms hydrogen bonds with oxygen atoms of fumarate and oxalate, O9–H9B···O4($x+1,y,z$), 2.90(4) Å, 147.7° and O9–H9···O1($-x+2,-y+2,-z+1$), 3.08(3) Å, 138.5°, respectively. Its site occupancy factor was fixed at 0.5 in agreement with the results of the elemental analysis. The coordinating water molecules form hydrogen bonds with oxygen atoms of fumarate and oxalate, O8–H8A···O4($x+1,y,z$), 3.360(7) Å, 154.6° and O8–H8B···O2($x,y,z+1$), 2.751(7) Å, 165.4°, respectively. The coordinating water molecules form also hydrogen bonds with lattice water molecules, O7–H7B···O9($-x+1,-y+1,-z+1$), 3.06(3) Å, 134.8°. In addition, hydrogen bonds exist between coordinating water molecules themselves, O7–H7B···O8($-x+1,-y+1,-z+1$), 3.131(7) Å, 120.2°. As a result, the 3D supramolecular structure is stabilized by the hydrogen bonds.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.12 × 0.16 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	69.16 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, ω/φ
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2204, 1497
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1374
$N(param)_{refined}$:	136
Programs:	SHELXS-97 [2], SHELXL-97 [3]

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Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{iso}
H(3)	2*i*		0.0874	0.4381	0.3703	0.029
H(5)	2*i*		1.1077	0.6907	0.1183	0.029
H(7A)	2*i*		0.5770	0.4760	0.3635	0.049
H(7B)	2*i*		0.3736	0.4364	0.3189	0.049
H(8A)	2*i*		0.8707	0.8985	0.5764	0.037
H(8B)	2*i*		0.7097	0.8998	0.6511	0.037
H(9A)	2*i*	0.5	1.0256	0.9330	0.9518	0.207
H(9B)	2*i*	0.5	0.9855	0.7951	0.7850	0.207

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Y(1)	2*i*		0.57046(7)	0.79907(7)	0.26853(7)	0.0159(3)	0.0163(3)	0.0171(3)	0.0093(2)	0.0071(2)	0.0070(2)
O(1)	2*i*		0.6432(7)	0.8780(7)	0.0022(6)	0.028(1)	0.029(1)	0.028(1)	0.0143(9)	0.0071(9)	0.0108(9)
O(2)	2*i*		0.5897(6)	1.0199(6)	–0.1878(6)	0.024(1)	0.024(1)	0.023(1)	0.0115(9)	0.0073(9)	0.0089(9)
C(1)	2*i*		0.5682(8)	0.9716(9)	–0.0524(8)	0.019(2)	0.018(2)	0.018(2)	0.008(1)	0.005(1)	0.007(1)
O(3)	2*i*		0.3478(7)	0.7809(7)	0.4370(6)	0.027(1)	0.028(1)	0.027(1)	0.0103(9)	0.0084(9)	0.0104(9)
O(4)	2*i*		0.1859(7)	0.8718(7)	0.6265(7)	0.031(1)	0.029(1)	0.031(1)	0.012(1)	0.0109(9)	0.009(1)
C(2)	2*i*		0.2099(8)	0.7412(9)	0.5120(8)	0.019(2)	0.019(2)	0.019(2)	0.008(1)	0.006(1)	0.007(1)
C(3)	2*i*		0.0724(9)	0.532(1)	0.4613(9)	0.025(2)	0.024(2)	0.024(2)	0.011(1)	0.007(1)	0.008(1)
O(5)	2*i*		0.8215(6)	0.7287(7)	0.2038(6)	0.025(1)	0.026(1)	0.026(1)	0.0143(9)	0.0064(9)	0.0074(9)
O(6)	2*i*		0.6591(7)	0.4427(8)	–0.0217(7)	0.031(1)	0.036(1)	0.036(1)	0.017(1)	0.008(1)	0.008(1)
C(4)	2*i*		0.8114(8)	0.5824(9)	0.0799(8)	0.018(2)	0.019(2)	0.019(2)	0.010(1)	0.004(1)	0.006(1)
C(5)	2*i*		0.9945(9)	0.578(1)	0.0545(9)	0.023(2)	0.024(2)	0.025(2)	0.011(1)	0.006(1)	0.008(1)
O(7)	2*i*		0.4855(8)	0.4820(7)	0.3056(7)	0.043(2)	0.039(2)	0.040(2)	0.018(1)	0.011(1)	0.015(1)
O(8)	2*i*		0.7506(7)	0.8567(7)	0.5614(6)	0.031(1)	0.032(1)	0.030(1)	0.015(1)	0.0085(9)	0.009(1)
O(9)	2*i*	0.5	0.928(5)	0.834(5)	0.864(5)	0.17(1)	0.17(1)	0.17(1)	0.077(5)	0.041(3)	0.062(4)

Acknowledgments. We are grateful to the Science and Technology Program, Beijing Municipal Education Commission (grant no. KM200510028007) and the Scientific Research Foundation for Returned Overseas Chinese Scholars, Beijing Municipal Government.

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