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Structural Studies of Steric Effects in Phosphine Complexes: Dimers of Bis-{dithiocyanato(1-phenyldibenzophosphole)mercury(II)} Associate with Significant Hg–N and Hg–S Interdimer Interactions*

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The title compound, $[\text{Hg}(\text{SCN})_2(\text{C}_6\text{H}_5)\text{P}(\text{C}_{12}\text{H}_8)]_2$, exists as a dimer with two-fold crystallographic symmetry in the solid state with the Hg atoms linked by bridging N- and S-thiocyanato atoms. There are four primary bonds to each Hg atom, Hg–N, 2.771(4) Å, Hg–P, 2.4084(11) Å and two Hg–S, 2.4565(10) Å and 2.6055(13) Å, resulting in a distorted trigonal pyramidal geometry about the metal centre. The dimers associate about inversion centres to form infinite one-dimensional chains by weaker Hg···N 3.178(5) Å and Hg···S 3.6027(14) Å interactions, giving an overall distorted octahedral coordination geometry for each Hg atom. The Hg–P bond lies approximately orthogonal to the ··Hg··Hg·· chain and the benzophosphole group forms a ‘sandwich’ preventing interactions between the $\text{Hg}(\text{SCN})_2$ moieties in neighbouring chains.

Key words: mercury, phosphine, thiocyanato, phenyldibenzophosphole, interdimer, interactions, stereochemistry.

* Dedicated to Professor Boris Kamenar on the occasion of his 70th birthday.

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INTRODUCTION

The electronic and steric effects of bulky phosphines in metal complexes such as those of Hg(II),¹ Au(I),² and Mo(0),³ have attracted our attention for several years. Our interest stems primarily from the effects that these phosphines exert on the stereochemistry of the metal atoms to which they are bonded. Mercury phosphine complexes embody a wide range of structural types, with those of 1:1 complexes being especially diverse.⁴ We now report on the structure of $[\text{Hg}(\text{SCN})_2(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_{12}\text{H}_8)]_2$, $\{= [\text{Hg}(\text{SCN})_2(\text{PhDBP})_2]_2$ or **I**\}.

EXPERIMENTAL

Compound **I** was synthesized from $\text{Hg}(\text{SCN})_2$ and 1-phenyldibenzophosphole in aqueous ethanol solution; recrystallization from ethanol/ CH_2Cl_2 solution afforded colorless crystals suitable for X-ray analysis. IR and Raman spectral peaks at 2122 and 2089 cm^{-1} indicated the presence of both terminal and bridging thiocyanato groups.

Molecule (**I**) crystallizes in the monoclinic system, space group $C2/c$ or Cc from the systematic absences, $C2/c$ chosen and confirmed by the analysis. Table I summarizes general, crystallographic and refinement data; final fractional coordinates are listed in Table II.*

Data collection: CAD-4.⁵ Cell refinement: SET4 & CELDIM.⁵ Data reduction: DATRD2 in NRCVAX96.⁶ Program(s) used to solve the structure: NRCVAX96 *via* Patterson heavy-atom method.⁶ Program(s) used to refine the structure: NRCVAX96,⁶ and SHELXL97.⁷ Molecular graphics: NRCVAX96,⁶ ORTEP,⁸ and PLATON.⁹ Software used to prepare material for publication: NRCVAX96,⁶ SHELXL97,⁷ and WordPerfect macro PREP8.¹⁰

RESULTS AND DISCUSSION

A view of **I** with N and S atoms from adjacent dimers and our numbering scheme is in Figure 1; selected dimensions are in Table III. The dimer lies about a two-fold axis and the coordination geometry about Hg is distorted trigonal pyramidal with four primary bonds consisting of Hg–N, 2.771(4) Å, Hg–P, 2.4084(11) Å and two Hg–S, 2.4565(10) Å and 2.6055(13) Å. The angles which these atoms make about the mercury atom are in the range 85.31(9)° (P1–Hg–N1ⁱ, $i = -x, y, \frac{1}{2} - z$) to 149.46(4)° (P1–Hg–S1) which deviate considerably from angles of 90° and 120° in an idealised trigonal pyramidal geometry.

* Crystallographic data for the structure reported in this paper have been deposited with Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK and can be obtained on request, free of charge, by quoting the publication citation and the deposition number 103104.

TABLE I

The details of general, crystal, X-ray and refinement data for compound I

<i>General and crystal data</i>	
Molecular formula	C ₄₀ H ₂₆ Hg ₂ N ₄ P ₂ S ₄
Formula weight, M_r	1154.00
Crystal shape and colour ^a	block, colourless
Crystal size/mm	0.39 x 0.18 x 0.17
Crystal system and space group	Monoclinic, $C2/c$
Unit cell parameters ^b	
$a/\text{\AA}$	14.899(2)
$b/\text{\AA}$	17.815(2)
$c/\text{\AA}$	16.131(4)
$\beta/^\circ$	114.400(10)
Volume/ \AA^3	3899.2(12)
Unit cell content, Z	4
Calculated density, $D_x/\text{g cm}^{-3}$	1.966
X-ray wavelength, $\lambda(\text{Mo-K}\alpha)/\text{\AA}$	0.7107
Linear absorption coefficient, $\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	8.197
<i>Data collection</i>	
Diffractometer	Enraf-Nonius CAD-4
Data collection range and scan mode [$T = 294(1) \text{ K}$]	$\theta_{\text{max}} = 27.90^\circ$; $\omega - 2\theta$
Min. and max. transmission factors ^c	0.236; 0.337
Reflections measured ^d	4853
Independent reflections [$R_{\text{int}} = 0.024$] ^e	4699
Observed reflections, $I_{\text{net}} \geq 2\sigma(I_{\text{net}})$	3120
<i>Refinement</i>	
Residuals, $R[F^2 > 2\sigma(F^2)]$; $wR(F^2)$ ^f	0.0259; 0.0643
Goodness-of-fit, S	0.956
Extinction coefficient (SHELXL97)	0.00035(3)
Min. and max. electron densities in the last δF -map / e \AA^{-3}	-0.897; 0.865
Parameters refined	236
Max. variable shift/error ratio	0.001

^a The compound was synthesized and the crystals were prepared by the authors. See Experimental.

^b Cell parameters from 25 reflections in θ range 8.0 to 19.0°.

^c Gaussian absorption corrections by integration were applied.⁶

^d Three standard reflections measured every 2 hours showed no decay. Intensity variation $\pm 2\%$. Miller indices range: $h = -19 \rightarrow 17$; $k = 0 \rightarrow 13$; $l = 0 \rightarrow 21$.

^e Scattering factors from the *International tables for X-ray crystallography* (Vol. C).

^f Refinement on F^2 . Weighting scheme: $w = 1 / [\sigma^2(F_o^2) + (0.0363P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. Hydrogen atom parameters were constrained.

TABLE II
 Fractional atomic coordinates and equivalent isotropic displacement
 parameters $U_{\text{eq}}/\text{\AA}^2$ for compound **I**

Atom	x	y	z	U_{eq}^{a}
Hg	0.097903(11)	-0.006745(9)	0.143211(11)	0.04190(7)
S1	-0.03258(8)	0.08792(6)	0.07876(8)	0.0412(2)
S2	-0.00161(11)	-0.12891(6)	0.13489(10)	0.0651(4)
P1	0.27032(7)	-0.03879(5)	0.20661(7)	0.0323(2)
N1	-0.1355(3)	0.0474(3)	0.1846(3)	0.0579(11)
N2	-0.1729(3)	-0.0857(2)	-0.0155(3)	0.0614(11)
C1	-0.0924(3)	0.0625(2)	0.1434(3)	0.0408(10)
C2	-0.1022(4)	-0.1032(2)	0.0463(3)	0.0479(11)
C11	0.3115(3)	-0.0909(2)	0.1331(3)	0.0364(9)
C12	0.3435(3)	-0.1624(2)	0.1695(3)	0.0430(10)
C13	0.3740(4)	-0.2123(3)	0.1198(4)	0.0654(15)
C14	0.3755(4)	-0.1908(3)	0.0382(4)	0.0705(16)
C15	0.3432(4)	-0.1208(3)	0.0036(3)	0.0599(13)
C16	0.3107(3)	-0.0696(3)	0.0495(3)	0.0451(10)
C21	0.2979(3)	-0.1150(2)	0.2856(3)	0.0381(9)
C22	0.3360(3)	-0.1756(2)	0.2565(3)	0.0408(10)
C23	0.3646(4)	-0.2398(2)	0.3092(4)	0.0561(13)
C24	0.3518(4)	-0.2421(3)	0.3899(4)	0.0637(15)
C25	0.3113(4)	-0.1833(3)	0.4171(3)	0.0570(13)
C26	0.2829(3)	-0.1188(2)	0.3650(3)	0.0473(11)
C31	0.3514(3)	0.0386(2)	0.2630(3)	0.0345(9)
C32	0.3201(3)	0.1109(2)	0.2412(3)	0.0447(11)
C33	0.3819(4)	0.1701(2)	0.2848(3)	0.0548(13)
C34	0.4740(4)	0.1556(3)	0.3500(3)	0.0541(12)
C35	0.5058(3)	0.0833(3)	0.3720(3)	0.0579(13)
C36	0.4447(3)	0.0245(2)	0.3287(3)	0.0484(11)

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

The dimers associate about inversion centres to form infinite one-dimensional chains through weaker Hg...N 3.178(5) Å and Hg...S 3.6027(14) Å interactions with alternating Hg...Hg distances of 5.3558(9) Å (within each dimer) and 4.3335(11) Å (between pairs of dimers). The overall coordination geometry about the mercury is thus distorted octahedral, consisting of four primary bonds and two weaker interactions {the three trans angles are

$138.09(8)^\circ$ S2–Hg–N2ⁱⁱ, $149.46(4)^\circ$ P1–Hg–S1, and $174.89(9)^\circ$ N1ⁱ–Hg–S1ⁱⁱ; ii = $-x, -y, -z$ }, representing a considerable deviation away from ideal octahedral geometry.

The phenyl ring is at an angle of $77.00(9)^\circ$ to the benzophosphole group and the P atom is displaced $0.017(6)$ Å and $0.028(3)$ Å from the mean planes of these rings respectively. In chloro(trimesitylphosphine)gold(I) the P atom is 0.34 Å from the aromatic ring planes due to steric effects within the bulky phosphine mesityl groups.² In **I**, the Hg–P bond lies approximately orthogonal to the $\cdot\text{Hg}\cdot\text{Hg}\cdot$ chain and the PhDBP ligand forms a sandwich about this chain preventing the Hg(SCN)₂ groups in neighbouring chains from interacting with one another. The $\cdot\text{Hg}(\text{SCN})_2(\text{PhDBP})\cdot$ chains stack with the phenyl and benzophosphole groups dove-tailed between the grooves formed by the phosphole ligands in neighbouring chains. The shortest *intermolecular* contact involves C16 with an inversion symmetry related N2ⁱⁱ such that

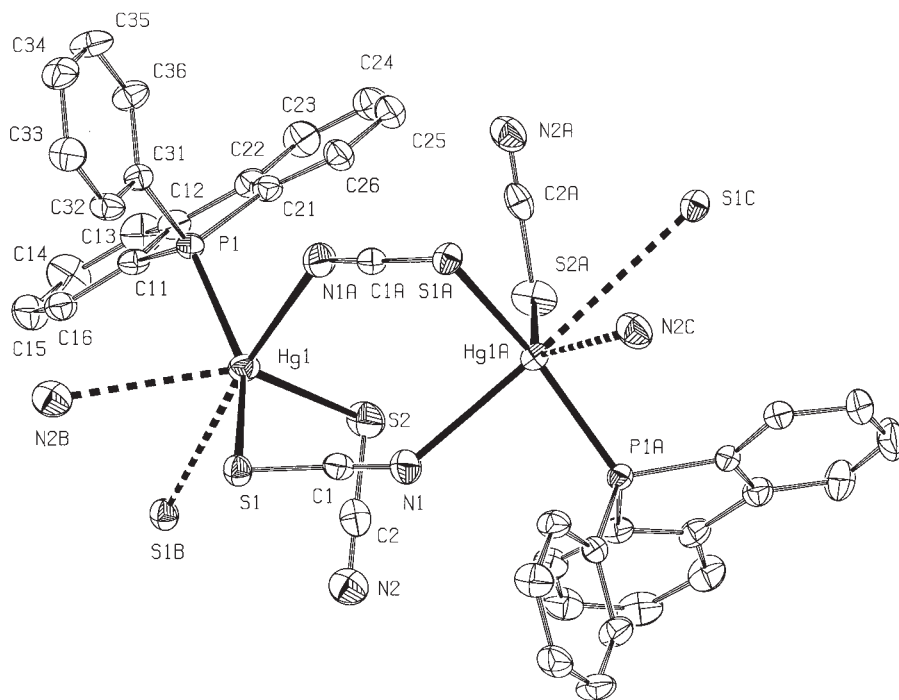


Figure. 1. A view of dimer **I** with N and S atoms from adjacent dimers and our numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Atoms in dimer **I** labelled with an A suffix are related to those in the asymmetric unit by the symmetry operators, $-x, y, \frac{1}{2} - z$; the S1 and N2 atoms with a B and C suffix by $-x, -y, -z$ and $x, -y, \frac{1}{2} + z$ respectively.

TABLE III
Selected molecular geometric parameters for compound **I**

Bond lengths / Å			
Hg–P1	2.4084(11)	S1–C1	1.689(5)
Hg–S1	2.4565(10)	S2–C2	1.652(5)
Hg–S2	2.6055(13)	P1–C11	1.801(4)
Hg–N1 ⁱ	2.771(4)	P1–C21	1.790(4)
Hg–N2 ⁱⁱ	3.178(5)	P1–C31	1.811(4)
Hg–S1 ⁱⁱ	3.6027(14)	N1–C1	1.131(5)
Hg–Hg ⁱⁱ	4.3335(11)	N2–C2	1.154(6)
Hg–Hg ⁱ	5.3558(9)		
Bond angles / °			
P1–Hg–S1	149.46(4)	N1 ⁱ –Hg–S1 ⁱⁱ	174.89(9)
P1–Hg–S2	107.96(4)	N2 ⁱⁱ –Hg–S1 ⁱⁱ	65.59(8)
S1–Hg–S2	102.57(4)	N1 ⁱ –Hg–N2 ⁱⁱ	119.31(11)
P1–Hg–N1 ⁱ	85.31(9)	Hg–P1–C11	115.87(13)
S1–Hg–N1 ⁱ	88.98(9)	Hg–P1–C21	111.91(14)
S2–Hg–N1 ⁱ	102.58(9)	Hg–P1–C31	113.96(13)
P1–Hg–N2 ⁱⁱ	78.42(9)	C11–P1–C21	92.16(19)
S1–Hg–N2 ⁱⁱ	78.38(8)	C11–P1–C31	112.61(18)
S2–Hg–N2 ⁱⁱ	138.09(8)	C21–P1–C31	108.09(18)
P1–Hg–S1 ⁱⁱ	97.45(3)	S1–C1–N1	177.2(4)
S1–Hg–S1 ⁱⁱ	90.76(3)	S2–C2–N2	179.5(5)
S2–Hg–S1 ⁱⁱ	72.49(4)	Hg ⁱⁱ –Hg–Hg ⁱ	112.344(17)

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

the H16...N2ⁱⁱ distance is 2.55 Å and the C–H...N angle 145° (ii = $-x, -y, -z$). Examination of the structure with PLATON showed that there were no solvent accessible voids in the crystal lattice.⁹

A search of the latest (April, 1998) release of the Cambridge Structural Database,¹¹ revealed only a few related PHg(SCN)₂ structures. Two forms of the triphenylphosphine complex {Hg(SCN)₂(PPh₃)_n **A**,¹² **B**,¹³ have been reported. In complex **A**, the Hg has a distorted trigonal bipyramidal geometry resulting from three bonds to Hg in a trigonal planar arrangement and consisting of Hg–P and two Hg–S bonds; two weaker and unequal Hg–N bonds complete the Hg–X bonding. In complex **B**, two independent infinite chains of thiocyanate-bridged Hg atoms are present in the crystal structure; the Hg atom is in a distorted trigonal bipyramidal environment in one chain

and similar to that reported for complex **A**, while the second chain contains Hg in a distorted tetrahedral arrangement bridged by SCN groups. The triphenylarsine $\{\text{Hg}(\text{SCN})_2(\text{AsPh}_3)\}_n$ complex,¹⁴ is isostructural with complex **A**, although the Hg–As bond is 0.10 Å longer than the Hg–P in **A**.¹²

The tricyclohexylphosphine complex $\{\text{Hg}(\text{SCN})_2(\text{Pcy}_3)\}_n$,¹⁵ has the Hg atom in a distorted trigonal pyramidal environment and is closest in structure to that found in one of the chains of **B** in $\{\text{Hg}(\text{SCN})_2(\text{PPh}_3)\}_n$.¹³ All four structures differ from the distorted octahedral geometry observed for the Hg atom in the present structure where four primary bonds and two weaker interactions are observed. This is almost certainly due to the steric size of the 1-phenyldibenzophosphole ligand as compared with the bulkier triphenylphosphine, triphenylarsine and tricyclohexylphosphine ligands which prevent an increase in the overall coordination number at the Hg atom.

Two polymorphs of the 1-phenyldibenzophosphole ligand are known, **II**,¹⁶ and **III**.¹⁷ The P–C bond lengths in the present structure **I** are 1.790(4) to 1.811(4) Å and comparable with 1.808(9) to 1.846(10) Å in **II** and 1.808(3) to 1.828(3) Å in **III**. The orientation of the phenyl ring relative to the benzophosphole ring is defined by *e.g.* the torsion angle C11–P1–C31–C36, 68.8(4)°, which is comparable with **III**, 68.3(3)° and different from the 32.0(5)° and 34.1(6)° observed in the two independent molecules of **II**.

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REFERENCES

1. G. Ferguson, P. J. Roberts, E. C. Alyea, and M. A. Khan, *Inorg. Chem.* **17** (1978) 2965–2967.
2. E. C. Alyea, G. Ferguson, J. F. Gallagher, and J. Malito, *Acta Crystallogr., Sect. C* **49** (1993) 1473–1476.
3. E. C. Alyea and S.-Q. Song, *Can. J. Chem.* **74** (1996) 2304–2320.
4. G. A. Bowmaker, H. J. Clase, N. W. Alcock, J. M. Kessler, J. H. Nelson, and J. S. Frye, *Inorg. Chim. Acta* **210** (1993) 107–124.
5. Enraf-Nonius CAD4-PC Software, Version 1.1. Enraf-Nonius, Delft, Holland, 1992.
6. E. J. Gabe, Y. Le Page, J.-P. Charland, F. L. Lee, and P. S. White, *J. Appl. Cryst.* **22** (1989) 384–387.
7. G. M. Sheldrick, SHELXL97, program for the refinement of crystal structures, University of Göttingen, Germany, 1997.
8. C. K. Johnson, ORTEP – A Fortran Thermal Ellipsoid Plot Program, Technical Report ORNL-5138, Oak Ridge National Laboratory, U.S.A., 1976.
9. A. L. Spek, PLATON Molecular Geometry Program, version: June 1998, University of Utrecht, Holland, 1998.

10. G. Ferguson, PREP8 – a WordPerfect-5.1 macro to merge and polish CIF format files from NRCVAX and SHELXL97 programs, University of Guelph, Canada, 1998.
11. F. H. Allen, O. Kennard, and R. Taylor, *Acc. Chem. Res.* **16** (1993) 146–153.
12. C. Gagnon and A. L. Beauchamp, *Acta Crystallogr., Sect. B* **35** (1979) 166–169.
13. R. C. Makhija, R. Rivest, and A. L. Beauchamp, *Can. J. Chem.* **57**, (1979) 2555–2559.
14. J. Hubert, A. L. Beauchamp, and R. Rivest, *Can. J. Chem.* **53** (1975) 3383–3387.
15. E. C. Alyea, G. Ferguson, and R. J. Restivo, *J. Chem. Soc., Dalton Trans.* (1977) 1845–1848.
16. E. C. Alyea, G. Ferguson, and J. F. Gallagher, *Acta Crystallogr., Sect. C* **48** (1992) 959–961.
17. P. R. Meehan, E. C. Alyea, and G. Ferguson, *Acta Crystallogr., Sect. C* **53** (1997) IUC9700001.

SAŽETAK

Strukturno istraživanje steričkih učinaka u fosfinskim kompleksima. Dimeri bis-{ditiocianato(1-fenildibenzofosfol)žive(II)} s izraženim Hg–N i Hg–S međudjelovanjima unutar dimera

John F. Gallagher, Elmer C. Alyea i George Ferguson

Kompleksni spoj $[\text{Hg}(\text{SCN})_2(\text{C}_6\text{H}_5)\text{P}(\text{C}_{12}\text{H}_9)]_2$ u krutom stanju postoji kao dimer-na molekula koja posjeduje simetrijsku os drugog reda s atomima žive premošćenim tiocianatnim N i S atomima. Neravnomjernost duljina valencijskih veza atoma žive Hg–N 2,771(4) Å, Hg–P 2,4084(11) Å i dvije Hg–S, 2,4565(10) Å i 2,6055(13) Å, ima za posljedicu nepravilnost trigonsko-piramidskog okruženja središnjeg atoma metala. Dimerne se molekule slabim međudjelovanjima Hg...N 3,178(5) Å i Hg...S 3,6027(14) Å udružuju oko centara inverzije u beskonačne jednodimenzijske lance. Na taj način dolazi do povećanja koordinacijskog broja atoma žive pri čemu koordinacijski polieder metala poprima oblik nepravilnog oktaedra. Veze Hg–P usmjerene su približno okomito na pravac prostiranja lanaca $\cdot\text{Hg}\cdot\text{Hg}\cdot$, dok benzofosfolne skupine, svojom međusobnom usporednošću, sprječavaju međudjelovanja fragmenata $\text{Hg}(\text{SCN})_2$ susjednih lanaca.