Crystal structure of tetraaquasamarium(III) tri(2-chlorofumarate) hexahydrate, $Sm_2(COOCHCClCOO)_3(H_2O)_4 \cdot 6H_2O$, *with two-dimensional net structure*

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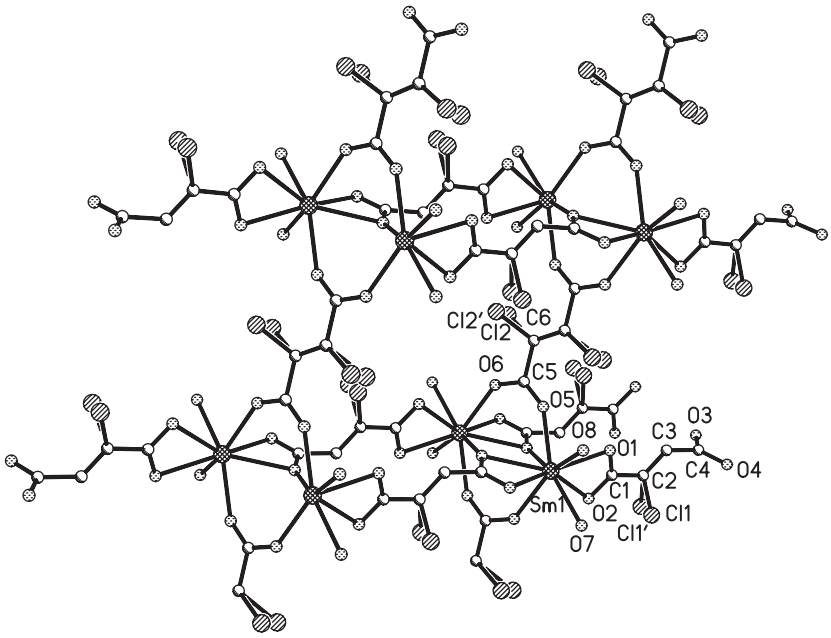

Abstract

$C_{12}H_{23}Cl_3O_{22}Sm_2$, triclinic, $P\bar{1}$ (No. 2), $a = 8.877(3)$ Å, $b = 9.413(3)$ Å, $c = 9.554(3)$ Å, $\alpha = 103.778(5)°$, $\beta = 101.315(5)°$, $\gamma = 93.954(5)°$, $V = 754.7$ Å^3, $Z = 1$, $R_{gt}(F) = 0.056$, $wR_{ref}(F^2) = 0.152$, $T = 293$ K.

Source of material

0.5218 g (0.937 mmol) $Sm(ClO_4)_3 \cdot 6H_2O$, 0.1432 g (0.951 mmol) 2-chlorofumaric acid and 0.0885 g (0.478 mmol) 2,3-dichlorofumaric acid were dissolved in 20 ml H_2O and the dilute solution of NaOH was added in drops into the solution until the pH value of the solution is close to 4.2. The colorless single crystals were obtained after the solution was allowed to stand at room temperature for about three weeks.

Experimental details

All chlorine atom positions were found to be disordered in the structure. The sum of position occupation parameters of Cl1 and Cl1′ were fixed to 1.0 in the refinement and that of Cl2 and Cl2′ in the molecule with symmetric center were fixed to 0.5 (If not fixed, refined value was near 0.5), a hydrogen atom (H6A) occupies another 0.5 position. These indicates that there is position disorder between Cl and H atoms in the molecule with symmetric center. In the refinement three O atoms of uncoordinated solvant waters in the asymmetric unit were found to be disordered and their sum of position occupation of O9 and O9′, O10 and O10′, O11 and O11′ were refined to near 1.0, and so fixed to 1.0, respectively. The structure was also solved in *P*1 space group, but the refinement was unstable and not converged to reasonable result.

Discussion

The structure of the title complex consists of trivalent samarium cation coordinated by nine oxygen atoms. These coordinating oxygen atoms originate from two H_2O molecules and five carboxylate groups. The Sm—O bond distances vary in the range from 2.38(1) Å to 2.596(9) Å, while the associated angles range from 50.2(3)° to 148.5(4)°. The *d*(C2—C3) bond distance is 1.30(2) Å, the distance *d*(C6—C6E) is 1.34(2) Å, and the *d*(C=C) double bond distances are close to that of the europium complex that 2-chlorofumarate acts as bridging ligand [1]. In the crystal the carboxylate groups coordinate samarium cations in chelation way, in bridging way and in chelation and bridging way. In this way a two-dimensional net was formed in the (100) plane and the layers pile up along the *c* direction to form a three-dimensional net structure with countless microproposities, and the crystal H_2O molecules are trapped in the microporosities throught hydrogen

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bonding. In addition, the unit cell contains three 2-chlorofumarate anions, two are related by symmetric center, one possesses symmetric center on C=C double bond.

Table 1. Data collection and handling.

Crystal:	colourless prism, size 0.10 × 0.10 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	42.91 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	46.62°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3482, 2167
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1708
$N(param)_{refined}$:	185
Programs:	SHELXS-97 [2] SHELXL-97 [3]

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(3A)	2*i*		0.31(2)	0.61(1)	0.41(2)	0.14(8)
H(7A)	2*i*		0.0197	0.2381	0.7705	0.08
H(7B)	2*i*		0.0379	0.2907	0.6519	0.08
H(8A)	2*i*		0.0983	0.7223	0.8692	0.08
H(8B)	2*i*		0.0002	0.6020	0.8669	0.08
Cl(1)	2*i*	0.51(2)	0.364(2)	0.2321(9)	0.3070(9)	0.051(3)
Cl(1′)	2*i*	0.49	0.284(2)	0.2200(9)	0.284(1)	0.051(4)
Cl(2)	2*i*	0.22(2)	0.693(3)	1.057(3)	1.192(2)	0.10(1)
Cl(2′)	2*i*	0.23	0.751(2)	1.027(2)	1.106(3)	0.096(9)
H(6A)	2*i*	0.50	0.6506	1.0221	1.0932	0.08
O(9)	2*i*	0.68(4)	0.097(3)	0.771(4)	0.565(2)	0.20(2)
H(9A)	2*i*	0.68	0.0890	0.7575	0.6518	0.08
H(9B)	2*i*	0.68	0.1732	0.8393	0.5776	0.08
O(9′)	2*i*	0.32	0.045(4)	0.714(3)	0.550(3)	0.05(1)
H(9C)	2*i*	0.32	–0.0019	0.6401	0.5738	0.08
H(9D)	2*i*	0.32	0.1065	0.7694	0.6297	0.08
O(10)	2*i*	0.42(2)	0.068(7)	0.015(7)	0.910(7)	0.22(3)
H(10A)	2*i*	0.42	0.1257	0.1015	0.9387	0.08
H(10B)	2*i*	0.42	0.0548	–0.0004	0.8098	0.08
O(10′)	2*i*	0.58(3)	–0.137(3)	0.150(3)	0.863(3)	0.09(1)
H(10C)	2*i*	0.58	–0.1684	0.0699	0.8845	0.08
H(10D)	2*i*	0.58	–0.2160	0.1626	0.7977	0.08
O(11)	2*i*	0.35(3)	0.788(4)	0.169(5)	0.790(5)	0.12(2)
H(11A)	2*i*	0.35	0.7123	0.2193	0.7673	0.08
H(11B)	2*i*	0.35	0.7479	0.0844	0.8010	0.08
O(11′)	2*i*	0.65	0.592(4)	0.127(3)	0.645(3)	0.15(1)
H(11C)	2*i*	0.65	0.5356	0.1837	0.5988	0.08
H(11D)	2*i*	0.65	0.5228	0.0959	0.6928	0.08

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

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sm(1)	2*i*	0.29639(7)	0.47117(7)	0.85482(7)	0.0299(4)	0.0493(5)	0.0255(4)	0.0105(3)	0.0099(3)	0.0186(3)
C(1)	2*i*	0.304(2)	0.420(2)	0.551(1)	0.034(8)	0.055(9)	0.032(7)	0.003(7)	0.014(6)	0.021(7)
C(2)	2*i*	0.310(2)	0.401(2)	0.392(1)	0.037(8)	0.055(9)	0.032(7)	0.004(7)	0.011(6)	0.014(7)
C(3)	2*i*	0.304(2)	0.508(2)	0.329(1)	0.035(8)	0.059(9)	0.025(7)	0.012(7)	0.017(6)	0.021(7)
C(4)	2*i*	0.304(2)	0.495(1)	0.167(1)	0.040(8)	0.042(8)	0.024(7)	0.011(6)	0.016(7)	0.016(6)
C(5)	2*i*	0.525(2)	0.799(2)	1.023(1)	0.052(9)	0.045(9)	0.033(7)	0.018(8)	0.022(7)	0.019(7)
C(6)	2*i*	0.553(2)	0.965(2)	1.034(2)	0.08(1)	0.05(1)	0.05(1)	0.017(9)	0.013(9)	0.024(8)
O(1)	2*i*	0.279(1)	0.543(1)	0.6217(9)	0.063(7)	0.064(7)	0.020(4)	0.023(5)	0.014(5)	0.016(5)
O(2)	2*i*	0.323(1)	0.315(1)	0.6074(9)	0.075(7)	0.043(6)	0.030(5)	0.008(5)	0.016(5)	0.017(5)
O(3)	2*i*	0.4302(9)	0.5184(9)	0.1326(9)	0.030(5)	0.045(5)	0.033(5)	0.010(4)	0.013(4)	0.015(4)
O(4)	2*i*	0.180(1)	0.462(1)	0.073(1)	0.031(6)	0.106(8)	0.026(5)	0.008(5)	0.010(5)	0.026(5)
O(5)	2*i*	0.400(1)	0.723(1)	0.952(1)	0.043(6)	0.040(6)	0.054(6)	0.005(5)	0.001(5)	0.013(5)
O(6)	2*i*	0.638(1)	0.756(1)	1.096(1)	0.049(6)	0.058(6)	0.040(5)	0.019(5)	0.005(5)	0.027(5)
O(7)	2*i*	0.054(1)	0.313(1)	0.746(1)	0.044(6)	0.081(8)	0.061(7)	–0.001(6)	0.011(6)	0.016(6)
O(8)	2*i*	0.090(1)	0.628(1)	0.855(1)	0.037(6)	0.062(7)	0.080(7)	0.021(5)	0.024(6)	0.032(6)

References

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