metal-organic papers

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Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean σ(C–C) = 0.011 Å
R factor = 0.034
wR factor = 0.079
Data-to-parameter ratio = 17.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Poly[[bis(triphenylphosphine)mercury(II)]-μ-thiocyanato-cadmium(II)-tri-μ-thiocyanato]

The title complex, $[CdHg(NCS)_4(C_{18}H_{15}P)_2]_n$, contains slightly distorted trigonal bipyramidal CdN_4S and tetrahedral HgP_2S_2. The Cd^{II} atom is coordinated by the N atoms of four thiocyanate ions and the S atom of one thiocyanate ion. The Hg^{II} atom is coordinated by two triphenylphosphine P atoms and two thiocyanate S atoms. The two metal atoms, *viz*. Cd^{II} and Hg^{II}, are connected by an —S=C=N— bridge, forming an infinite three-dimensional network.

Comment

In studies of coordination compounds, the supramolecular architecture of multidimensional networks is most attractive from a technological point of view because these networks may have electronic, magnetic, optical or catalytic applications (Batten & Robson, 1998). The thiocyanate ion is often used for designing infinite inorganic and organic frameworks. Due to its versatility in acting as a monodentate, bidentate or bridging ligand, it can be used to build multidimensional framework structures by alternately linking one metal atom (M) to another metal atom (M').

CMTTP
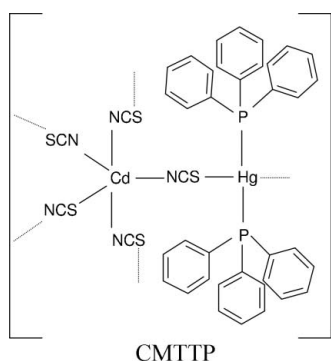
Cadmium mercury thiocyanate (CMTC) and its Lewis-base adducts are known to exist in a variety of polymeric structures. CMTC consists of flattened CdN_4 and HgS_4 tetrahedra (Yuan *et al.*, 1997), while its three reported Lewis-base adducts contain distorted CdN_4O_2 octahedra and HgS_4 tetrahedra (Zhou *et al.*, 2000; Guo *et al.*, 2001; Wang *et al.*, 2002). In the context of this research, the title complex, polymeric tetrakis(thiocyanato)bis(triphenylphosphine)cadmium(II)-mercury(II) (abbreviated as CMTTP), the triphenylphosphine (Ph_3P) adduct of CMTC, has been prepared. The coordination geometry of this new Lewis-base adduct is obviously different from that of the Lewis-base adducts reported earlier. In this structure, each Cd^{II} atom is penta-coordinated *via* 4N(SCN),S(SCN) in a distorted trigonal bipyramidal geometry, and each Hg^{II} atom is tetracoordinated *via* 2S(SCN),2P(Ph_3P) in a distorted tetrahedral geometry.

The coordination geometries of Cd and Hg can be explained using the hard and soft acid and bases (HSAB) concept (Pearson, 1966; Balarew & Duhlew, 1984). The harder metals show a pronounced affinity for coordination with harder ligands, while softer metals prefer coordination with softer ligands. An intermediate ligand is ambidentate, and can coordinate with different metals at the same time. The N, S and P atoms are harder, intermediate and softer ligands, while Cd and Hg are relatively hard and soft metals.

Each Cd^{II} atom is bound to four N and one atom S belonging to thiocyanate groups. The resulting pentacoordinated Cd^{II} atom is highly distorted from ideal trigonal bipyramidal. Among the four N atoms, N1 and N2 are equatorial, while N3 and N4 are axial. The two equatorial distances [Cd1—N1 and Cd1—N2 of 2.209 (5) and 2.174 (6) Å, respectively] are slightly shorter than the sum of the single-bond covalent radii, *i.e.* 2.23 Å. The third equatorial distance [Cd1—S3 = 2.5409 (17) Å] is somewhat longer than the sum of the single-bond covalent radii, *i.e.* 2.50 Å. The two axial distances [Cd1—N3 and Cd1—N4 of 2.368 (5) and 2.363 (5) Å, respectively] are almost equal and the bonds are essentially collinear [N3—Cd—N4 = 175.79 (18)°]. Both are a little longer than the sum of the single-bond covalent radii and obviously longer than the equatorial Cd—N distances. The N_{eq}—Cd—N_{ax} angles and the N_{ax}—Cd—S3 angles (Table 1) span the range 86.1 (2)–94.39 (12)°. The equatorial angles are not ideal trigonal angles of 120°. One of them is significantly smaller, while the other two are slightly larger than the normal value.

Each Hg^{II} atom, coordinated by two Ph_3P P atoms and two thiocyanate S atoms, is in a tetrahedral geometry. The tetrahedron is also distorted. The Hg—P bond lengths (average 2.4918 Å) are shorter than the sum of single-bond covalent radii, *i.e.* 2.55 Å, and the Hg—S bond lengths (average 2.6301°) are much longer than the sum of single-bond covalent radii, *i.e.* 2.51 Å. The bond angles at Hg deviate markedly from a typical tetrahedral angle.

The thiocyanate groups are quasi-linear [N—C—S = 177.2 (5)–178.8 (7)°], which is the striking feature of these kinds of complexes. The —S≡C≡N— bridges connect the two metals, forming an infinite three-dimensional network.

Experimental

The title compound was obtained by the reaction of CMTC and Ph_3P in acetonitrile. All reagents were of analytical grade. The reaction mixture was stirred for 12 h. The crystals used for the X-ray structure analysis were obtained from an acetonitrile solution by evaporation at room temperature.

Crystal data

[CdHg(NCS)4(C18H15P)2]
$M_r = 1069.85$
Triclinic, $P\bar{1}$
$a = 11.5181 (18)$ Å
$b = 13.8876 (15)$ Å
$c = 13.9889 (10)$ Å
$\alpha = 93.532 (7)°$
$\beta = 95.868 (9)°$
$\gamma = 109.014 (9)°$
$V = 2093.7 (4)$ Å^3

$Z = 2$
$D_x = 1.697$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 42 reflections
$\theta = 4.6$–12.5°
$\mu = 4.48$ mm^{-1}
$T = 293 (2)$ K
Prism, colourless
$0.42 \times 0.38 \times 0.20$ mm

Data collection

Bruker $P4$ diffractometer
ω scans
Absorption correction: ψ scan (*XSCANS*; Siemens, 1996)
$T_{min} = 0.156$, $T_{max} = 0.410$
9487 measured reflections
8195 independent reflections
6871 reflections with $I > 2\sigma(I)$

$R_{int} = 0.028$
$\theta_{max} = 26.0°$
$h = -1 \rightarrow 13$
$k = -17 \rightarrow 16$
$l = -17 \rightarrow 17$
3 standard reflections
every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.079$
$S = 1.05$
8195 reflections
470 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0368P)^2 + 1.0625P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.83$ e Å^{-3}
$\Delta\rho_{min} = -0.54$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0042 (2)

Table 1
Selected geometric parameters (Å, °).

C1—N1	1.138 (7)	C29—P2	1.803 (5)
C1—S1	1.648 (6)	C35—P2	1.801 (6)
C2—N2	1.123 (8)	N1—Cd1	2.209 (5)
C2—S2	1.599 (7)	N2—Cd1	2.174 (6)
C3—N3^i	1.137 (7)	N3—Cd1	2.368 (5)
C3—S3	1.659 (6)	N4—Cd1^{ii}	2.363 (5)
C4—N4	1.155 (7)	P1—Hg1	2.5012 (13)
C4—S4	1.657 (6)	P2—Hg1	2.4825 (13)
C5—P1	1.811 (5)	S1—Hg1	2.6230 (14)
C11—P1	1.799 (5)	S3—Cd1	2.5409 (17)
C17—P1	1.795 (5)	S4—Hg1	2.6372 (14)
C23—P2	1.801 (6)		
N1—C1—S1	177.2 (5)	C1—S1—Hg1	103.24 (18)
N2—C2—S2	178.8 (7)	C3—S3—Cd1	99.77 (18)
N3^i—C3—S3	177.7 (6)	C4—S4—Hg1	101.47 (18)
N4—C4—S4	177.4 (5)	N2—Cd1—N1	111.6 (2)
C1—N1—Cd1	166.1 (5)	N2—Cd1—N4^{ii}	90.0 (2)
C2—N2—Cd1	170.5 (5)	N1—Cd1—N4^{ii}	89.82 (18)
C3^i—N3—Cd1	163.5 (5)	N2—Cd1—N3	86.1 (2)
C4—N4—Cd1^{ii}	163.4 (5)	N1—Cd1—N3	89.93 (18)
C17—P1—C11	105.2 (3)	N4^{ii}—Cd1—N3	175.79 (18)
C17—P1—C5	106.7 (2)	N2—Cd1—S3	125.04 (17)
C11—P1—C5	108.2 (2)	N1—Cd1—S3	123.34 (15)
C17—P1—Hg1	111.43 (18)	N4^{ii}—Cd1—S3	89.26 (14)
C11—P1—Hg1	112.28 (18)	N3—Cd1—S3	94.39 (12)
C5—P1—Hg1	112.03 (17)	P2—Hg1—P1	127.29 (4)
C23—P2—C35	107.5 (3)	P2—Hg1—S1	114.79 (5)
C23—P2—C29	105.3 (3)	P1—Hg1—S1	104.62 (5)
C35—P2—C29	107.0 (2)	P2—Hg1—S4	110.13 (5)
C23—P2—Hg1	110.33 (19)	P1—Hg1—S4	100.82 (5)
C35—P2—Hg1	112.50 (16)	S1—Hg1—S4	93.09 (4)
C29—P2—Hg1	113.83 (17)		

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

H atoms were positioned geometrically (C—H = 0.93 Å) and refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.
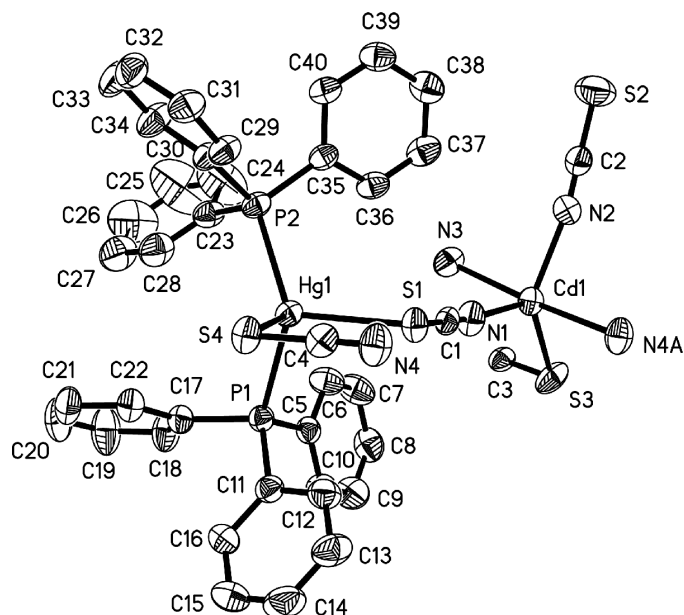
Figure 1
Part of the polymeric structure of the title compound. Displacement ellipsoids are drawn at the 20% probability level and H atoms have been omitted for clarity. Atom N4A is at the symmetry position $(2 - x, 1 - y, 2 - z)$.

Figure 2
Packing diagram for CMTTP, showing the three-dimensional network. H atoms have been omitted.

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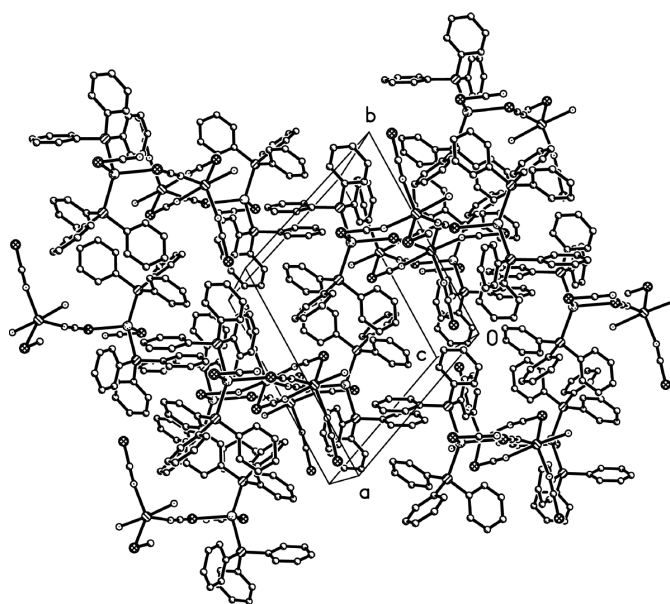Pearson, R. G. (1966). *Science*, pp. 172–177.
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