metal-organic papers

Poly[bis[aquamercury(I)]-di-μ-aqua-μ-1,5-naphthalenedisulfonato]

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In the crystal structure of the title polymeric complex, $[Hg_2(C_{10}H_6O_6S_2)(H_2O)_4]_n$, the metal atom of an $H_2O{\rightarrow}Hg{\cdots}Hg{\leftarrow}H_2O$ unit $[Hg{\leftarrow}O_{water} = 2.124\,(7)$ Å] is linked to the metal atom of an adjacent unit by two water molecules $[Hg{\leftarrow}O_{water} = 2.619\,(7)$ and $2.872\,(7)$ Å], giving rise to a polycationic chain. Adjacent chains are linked through the dianion *via* a weaker interaction $[Hg{\cdots}O_{sulfonate} = 3.062\,(7)$ Å] to form layers. The $H_2O{\rightarrow}Hg{\cdots}Hg{\leftarrow}H_2O$ unit, the $(H_2O{\rightarrow}Hg)_2$ parallelogram and the dianion all lie on centres of inversion. Hydrogen bonding consolidates the layers of the structure into a three-dimensional network architecture.

Comment

A preceeding report (Gao *et al.*, 2005) mentions examples of metal derivatives of naphthalenedisulfonic acids, in which the metal atoms interact with the dianion through the coordinated water molecules. The title mercury(I) derivative, (I), of 1,5-naphthalenedisulfonic acid similarly exists as a water-coordinated compound, but, as the distance between the Hg atom and the O atom of the centrosymmetric dianion is 3.062 (7) Å, the interaction is regarded as corresponding to a formal bond.


(I)
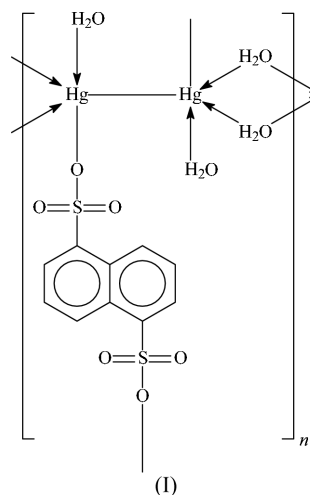
Compound (I) features an $H_2O{\rightarrow}Hg{\cdots}Hg{\leftarrow}H_2O$ unit, which is linked to another unit by two water molecules to give rise to a polycationic chain. Adjacent chains are linked through the dianion (Fig. 1) to form layers. The compound has a metal–metal interaction that is characteristic of mercurous systems, and the Hg$\cdots$Hg distance is similar to those found in a number of such systems (Allen, 2002).

The structure of (I) represents a rare example of a water-coordinated Hg$_2$ system, this feature having been previously
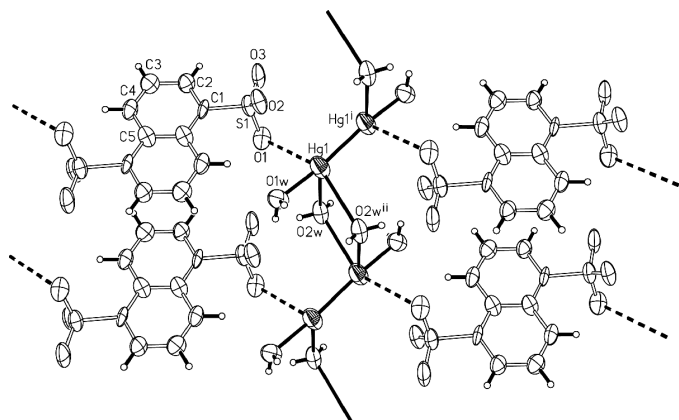
Figure 1
A plot of a portion of the structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 70% probability level, and H atoms are shown as small spheres of arbitrary radii. Dashed lines are used for the sulfonate coordination. Symmetry codes are as in Table 1.

Table 1
Selected geometric parameters (Å, °).

Hg1—Hg1^i	2.4488 (9)	Hg1—O2w	2.619 (7)
Hg1—O1	3.062 (7)	Hg1—O2w^{ii}	2.872 (7)
Hg1—O1w	2.124 (7)		
O1—Hg1—O1w	86.8 (2)	O1w—Hg1—O2w^{ii}	76.8 (2)
O1—Hg1—O2w	78.2 (2)	O2w—Hg1—O2w^{ii}	72.9 (2)
O1—Hg1—O2w^{ii}	146.9 (2)	Hg1—O2w—Hg1^{ii}	107.1 (2)
O1w—Hg1—O2w	88.5 (2)		

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1w1···O1^{iii}	0.85	1.87	2.68 (1)	157
O1W—H1w2···O2^{iv}	0.85	1.81	2.62 (1)	158
O2W—H2w1···O1^v	0.85	2.09	2.82 (1)	144
O2W—H2w2···O3^{iv}	0.85	1.87	2.71 (1)	169

Symmetry codes: (iii) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (iv) $x, y + 1, z$; (v) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$.

documented only in the black 3-pyridylsulfonate (Brodersen *et al.*, 1980) and the colourless methanesulfonate (Malleier *et al.*, 2001) complexes.

Experimental

Mercurous nitrate dihydrate (2.81 g, 5 mmol) was reacted with 1,5-naphthalenedisulfonic acid (1.65 g, 5 mmol) in water; a proton-abstracting reagent was not used. Colourless crystals of (I) were isolated from the solution after several days. Analysis, calculated for $C_{10}H_{14}O_{10}S_2Hg_2$: C 15.81, H 1.86%; found: C 15.84, H 1.78%.

Crystal data

[Hg2(C10H6O6S2)(H2O)4]
$M_r = 759.51$
Monoclinic, $P2_1/c$
$a = 13.199 (3)$ Å
$b = 5.699 (1)$ Å
$c = 11.039 (2)$ Å
$\beta = 112.79 (3)°$
$V = 765.5 (3)$ Å^3
$Z = 2$

$D_x = 3.295$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3608 reflections
$\theta = 3.8–26.2°$
$\mu = 20.36$ mm^{-1}
$T = 295 (2)$ K
Block, colourless
$0.31 \times 0.26 \times 0.13$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: numerical (*NUMABS* in *ABSCOR*; Higashi, 1995)
$T_{min} = 0.002$, $T_{max} = 0.177$
4829 measured reflections

1759 independent reflections
1526 reflections with $I > 2\sigma(I)$
$R_{int} = 0.090$
$\theta_{max} = 27.5°$
$h = -17 \rightarrow 17$
$k = -7 \rightarrow 7$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.136$
$S = 1.11$
1759 reflections
111 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0734P)^2 + 3.8951P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.62$ e Å^{-3}
$\Delta\rho_{min} = -1.72$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0069 (8)

The C—C distances were restrained to 1.39 (1) Å, to prevent too wide a spread of values. Additionally, the displacement parameters of these C atoms were restrained to be approximately isotropic. The two H atoms of atom O1W were rotated around the Hg—O1W bond to fit the electron density; those belonging to atom O2W were generated by assuming sp^3 hybridization (O—H = 0.85 Å). Aromatic H atoms were placed in calculated positions (C—H = 0.93 Å). All H atoms were included in the refinement in the riding-model approximation, with $U_{iso}(\text{H}) = 1.2U_{eq}$(parent). In the final difference Fourier map, the largest peak and deepest hole were about 1 Å from atom Hg1.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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