Crystal and Molecular Structure of Dithiocyanatobis(triphenylphosphine)-mercury(II)

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The crystal and molecular structure of the title compound has been determined from three-dimensional X-ray data. Crystals are monoclinic, space group $P2_1/c$, $a = 17·385(9)$, $b = 10·581(4)$, $c = 19·304(5)$ Å, $\beta = 91·41(6)°$, and $Z = 4$. The structure was solved from diffractometer data by the heavy-atom method and refined by least-squares procedures to R 0·048 for 2769 observed reflections. The cell contains monomeric molecules and the mercury atom is in a distorted tetrahedral environment, as previously suggested on the basis of the i.r. spectrum. Bond lengths are: Hg–S 2·565 and 2·577, and Hg–P 2·487 and 2·484 Å.

MERCURY(II) halide complexes with tertiary aliphatic phosphines and arsines are well known.[1] Similar triphenylphosphine complexes of empirical formulae $HgX_2(PPh_3)$ and/or $HgX_2(PPh_3)_2$ have been reported [2-4] for X = SCN, CN, Cl, Br, I, NO_3, and ClO_4; structural information available has generally been obtained from their vibrational spectra.[2,5]

We have recently determined the crystal structure of $Hg(SCN)_2(AsPh_3)$,[6] for which a dimeric structure with bridging thiocyanato-groups had been suggested on the basis of the i.r. spectrum.[5] The crystal was found to contain discrete three-co-ordinate molecules. This prompted us to investigate the structure of a 1:2 addition complex and the triphenylphosphine compound was selected.

EXPERIMENTAL

Preparation.—The complex was prepared according to the procedure of ref. 2. It was twice recrystallized from acetone and slow evaporation of the solvent yielded diamond-shaped crystals suitable for X-ray work.

Crystal Data.—$C_{38}H_{30}HgN_2S_2P_2$, $M = 840·6$, Monoclinic $a = 17·385(9)$, $b = 10·581(4)$, $c = 19·304(5)$ Å, $\beta = 91·41(6)°$, $U = 3448$ Å^3, $D_m = 1·58(1)$ g cm^{-3} (by flotation), $Z = 4$, $D_c = 1·585$ g cm^{-3}. $\lambda(\text{Cu-}K_{\bar{\alpha}}) = 1·5418$, $\lambda(\text{Cu-}K_\beta) = 1·3922$ Å; $\mu(\text{Cu-}K_{\bar{\alpha}}) = 104·1$ cm^{-1}. Space group $P2_1/c$.

Crystallographic Measurements.—Cell parameters were obtained by least-squares refinement [7] of the setting angles for 12 independent Cu-K_β peaks automatically centred on a Picker FACS 1 diffractometer ($52° < 2\theta < 64°$). The estimated standard deviations, given in parentheses, are set equal to twice the values calculated in the last cycle of refinement, which reflects our experience with reproducibility.

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A crystal of dimensions $0{\cdot}30 \times 0{\cdot}31 \times 0{\cdot}32$ mm^3 was mounted on a glass fibre and left exposed to the atmosphere. A detailed description of the instrument and methods used for data collection is given elsewhere.[8] Three standard reflections ($10,\bar{1},\bar{4}$; $1,7,\bar{2}$; $10,0,0$), measured every 30 reflections, did not show a variation of $>6\%$ from their respective means. 3589 measurements (hkl, $\bar{h}kl$) were obtained within a sphere of $2\theta \leqslant 90°$ by use of Ni-filtered Cu-K_α radiation, giving 2916 independent measurements after removal of systematically absent reflections, and equivalent reflections were averaged. 2769 Observed reflections were obtained having $I > 8$ decacounts and $>10\%$ of the background count. They were corrected for Lorentz and polarization effects. Because of the nearly spherical crystal, no absorption correction was applied.

Refinement.—The structure was solved by the standard heavy-atom method and refined by full-matrix least-squares. Form factors used were from ref. 9 with anomalous dispersion terms $\Delta f'$ and $\Delta f''$ for mercury, phosphorus, and sulphur from ref. 10. Programs used are listed in ref. 11.

Isotropic refinement for all non-hydrogen atoms converged to R 0·086. Hydrogen atoms were placed in calculated positions (assuming C–H 1·00 Å) and were assigned temperature factors 0·5 units greater than those of the corresponding carbon atom. The hydrogen parameters were not refined, but the atoms were displaced according to the shift of the corresponding carbon atom. Mercury, phosphorus, and the SCN groups were then refined anisotropically and the carbon atoms of the rings isotropically. This reduced R to 0·059. Finally, anisotropic temperature factors were refined for all non-hydrogen atoms. In order to keep the least-squares matrix at a reasonable size, mercury, phosphorus, and the SCN groups were refined at each cycle, but the carbon atoms of only one triphenylphosphine molecule were refined at a time. Anisotropic refinement with unit weights converged to R 0·050. A weighting scheme of the form $\sqrt{w} = a + b|F_o| + c|F_o|^2$ (with $a = 11{\cdot}3$, $b = -0{\cdot}37$, and $c = 0{\cdot}0045$) was applied at the end of the refinement. The constants were adjusted to obtain minimum variation of the weighted mean residual as a function of sin θ/λ and of F_o. The refinement of the scale factor, positional parameters, and anisotropic temperature factors for all non-hydrogen atoms converged to R 0·048 and R' $\{=[\Sigma(w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)]^{\frac{1}{2}}\}$ 0·054 (observed reflections only). Average and maximum shifts in the last least-squares cycle were 0·1 and 0·3σ respectively. The final difference-Fourier map showed no peaks $> \pm 0{\cdot}7$ eÅ^{-3}, except for two of 2·0 and 1·7 eÅ^{-3} at *ca.* 0·5 Å from mercury and phosphorus respectively.

Final co-ordinates and temperature factors are listed in Table 1.* The carbon atoms are identified with C(ij) labels, where i is the ring number and j corresponds to sequential numbering of the ring vertices, the index $j = 1$ being assigned to the atoms bound to phosphorus. Hydrogen atoms are numbered with the same pair of indices as the carbon atom to which they are attached.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

Crystals of $Hg(SCN)_2(PPh_3)_2$ contain monomeric molecules (Figure), in which mercury is four-co-ordinated. Bond lengths and angles are listed in Table 2.

As commonly observed for mercury compounds, the SCN groups bind to the metal *via* the sulphur atom and define Hg–S–C angles of *ca.* 100°. They are linear and the S–C and C–N bond lengths are normal. The Hg–S distances (2·565 and 2·577 Å) are slightly longer than the sum of the covalent radii of sulphur (1·04 Å) and tetrahedrally co-ordinated mercury (1·48 Å).[12] Typical distances reported for HgS_4 tetrahedral units are 2·54 in HgS, $K_2Hg(SCN)_4$, and $NiHg(SCN)_4(H_2O)_2$,[12]

TABLE 1

Final fractional co-ordinates and anisotropic thermal parameters ($\times 10^3$) with estimated standard deviations (in parentheses)

Atom	*x*	*y*	*z*
Hg	0·23836(3)	0·02642(4)	0·05461(2)
P(1)	0·3474(2)	0·0979(3)	0·1313(1)
P(2)	0·1592(2)	−0·1540(3)	0·0940(1)
S(1)	0·1396(2)	0·1958(3)	0·0185(2)
S(2)	0·2878(2)	−0·0179(3)	−0·0676(1)
C(1)	0·1409(8)	0·2842(14)	0·0912(8)
C(2)	0·3105(8)	−0·1682(15)	−0·0573(6)
N(1)	0·1427(9)	0·3478(14)	0·1378(8)
N(2)	0·3250(9)	−0·2744(16)	−0·0517(6)
C(11)	0·4277(6)	−0·0119(11)	0·1356(6)
C(12)	0·4708(7)	−0·0347(14)	0·1947(7)
C(13)	0·5299(8)	−0·1207(17)	0·1912(8)
C(14)	0·5477(8)	−0·1838(14)	0·1312(10)
C(15)	0·5021(8)	−0·1580(15)	0·0732(7)
C(16)	0·4439(6)	−0·0750(12)	0·0728(6)
C(21)	0·3130(6)	0·1184(12)	0·2191(5)
C(22)	0·2901(7)	0·2377(12)	0·2408(6)
C(23)	0·2565(7)	0·2510(15)	0·3053(8)
C(24)	0·2486(8)	0·1467(20)	0·3466(7)
C(25)	0·2703(8)	0·0286(16)	0·3254(7)
C(26)	0·3029(7)	0·0118(12)	0·2609(7)
C(31)	0·3881(7)	0·2480(12)	0·1054(6)
C(32)	0·3424(9)	0·3311(14)	0·0647(8)
C(33)	0·3721(15)	0·4458(15)	0·0445(9)
C(34)	0·4474(17)	0·4792(19)	0·0669(11)
C(35)	0·4931(11)	0·3958(23)	0·1057(10)
C(36)	0·4617(9)	0·2805(15)	0·1238(7)
C(41)	0·2139(6)	−0·2495(10)	0·1553(6)
C(42)	0·1860(8)	−0·2796(12)	0·2202(6)
C(43)	0·2319(8)	−0·3438(14)	0·2681(6)
C(44)	0·3049(9)	−0·3786(13)	0·2530(7)
C(45)	0·3332(7)	−0·3481(14)	0·1878(7)
C(46)	0·2876(7)	−0·2832(12)	0·1402(6)
C(51)	0·0770(7)	−0·0980(13)	0·1410(6)
C(52)	0·0848(8)	0·0019(13)	0·1854(8)
C(53)	0·0240(13)	0·0333(17)	0·2265(8)
C(54)	−0·0445(12)	−0·0320(25)	0·2222(12)
C(55)	−0·0519(10)	−0·1310(23)	0·1756(13)
C(56)	0·0066(7)	−0·1671(15)	0·1329(8)
C(61)	0·1254(6)	−0·2541(13)	0·0237(5)
C(62)	0·0944(7)	−0·1954(12)	−0·0360(7)
C(63)	0·0656(9)	−0·2691(17)	−0·0896(7)
C(64)	0·0678(10)	−0·3969(18)	−0·0864(8)
C(65)	0·0996(11)	−0·4533(15)	−0·0294(9)
C(66)	0·1286(8)	−0·3824(13)	0·0274(7)

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* Structure factors are listed in Supplementary Publication No. SUP 20787 (3 pp., 1 microfiche). See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

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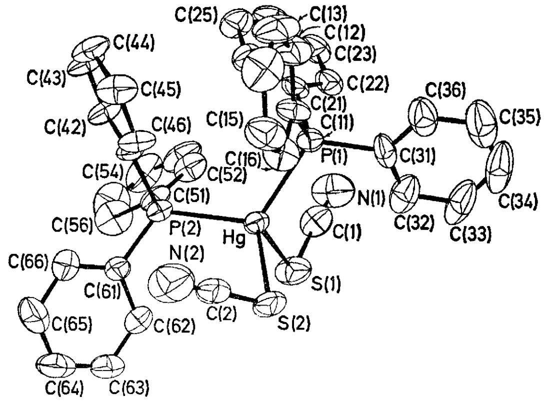
TABLE 1 (*continued*)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg	50·7(3)	38·4(3)	31·1(4)	0·3(3)	0·3(1)	2·2(2)
P(1)	50(2)	47(2)	28(2)	−4(2)	3(1)	−3(1)
P(2)	44(2)	44(2)	33(2)	3(2)	−1(1)	7(1)
S(1)	91(3)	67(2)	63(2)	25(2)	−8(1)	4(2)
S(2)	98(3)	61(2)	30(2)	−3(2)	4(2)	1(1)
C(1)	64(9)	59(12)	78(11)	23(7)	4(7)	8(8)
C(2)	80(9)	63(12)	30(7)	−1(4)	2(5)	−7(9)
N(1)	136(12)	89(11)	92(11)	41(9)	−5(7)	−19(9)
N(2)	142(13)	83(11)	70(10)	26(9)	7(6)	−14(9)
C(11)	25(6)	66(8)	42(8)	6(6)	−5(4)	−4(6)
C(12)	32(8)	101(11)	72(9)	7(7)	−10(5)	9(8)
C(13)	36(9)	138(15)	67(11)	4(9)	−11(4)	31(10)
C(14)	58(9)	87(11)	87(13)	12(8)	12(6)	5(9)
C(15)	60(9)	96(11)	46(10)	−9(10)	5(5)	−15(8)
C(16)	15(6)	72(9)	64(9)	11(6)	6(3)	−6(7)
C(21)	45(8)	56(10)	30(7)	−9(7)	−1(4)	−13(7)
C(22)	52(8)	56(9)	45(9)	−8(6)	1(4)	−14(6)
C(23)	69(12)	75(11)	49(9)	−10(7)	2(3)	−23(9)
C(24)	71(9)	112(15)	43(15)	1(8)	6(4)	−25(10)
C(25)	76(9)	95(12)	37(9)	−11(8)	10(4)	11(10)
C(26)	67(9)	55(9)	45(9)	−3(6)	2(5)	4(7)
C(31)	55(9)	56(9)	50(8)	−30(7)	15(4)	−21(7)
C(32)	99(12)	44(10)	84(11)	4(9)	14(5)	11(8)
C(33)	180(20)	38(11)	86(13)	−9(12)	30(8)	8(8)
C(34)	196(24)	65(14)	97(15)	−59(16)	58(10)	−33(11)
C(35)	115(15)	103(16)	96(13)	−59(14)	31(7)	−34(11)
C(36)	100(12)	74(14)	58(10)	−37(9)	14(5)	−18(8)
C(41)	39(8)	46(7)	35(7)	0(6)	−4(3)	12(6)
C(42)	52(8)	77(10)	41(7)	6(7)	3(3)	18(7)
C(43)	67(11)	101(11)	40(8)	15(8)	3(5)	33(9)
C(44)	87(12)	75(11)	42(10)	27(8)	−5(5)	14(7)
C(45)	55(9)	89(11)	55(9)	26(7)	−1(7)	−6(10)
C(46)	59(9)	75(10)	31(8)	14(7)	−2(4)	7(6)
C(51)	45(10)	57(9)	49(8)	11(7)	0(4)	18(8)
C(52)	76(11)	61(11)	63(9)	30(7)	7(5)	9(8)
C(53)	131(17)	93(13)	65(11)	58(13)	16(7)	14(10)
C(54)	73(14)	127(18)	139(17)	39(14)	36(7)	53(15)
C(55)	53(12)	121(18)	184(21)	−3(12)	14(8)	29(17)
C(56)	17(8)	122(12)	95(11)	13(8)	10(4)	13(9)
C(61)	47(8)	55(10)	35(7)	−6(6)	−1(3)	3(7)
C(62)	72(6)	59(9)	56(9)	2(7)	−4(4)	17(8)
C(63)	97(12)	99(15)	41(9)	−10(9)	−20(5)	9(9)
C(64)	129(14)	77(14)	58(11)	−4(12)	−17(6)	−6(10)
C(65)	138(14)	57(10)	90(13)	6(10)	−19(7)	−15(10)
C(66)	102(11)	42(11)	66(9)	0(8)	−7(5)	7(9)



Stereoscopic view of the molecule; ellipsoids represent 50% probability

and 2·56 Å in $CoHg(SCN)_4$,[12] $CoHg(SCN)_4(pyridine)_2$,[13] and $[Me_4N]_2Hg(SCN)_4$.[14] The terminal nitrogen atoms are free, which is consistent with the i.r. spectrum reported to indicate *S*-bonded non-bridging thiocyanate groups.[2,5]

TABLE 2

Interatomic distances (Å) and angles (°) and their respective standard deviations (in parentheses)

(*a*) Bond lengths around mercury

Hg–P(1)	2·489(3)	P(2)–C(41)	1·804(11)
Hg–P(2)	2·487(3)	P(2)–C(51)	1·815(12)
Hg–S(1)	2·565(4)	P(2)–C(61)	1·806(12)
Hg–S(2)	2·577(3)	S(1)–C(1)	1·689(16)
P(1)–C(11)	1·816(11)	S(2)–C(2)	1·648(16)
P(1)–C(21)	1·828(11)	C(1)–N(1)	1·119(22)
P(1)–C(31)	1·813(13)	C(2)–N(2)	1·155(23)

(*b*) Bond angles

P(1)–Hg–P(2)	118·1(1)	C(11)–P(1)–C(21)	107·9(5)
P(1)–Hg–S(1)	116·2(1)	C(11)–P(1)–C(31)	105·5(6)
P(1)–Hg–S(2)	109·3(1)	C(21)–P(1)–C(31)	107·0(6)
P(2)–Hg–S(1)	104·3(1)	C(41)–P(2)–C(51)	105·3(6)
P(2)–Hg–S(2)	110·1(1)	C(41)–P(2)–C(61)	108·6(5)
S(1)–Hg–S(2)	96·7(1)	C(51)–P(2)–C(61)	108·9(6)
Hg–S(1)–C(1)	99·6(5)	P(1)–C(11)–C(12)	123·4(9)
Hg–S(2)–C(2)	98·7(5)	P(1)–C(11)–C(16)	115·8(9)
		P(1)–C(21)–C(22)	119·4(9)
S(1)–C(1)–N(1)	176·8(15)	P(1)–C(21)–C(26)	119·3(9)
S(2)–C(2)–N(2)	177·7(15)	P(1)–C(31)–C(36)	121·3(11)
Hg–P(1)–C(11)	113·8(4)	P(1)–C(31)–C(32)	118·2(10)
Hg–P(1)–C(21)	108·8(4)	P(2)–C(41)–C(42)	121·7(9)
Hg–P(1)–C(31)	113·5(4)	P(2)–C(41)–C(46)	119·0(9)
Hg–P(2)–C(41)	110·1(4)	P(2)–C(51)–C(52)	120·0(10)
Hg–P(2)–C(51)	110·7(4)	P(2)–C(51)–C(56)	117·6(9)
Hg–P(2)–C(61)	113·0(4)	P(2)–C(61)–C(66)	122·3(10)
		P(2)–C(61)–C(62)	117·8(9)

(*c*) Intramolecular contacts

C(41) ··· C(51)	2·88(2)	C(21) ··· C(12)	3·23(2)
C(11) ··· C(31)	2·89(2)	C(12) ··· C(26)	3·26(2)
C(11) ··· C(21)	2·95(2)	C(31) ··· C(22)	3·16(2)
C(21) ··· C(31)	2·93(2)	C(42) ··· C(51)	3·07(2)
C(51) ··· C(61)	2·95(2)	C(61) ··· C(56)	3·13(2)
C(41) ··· C(61)	2·93(2)	C(41) ··· C(66)	3·17(2)
C(11) ··· C(26)	3·31(2)	C(11) ··· C(36)	3·16(2)
C(31) ··· H(22)	2·67(3)	C(51) ··· H(42)	2·57(3)
C(11) ··· H(26)	2·88(3)	C(12) ··· H(26)	2·81(3)
C(11) ··· H(36)	2·66(3)	C(12) ··· H(36)	2·78(3)
C(41) ··· H(66)	2·64(3)	C(34) ··· H(45)	2·85(3)
S(1) ··· H(32)	2·85(3)		

(*d*) Intermolecular contacts

C(34) ··· C(34) $1 - x, 1 - y, \bar{z}$	3·24(4)
S(1) ··· H(65) $x, -1 + y, z$	2·91(4)
S(2) ··· H(43) $x, -\frac{1}{2} - y, -\frac{1}{2} + z$	2·86(4)

Bond lengths and angles in the phenyl rings are in the range 1·34(2)—1·43(2) Å and 116(2)—123(2)°, means 1·38 Å and 120°. The rings are planar within 0·02 Å, but in several cases, the phosphorus atoms lie appreciably out of the planes: 0·01, 0·15, 0·04, 0·14, 0·21, and 0·06 Å for rings *i* = (1)—(6). Distortions of this magnitude exist in PPh_3 itself and in $NiBr_2(PPh_3)_2$[16] and $CdCl_2(PPh_3)_2$.[17] From the intramolecular contacts [Table 2(*c*)] it is clear that the immediate environment of phosphorus is overcrowded, but not exceptionally so for a phenylphosphine molecule. Except for the C(34) ··· H(45) contact (2·85 Å), which

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is not extremely short, all intramolecular contacts listed in Table 2(*c*) involve rings belonging to the same PPh_3 molecule. The lack of short non-bonded contacts *between* the two ligand molecules suggests that co-ordination of the two PPh_3 molecules to mercury does not appreciably increase steric strain within and between the PPh_3 molecules.

The Hg–P–C(*i*1) angles (mean 111·7°) tend to be larger than C(*i*1)–P–C(*i*′1) in the ligand molecule (mean 106·7°). In the crystals of PPh_3, the C(*i*1)–P–C(*i*′1) angles (mean 103·0°) are still smaller because of the steric influence of the phosphorus lone-pair. The Hg–P distances (2·489 and 2·487 Å) are *ca.* 0·1 Å shorter than expected from the covalent radii of mercury (1·48 Å) and phosphorus (1·10 Å).[12] The only other experimental values for Hg–P bond lengths (2·52—2·56 Å) come from the distorted tetrahedral HgP_4 unit in $PbHgP_{14}$.[18]

Besides the present mercury complex, $MX_2(PPh_3)_2$ complexes with $MX_2 = NiBr_2$,[16] $NiCl_2$,[19] and $CdCl_2$[17] are known to form tetrahedral molecules. In this series of compounds, the X–M–X angle shows a decrease with increasing size of the central atom: Br–Ni–Br 126·3,[16] Cl–Ni–Cl 123,[19] Cl–Cd–Cl 113·9,[17] and S–Hg–S 96·7°. The large angles in the nickel complexes have been explained by steric repulsions, the non-bonding Cl···Cl and Br···Br distances being relatively short because of the small nickel atom. With the larger cadmium atom, a normal Cl–Cd–Cl angle is compatible with sufficient separation of the chlorine atoms. In the present compound, the metal atom is still larger and even with an S–Hg–S angle as small as 97° the sulphur atoms are not in direct contact, since the S···S distance (3·85 Å) is more than twice the van der Waals radius of sulphur (1·85 Å). This small angle would favour an increase of the P–Hg–P angle (118·1°) beyond the normal value to decrease repulsions between the bulky PPh_3 groups.

We thank the National Research Council of Canada for financial support.

[3/516 *Received*, 12*th March*, 1973]

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