atoms on the benzene rings were placed at calculated positions. All calculations were performed using the *SHELXTL* program system (Sheldrick, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond angles and *p*-nitrobenzoate geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71835 (62 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1099]

References

Birnbaum, E. R. (1984). *Gmelin's Handbook of Inorganic Chemistry*, 8th edition. System No. 39, Part D5.

Ma, J.-F., Jin, Z.-S. & Ni, J.-Z. (1991*a*). *Jiegou Huaxue*, **10**, 56–59, 121–124, 125–128.

Sheldrick, G. M. (1983). *SHELXTL User's Manual*. Revision 4. Nicolet XRD Corporation, Madison, Wisconsin, USA.

Xing, Y., Jin, Z.-S., Duan, Z.-B. & Ni, J.-Z. (1987). *Acta Chim. Sin.* **45**, 1044–1047.

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Yttrium Salicylate Tetrahydrate

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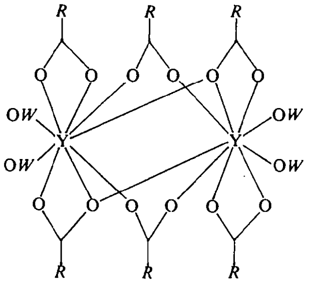
Abstract

The structure of tetraaqua-$1\kappa^2O,2\kappa^2O$-tetrakis-(μ-salicylato)-$1{:}2\kappa^2O,1\kappa O';1{:}2\kappa^2O,2\kappa O';1\kappa O{:}2\kappa O';1\kappa O{:}2\kappa O'$-bis(salicylato)-$1\kappa^2O,O';2\kappa^2O,O'$-diyttrium tetrahydrate, [$Y_2(C_7H_5O_3)_6(H_2O)_4$].$4H_2O$, is composed of dimeric Y_2(*o*-$HOC_6H_4CO_2)_6(H_2O)_4$ units in which the two metal ions are bridged by carboxylate groups. The carboxylate groups coordinate in three different modes: bridging, chelating and bridging–chelating. None of the phenolic O atoms is coordinated.

Comment

As rare earth complexes can be used as bonding models for the study of the interaction of rare earth elements with humic materials, structural information for these complexes is important. The structures of Sm(*o*-$HOC_6H_4CO_2)_3.H_2O$ (Burns & Baldwin, 1977) and [*M*(*o*-$HOC_6H_4CO_2)_3(H_2O)_2$].$2H_2O$ [*M* = Tb, Ho (Ma, Jin & Ni, 1991)] have been determined. In this paper we describe the structure of the title compound (I).



(I) R = 2-HO-C_6H_4—

Each Y ion is coordinated to seven carboxylate O atoms [O(11), O(12^i), O(21), O(22), O(31), O(31^i) and O(32^i)] from five salicylate ions and two O atoms [O(*W*1) and O(*W*2)] from water molecules. There are also two lattice water molecules per metal ion which are not coordinated to the metal ions. The coordination number of each Y ion is nine. None of the phenolic O atoms is coordinated to the metal ions. The carboxylate groups coordinate in three different modes. In the bridging mode two O atoms are coordinated to two different metal ions, forming a carboxylate bridge [C(17), O(11), O(12)]. In the chelating mode two O atoms are coordinated to the same metal ion, forming a four-membered ring [C(27), O(21), O(22)]. In the bridging–chelating mode two O atoms chelate one metal ion, with one of the O atoms also coordinated to another metal ion. Pairs of Y ions are bridged by two bridging carboxylate groups and two bridging–chelating carboxylate groups to form a dimeric molecule in which the Y···Y distance is 4.029 (1) Å.

The title compound has a different structure from those of the compounds of samarium (Burns & Baldwin, 1977), terbium and holmium (Ma, Jin & Ni, 1991), which have infinite chain structures. The Y—O distances are in the range 2.296 (4)–2.732 (4) Å, with an average value of 2.418 (4) Å. The average Y—O bond length within the bridging carboxylate groups [2.352 (4) Å] is shorter than the average Y—O bond length within the chelating carboxylate groups [2.433 (4) Å], as the four-membered chelate ring is less stable. The dihedral angles between the carboxylate planes and the benzene rings in the three salicylate ions are 19.3 (5), 5.7 (9) and 13.0 (7)°, respectively.

Although the H atoms were not located in this work, the existence of some hydrogen bonds can be inferred from the distances listed in Table 2. Both the coordinated and lattice water molecules can form hydrogen bonds with the carboxylate O atoms, and hydrogen bonds also exist between the water molecules. The dimers are connected by hydrogen bonds

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between the coordinated water molecules and the carboxylate O atoms [O(*W*1)···O(22^{iv})] or the phenolic O atoms [O(*W*2)···O(13^{ii})].

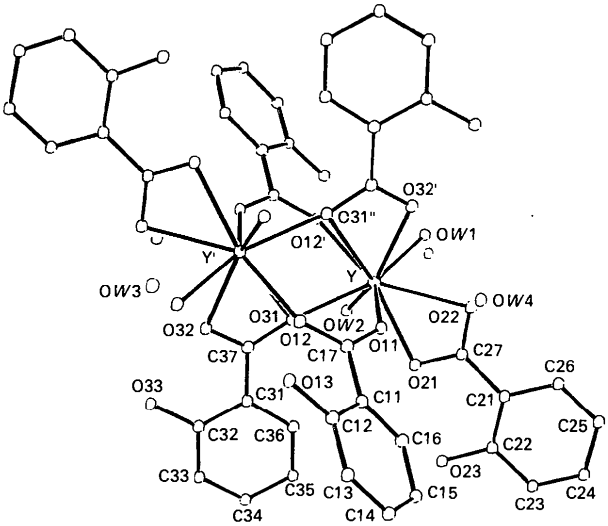

Fig. 1. A perspective view of the dimeric structure of the title compound.

Experimental

The title compound was prepared from an aqueous solution of YCl_3 and sodium salicylate.

Crystal data

$[Y_2(C_7H_5O_3)_6(H_2O)_4].4H_2O$
$M_r = 1144.62$
Triclinic
$P\bar{1}$
$a = 9.963\ (3)$ Å
$b = 14.344\ (4)$ Å
$c = 9.464\ (2)$ Å
$\alpha = 88.39\ (2)°$
$\beta = 115.83\ (2)°$
$\gamma = 80.93\ (2)°$
$V = 1195.0\ (5)$ Å^3
$Z = 1$

$D_x = 1.59$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 2.5\text{–}11.2°$
$\mu = 2.59$ mm^{-1}
$T = 293$ K
Needle
0.36 × 0.18 × 0.12 mm
Colourless

Data collection

Nicolet *R*3*m*/*E* diffractometer
ω scans
Absorption correction: empirical (ψ scan)
$T_{min} = 0.834$, $T_{max} = 0.978$
4659 measured reflections
4307 independent reflections
2815 observed reflections $[F_o > 3\sigma(F_o)]$

$R_{int} = 0.0234$
$\theta_{max} = 26°$
$h = 0 \rightarrow 13$
$k = -18 \rightarrow 18$
$l = -12 \rightarrow 12$
2 standard reflections monitored every 100 reflections
intensity variation: <3.3%

Refinement

Refinement on F
$R = 0.046$
$wR = 0.054$
$S = 1.236$
2815 reflections
316 parameters
Only H-atom *U*'s refined
$w = 1/[\sigma^2(F_o) + 0.00073(F_o)^2]$

$(\Delta/\sigma)_{max} = 0.018$
$\Delta\rho_{max} = 0.54$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974) Vol. IV

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Y	0.4102 (1)	0.0445 (1)	0.6458 (1)	0.025 (1)
O(11)	0.5887 (4)	0.1329 (3)	0.6473 (4)	0.036 (2)
O(12)	0.6666 (4)	0.0954 (3)	0.4636 (4)	0.037 (2)
O(13)	0.8501 (5)	0.1897 (3)	0.4301 (5)	0.052 (2)
O(21)	0.3117 (4)	0.2016 (3)	0.6683 (4)	0.037 (2)
O(22)	0.4949 (4)	0.1280 (3)	0.8894 (4)	0.037 (2)
O(23)	0.2032 (5)	0.3776 (3)	0.6409 (5)	0.058 (2)
O(31)	0.3674 (4)	0.0759 (3)	0.3889 (4)	0.034 (2)
O(32)	0.3725 (4)	0.0597 (3)	0.1621 (4)	0.037 (2)
O(33)	0.1666 (4)	0.1605 (3)	−0.0897 (4)	0.043 (2)
O(*W*1)	0.3253 (4)	−0.0260 (3)	0.8163 (4)	0.040 (2)
O(*W*2)	0.1378 (4)	0.0716 (3)	0.5062 (4)	0.040 (2)
O(*W*3)	0.9757 (5)	0.0087 (4)	0.2180 (5)	0.062 (2)
O(*W*4)	0.8450 (7)	0.1320 (5)	0.9477 (7)	0.130 (4)
C(11)	0.6933 (6)	0.2449 (4)	0.5565 (6)	0.032 (2)
C(12)	0.7918 (5)	0.2602 (4)	0.4920 (6)	0.038 (2)
C(13)	0.8313 (7)	0.3491 (4)	0.4921 (7)	0.051 (3)
C(14)	0.7704 (8)	0.4225 (4)	0.5479 (7)	0.057 (3)
C(15)	0.6705 (8)	0.4097 (4)	0.6077 (8)	0.056 (3)
C(16)	0.6333 (7)	0.3210 (4)	0.6150 (7)	0.047 (3)
C(17)	0.6466 (5)	0.1514 (4)	0.5578 (4)	0.031 (2)
C(21)	0.3917 (6)	0.2916 (4)	0.8883 (6)	0.034 (2)
C(22)	0.2917 (7)	0.3740 (4)	0.7991 (7)	0.041 (3)
C(23)	0.2835 (7)	0.4559 (4)	0.8721 (7)	0.053 (3)
C(24)	0.3657 (8)	0.4557 (4)	1.0278 (8)	0.060 (3)
C(25)	0.4630 (8)	0.3727 (5)	1.1218 (7)	0.060 (3)
C(26)	0.4752 (7)	0.2923 (4)	1.0503 (7)	0.049 (3)
C(27)	0.3998 (6)	0.2026 (4)	0.8138 (6)	0.032 (2)
C(31)	0.2078 (6)	0.1942 (4)	0.1736 (6)	0.033 (2)
C(32)	0.1388 (6)	0.2181 (4)	0.0100 (6)	0.034 (2)
C(33)	0.0364 (7)	0.3043 (4)	−0.0543 (7)	0.051 (3)
C(34)	0.0036 (8)	0.3634 (5)	0.0415 (8)	0.060 (3)
C(35)	0.0738 (8)	0.3407 (5)	0.2039 (8)	0.060 (3)
C(36)	0.1730 (7)	0.2574 (4)	0.2673 (7)	0.052 (3)
C(37)	0.3196 (5)	0.1053 (4)	0.2440 (6)	0.027 (2)

Table 2. *Selected geometric parameters* (Å)

Y—O(11)	2.337 (4)	Y—O(21)	2.367 (4)
Y—O(22)	2.498 (4)	Y—O(31)	2.296 (4)
Y—O(*W*1)	2.389 (5)	Y—O(*W*2)	2.403 (3)
Y—O(12^i)	2.366 (4)	Y—O(31^i)	2.732 (4)
Y—O(32^i)	2.371 (3)		
O(11)—C(17)	1.258 (8)	O(12)—C(17)	1.275 (7)
O(13)—C(12)	1.359 (8)	O(21)—C(27)	1.272 (6)
O(22)—C(27)	1.265 (6)	O(23)—C(22)	1.361 (7)
O(31)—C(37)	1.273 (6)	O(32)—C(37)	1.259 (7)
O(33)—C(32)	1.359 (8)	C(11)—C(12)	1.40 (1)
C(11)—C(16)	1.404 (9)	C(11)—C(17)	1.488 (8)
C(12)—C(13)	1.393 (9)	C(13)—C(14)	1.37 (1)
C(14)—C(15)	1.37 (1)	C(15)—C(16)	1.388 (9)
C(21)—C(22)	1.394 (7)	C(21)—C(26)	1.391 (7)
C(21)—C(27)	1.483 (8)	C(22)—C(23)	1.388 (9)
C(23)—C(24)	1.338 (9)	C(24)—C(25)	1.405 (8)
C(25)—C(26)	1.37 (1)	C(31)—C(32)	1.399 (7)
C(31)—C(36)	1.394 (9)	C(31)—C(37)	1.472 (7)
C(32)—C(33)	1.399 (7)	C(33)—C(34)	1.36 (1)
C(34)—C(35)	1.39 (1)	C(35)—C(36)	1.355 (8)

O(*W*2)···O(*W*1)	2.868 (5)	O(*W*2)···O(21)	2.775 (5)
O(*W*4)···O(11)	2.878 (7)	O(*W*2)···O(12^{i})	2.761 (5)
O(*W*3)···O(*W*1^{i})	2.841 (6)	O(*W*1)···O(12^{i})	2.885 (5)
O(*W*1)···O(32^{i})	2.888 (5)	O(*W*1)···O(22^{iv})	2.776 (5)
O(*W*2)···O(13^{ii})	2.866 (7)	O(*W*3)···O(*W*2^{v})	2.761 (6)
O(*W*4)···O(*W*3^{iii})	2.736 (9)		

Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $x - 1, y, z$; (iii) $x, y, 1 + z$; (iv) $1 - x, -y, 2 - z$; (v) $1 + x, y, z$.

Intensity data were corrected for Lp factors. The structure was solved by the heavy-atom method and refined by block-diagonal least-squares. All non-H atoms were refined anisotropically. H atoms on the benzene rings were located by theoretical calculation. All calculations were performed using the *SHELXTL* program system (Sheldrick, 1983).

Lists of structure factors, anisotropic displacement parameters and bond angles have been deposited with the IUCr (Reference: AB1097). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Burns, J. H. & Baldwin, W. H. (1977). *Inorg. Chem.* **16**, 289–294.
Ma, J.-F., Jin, Z.-S. & Ni, J.-Z. (1991). *Jiegou Huaxue*, **10**, 125–128.
Sheldrick, G. M. (1983). *SHELXTL User's Manual.* Revision 4. Nicolet XRD Corporation, Madison, Wisconsin, USA.

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A Mixed-Ligand Cadmium(II) Complex of Xanthic Acid and *N*,*N*′-Bis(4-methoxyphenyl)thiourea

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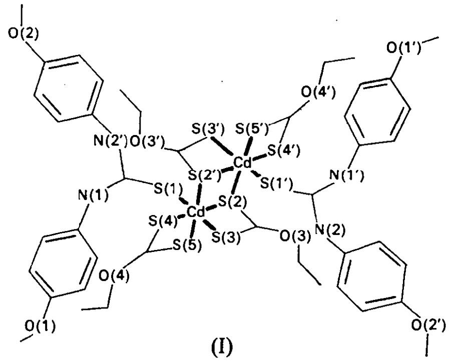
Abstract

The X-ray analysis reveals that the title compound, bis(μ-*O*-ethyl dithiocarbonato)-1κS,1:2$\kappa^2 S'$;2κS,-1:2$\kappa^2 S'$-bis{(*O*-ethyl dithiocarbonato-$\kappa^2 S,S'$)[*N*,*N*′-bis(4-methoxyphenyl)thiourea-κS]cadmium(II)}, $[Cd_2(C_3H_5OS_2)_4(C_{15}H_{16}N_2O_2S)_2]$, is a dimer of distorted octahedral Cd ions each coordinated to six S atoms: one non-bridging S atom of the thiourea ligand at a distance of 2.641 (1) Å, four non-bridging S atoms of the chelating/chelating–bridging xanthato (*O*-ethyl dithiocarbonato) ligands at distances of 2.606 (2)–2.765 (1) Å, and one bridging S atom of the chelating–bridging xanthato ligand at a much longer distance of 2.831 (2) Å. The shortest metal–sulfur distances involve the S atoms of one of the chelating moieties, while the S atoms of the chelating–bridging moiety form one of the shorter and the longest '2.831 Å' metal–sulfur distances. The other 'short' bond is subtended to an S atom of a symmetry-related bridging–chelating ligand. Cd, S(2), S(2^{i}) and Cd^{i} are coplanar [symmetry code: (i) $-x, -y, -z$].

Comment

Cadmium thiourea and xanthato derivative complexes have aroused considerable interest in recent years in view of their nonlinear optical properties (Xing, Jiang, Shao & Xu, 1987; Tao, Jian, Xu & Shao, 1987). Cd has a variety of coordination environments. In previous papers it appears that the coordination of Cd is most frequently tetrahedral or trigonal bipyramidal (Castineiras, Arguero, Masaguer, Ruiz-Amil, Martinez-Carrera & Garcia-Blanco, 1985; Casas, Sanchez, Bravo, Garcia-Fontan, Castellano & Jones, 1989). To study the Cd coordination environments and to determine the precise conditions which favour selective synthesis of asymmetric complexes, the crystal structure of a Cd^{II} complex, (I), of mixed ligands of xanthic acid and *N*,*N*′-bis(4-methoxyphenyl)thiourea is reported here.



(I)

The dimeric molecule is located on a centre of inversion. The Cd atom is octahedrally coordinated to one xanthato group functioning as a bidentate ligand, one bridging–bidentate xanthato and one monodentate *N*,*N*′-bis(4-methoxyphenyl)thiourea. The sixth coordination site around the Cd atom is

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† Visiting scholar from Hainan Normal College.