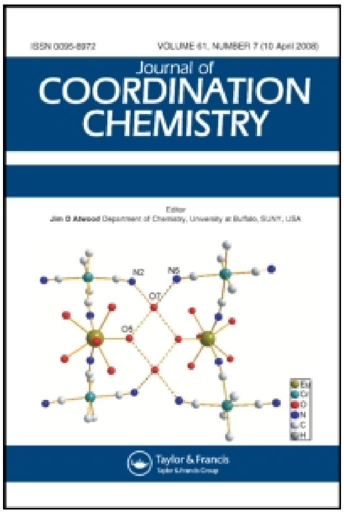

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X-RAY STRUCTURE OF DICHLORO-BIS(DIPHENYLPHOSPHINOTHIOLY) METHANEMERCURY(II)

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The mercury atom in the title compound, $[HgCl_2(Ph_2P(S)CH_2P(S)Ph_2)]$, exists in a distorted tetrahedral geometry defined by two Cl atoms (Hg–Cl 2.445(2) and 2.455(2) Å) and two S atoms derived from a chelating $Ph_2P(S)CH_2P(S)Ph_2$ ligand. The Hg–S bond distances are not equivalent at 2.557(2) and 2.613(2) Å, a fact which reflects the steric strain in the HgSPCPS six-membered ring. Crystals are triclinic, space group $P\bar{1}$, with unit cell dimensions $a = 9.755(1)$, $b = 16.049(1)$, $c = 8.436(2)$ Å, $\alpha = 96.33(1)$, $\beta = 90.17(1)$, $\gamma = 84.04(1)°$ and $Z = 2$. The structure was refined to final $R = 0.033$ for 2486 reflections with $I \geq 2.5\sigma(I)$.

Keywords: Mercury(II), tertiaryphosphine chalcogenide, $dppmS_2$, X-ray structure

INTRODUCTION

The coordination chemistry of tertiaryphosphine chalcogenides has been reviewed recently and, although a number of complexes with Zn, Cd and Hg are known, only relatively few have been characterized by X-ray crystallography.[1] Thus, the crystal structures of $[HgCl_2(Ph_3PSe)_2]$[2] and $\{HgCl[(Ph_2PS)_3CH]\}$[3] have been reported as have the structures of the following compounds emanating from our laboratories: $[Ph_2Hg.dppeS_2]$,[4] $[HgCl_2(dppeS_2)]$ and $[HgI_2(dppmS)]$,[5] where $dppeS_2$ is $Ph_2P(S)CH_2CH_2P(S)Ph_2$ and dppmS is $Ph_2P(S)CH_2PPh_2$. The $dppeS_2$ ligand in $[Ph_2Hg.dppeS_2]$[4] does not form significant Hg...S interactions, whereas in $[HgCl_2(dppeS_2)]$ the $dppeS_2$ ligand chelates the Hg atom, *via* both S atoms, thereby forming a seven-membered ring.[5] These results clearly reflect the different Lewis acidities of the mercury atoms in the diphenyl and dichloro compounds. In the $[HgI_2(dppmS)]$ compound in which the dppmS ligand coordinates *via* the P*S* and P atoms, a highly-strained five-membered ring HgSPCP is found.[5] The Hg–S separation of 2.760(4) Å in this compound is such that the geometry about the Hg atom is best described as flattened tetrahedral. Subsequent to these studies, we have isolated crystals of $[HgCl_2(dppmS_2)]$ ($dppmS_2$ is $Ph_2P(S)CH_2P(S)Ph_2$), a known compound,[6] and determined its crystal structure, the subject of this communication. The purpose of this study was to compare this structure with those of $[HgCl_2(dppeS_2)]$

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and [HgI_2(dppmS)][5] to enable a comparison of the coordinating ability of i) the dppeS_2 and dppmS_2 ligands, which differ by one $-CH_2-$ link, and ii) the dppmS and dppmS_2 ligands, which differ by one S atom.

EXPERIMENTAL

[$HgCl_2$(dppmS_2)] was prepared according to the literature method and crystals suitable for X-ray studies were grown by the slow evaporation of a $CH_3CN/CHCl_3$ mixture (1/1, V/V). Intensity data were measured at 295 K for a crystal 0.25 × 0.05 × 0.52 mm on an Enraf-Nonius CAD4F diffractometer fitted with graphite monochromatized Mo$K\alpha$ radiation, $\lambda = 0.7107$ Å. The ω:1/3θ scan technique was employed to measure the intensities for 3982 reflections up to a maximum Bragg angle of 22.5°. The data were corrected for Lorentz and polarization effects and for absorption with the use of an analytical procedure.[7] Of the 3404 unique reflections, 2486 satisfied the $I \geq 2.5\sigma(I)$ criterion of observability and were used in the subsequent analysis.

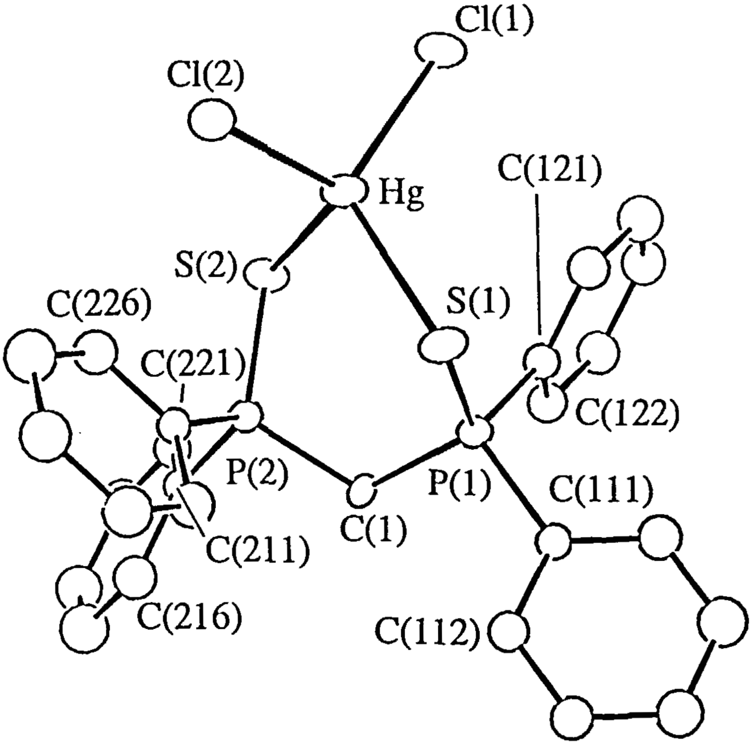

FIGURE 1 Molecular structure and crystallographic numbering scheme employed for [$HgCl_2$(dppmS_2)].

Crystal data:

[$HgCl_2$(dppmS_2)], $C_{25}H_{22}Cl_2HgP_2S_2$, $M_r = 720.0$, triclinic, space group $P\bar{1}$, $a =$ 9.755(1), $b =$ 16.049(1), $c =$ 8.436(2) Å, $\alpha =$ 96.33(1), $\beta =$ 90.17(1), $\gamma =$ 84.04(1)°,

$V = 1305.5$ Å^3, $Z = 2$, $D_c = 1.832\,\mathrm{g\,cm^{-3}}$, $F(000) = 696$, $\mu = 63.38\,\mathrm{cm^{-1}}$, max. and min. transmission factors: 0.731 and 0.229.

The structure was solved by interpretation of the Patterson synthesis and refined by a full-matrix least-squares procedure based on F.[7] All non-phenyl and non-H atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in the model at their calculated positions (C–H 0.97 Å). After the inclusion of a weighting scheme of the form, $w = k/[\sigma^2(F) + g|F|^2]$, the refinement was continued until convergence; $R = 0.033$, $k = 1.9$, $g = 0.0005$, and $R_w = 0.035$. The analysis of variance showed no special features. Fractional atomic coordinates are listed in Table I and the numbering scheme employed is shown in Figure 1 drawn with ORTEP at 25% probability ellipsoids.[8] Scattering factors for neutral Hg, corrected for f' and f'', were from the *International Tables for X-ray Crystallography*[9] and those for the remaining atoms were as incorporated in the SHELX76 program.[7] Calculations were performed on a SUN4/280 computer. Listings of thermal parameters, H-atom parameters, all bond distances and angles, and the observed and calculated structure factors are available from the Editor.

TABLE I
Fractional atomic coordinates ($\times 10^5$ for Hg; $\times 10^4$ for others) for $[HgCl_2(dppmS_2)]$.

Atom	*x/a*	*y/b*	*z/c*
Hg	26296(4)	24347(2)	14200(4)
Cl(1)	4009(2)	3285(2)	3258(3)
Cl(2)	1147(2)	1627(2)	2873(3)
S(1)	3822(2)	1431(1)	−843(3)
S(2)	1292(2)	3619(1)	−42(3)
P(1)	4041(2)	2214(1)	−2495(2)
P(2)	909(2)	2933(1)	−2071(2)
C(1)	2404(6)	2636(5)	−3346(9)
C(111)	4979(4)	1641(3)	−4172(6)
C(112)	4318(4)	1117(3)	−5289(6)
C(113)	5060(4)	665(3)	−6572(6)
C(114)	6464(4)	736(3)	−6738(6)
C(115)	7126(4)	1261(3)	−5621(6)
C(116)	6383(4)	1713(3)	−4338(6)
C(121)	4955(5)	3096(3)	−1792(5)
C(122)	4924(5)	3783(3)	−2677(5)
C(123)	5662(5)	4461(3)	−2164(5)
C(124)	6430(5)	4452(3)	−768(5)
C(125)	6461(5)	3766(3)	117(5)
C(126)	5723(5)	3088(3)	−396(5)
C(211)	−226(5)	3546(3)	−3269(6)
C(212)	−439(5)	4421(3)	−2936(6)
C(213)	−1334(5)	4890(3)	−3874(6)
C(214)	−2015(5)	4485(3)	−5145(6)
C(215)	−1801(5)	3610(3)	−5478(6)
C(216)	−906(5)	3141(3)	−4540(6)
C(221)	119(6)	1997(4)	−1790(6)
C(222)	373(6)	1247(4)	−2799(6)
C(223)	−306(6)	550(4)	−2542(6)
C(224)	−1239(6)	602(4)	−1277(6)
C(225)	−1493(6)	1351(4)	−268(6)
C(226)	−814(6)	2049(4)	−524(6)

RESULTS AND DISCUSSION

The molecular structure of [$HgCl_2(dppmS_2)$] is shown in Figure 1, selected bond distances and angles are listed in Table II and Table III collects interatomic parameters for the four compounds relevant to this comparative study. The structure is molecular, there being no close intermolecular contacts in the crystal lattice. The Hg atom is coordinated by two Cl atoms (Hg–Cl 2.445(2) and 2.455(2) Å) and two S atoms (Hg–S 2.557(2) and 2.613(2) Å) derived from a chelating $dppmS_2$ ligand leading to the formation of a puckered six-membered ring. The coordination geometry about the Hg atom is distorted tetrahedral; the tetrahedral bond angles range from 103.8(1)° for S(1)–Hg–S(2), *i.e.* the chelate angle, to 119.6(1)° for Cl(1)–Hg–S(1).

TABLE II

Selected bond distances (Å) and angles (°) for [$HgCl_2(dppmS_2)$].

Hg–Cl(1)	2.445(2)	Hg–Cl(2)	2.455(2)
Hg–S(1)	2.557(2)	Hg–S(2)	2.613(2)
S(1)–P(1)	2.003(3)	S(2)–P(2)	1.986(3)
Cl(1)–Hg–Cl(2)	111.1(1)	Cl(1)–Hg–S(1)	119.6(1)
Cl(1)–Hg–S(2)	100.1(1)	Cl(2)–Hg–S(1)	107.8(1)
Cl(2)–Hg–S(2)	114.2(1)	S(1)–Hg–S(2)	103.8(1)
Hg–S(1)–P(1)	101.5(1)	Hg–S(2)–P(2)	98.7(1)
P(1)–C(1)–P(2)	119.8(4)		

TABLE III

Selected bond distances (Å) and angles (°) for Hg chalcogenide complexes.

Parameter	[$HgI_2(dppmS)$][5]	[$HgCl(dppmS_2)$]	[$Ph_2Hg.dppeS_2$][4a]	[$HgCl(dppeS_2)$][5]
Hg–X(1)	2.727(2)	2.445(2)	2.069(7)	2.447(3)
Hg–X(2)	2.693(2)	2.455(2)	2.069(7)	2.442(3)
Hg–P(2)	2.503(5)			
Hg–S(1)	2.760(4)	2.557(2)	3.913(4)	2.559(3)
Hg–S(2)		2.613(2)	3.913(4)	2.546(3)
P(1)–S(1)	1.968(6)	2.003(3)	1.956(2)	1.998(3)
P(2)–S(2)		1.986(3)	1.956(2)	1.990(4)
X(1)–Hg–X(2)	113.0(1)	111.1(1)	180(–)	111.4(1)
P(2)–Hg–S(1)	88.8(1)			
S(1)–Hg–S(2)		103.8(1)		122.3(1)

[a] X = C; molecule has crystallographic $\bar{1}$ symmetry.

The Hg–Cl distances, which are equivalent within experimental error, are significantly shorter than the Hg–Cl bond distances found in a number of [$HgCl_2(PR_3)_2$] complexes thus indicating substantial Hg–Cl interactions. The Hg–S bond distances however, are slightly longer than the sum of the covalent radii of tetrahedral Hg and S (2.52 Å).[10] Evidence that the Hg–S bonds have some covalent character is found in the significant lengthening of the P–S bond distances to 2.003(3) and 1.986(3) Å, respectively, compared to the P=S distance of 1.956(2) Å found in the adduct [$Ph_2Hg.dppeS_2$],[4] in which there are no significant Hg. . .S interactions. That the two

P–S bond distances are different in $[HgCl_2(dppmS_2)]$ reflects the slight asymmetry in the mode of coordination of the $dppmS_2$ ligand to the Hg atom.

The structure found here for $[HgCl_2(dppmS_2)]$ can be related to the $dppeS_2$ analogue $[HgCl_2(dppeS_2)]$[5] which features a seven-membered ring. The Hg–Cl bond distances are equal within experimental error in both structures. By contrast, the longer Hg–S bond distance in $[HgCl_2(dppmS_2)]$ (*i.e.* Hg–S(2) 2.613(2) Å) is longer than the Hg–S(1) bond in this compound and both Hg–S bond distances in $[HgCl_2(dppeS_2)]$.[5] The slight asymmetry (*ca* 0.056 Å) in the Hg–S bond distances in the former compound probably reflects the extra strain in the six-membered ring.

The $dppmS_2$ ligand has also been characterized in the crystal structure of $[CuCl(dppmS_2)]$. In this compound the Cu–S bond distances differ by 0.06 Å and similar arguments are applicable to account for the disparity in the Cu–S bond distances.

The structure determinations for the $[HgI_2(dppmS)]$,[5] $[HgCl_2(dppeS_2)]$,[5] and $[HgCl_2(dppmS_2)]$ compounds enable a comparison of the coordinating ability of the dppmS, $dppmS_2$ and $dppeS_2$ ligands. For the dppmS ligand in $[HgI_2(dppmS)]$ the steric strain that would exist for the HgSPCP five-membered ring is offset by the significant lengthening of the Hg–S bond. As mentioned above, the lengthening of this bond is such that the coordination geometry about the Hg atom in $[HgI_2(dppmS)]$ is best described as flattened tetrahedral.[5] For the $dppeS_2$ ligand in the $[HgCl_2(dppeS_2)]$ compound there is minimal steric strain in the seven-membered ring however, and thus the S atoms of the $dppeS_2$ ligand form symmetrical Hg–S bond distances. An intermediate mode of coordination is found for the $dppmS_2$ ligand in $[HgCl_2(dppmS_2)]$ where the steric strain in the six-membered ring is alleviated by the slight elongation of the Hg–S(2) bond distance compared with the Hg–S(1) bond distance.

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