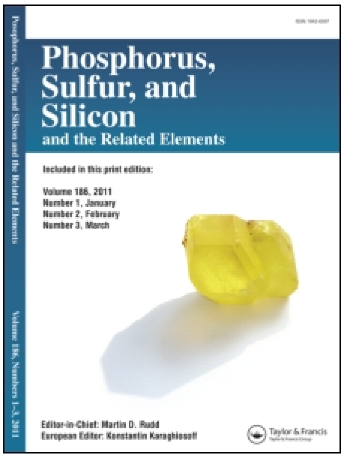

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Taş, Murat , Yağan, Mehtap , Batı, Hümeyra , Batı, Bekir and Büyükgüngör, Orhan(2010) 'Supramolecular Self-Organization in Mercury(II) Dicyclopentyldithiophosphate Polynuclear Complex', Phosphorus, Sulfur, and Silicon and the Related Elements, 185: 1, 242 — 248

To link to this Article: DOI: 10.1080/10426500902758501

URL: http://dx.doi.org/10.1080/10426500902758501

Phosphorus, Sulfur, and Silicon, 185:242–248, 2010

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500902758501

SUPRAMOLECULAR SELF-ORGANIZATION IN MERCURY(II) DICYCLOPENTYLDITHIOPHOSPHATE POLYNUCLEAR COMPLEX

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In the monomeric unit [Hg(μ-$S_2P(OCp)_2$) ($S_2P(OCp)_2$)] (Cp = cyclopentyl) moiety, the one dithiophosphate ligand acts as a chelating ligand and the other one acts as a bridging ligand by their sulfur atoms. The monomeric units arrange in order to give rise to an infinite polymeric structure along the direction of the b axis by the two-fold screw axis. The compound displays a supramolecular self-organization in the solid state through the additional Hg····S (3.516 Å) secondary interactions with formation of chain-like polymeric arrays. Also, there are some weak intra- and intermolecular hydrogen bonds between some of the hydrogen atoms of Cp and S atoms. The intermolecular hydrogen bonds form infinite polymeric chains that lie along the b axis, to each other, and along the c axis to contribute to the supramolecular association.

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Keywords Coordination polymer; dithiophosphate; mercury(II); supramolecular chemistry

INTRODUCTION

Organodithio-derivatives of phosphorus, which are known as phosphorodithioates or dithiophosphates (Scheme 1a), phosphonodithioates (Scheme 1b), and phosphinodithioates (Scheme 1c), have been widely studied since the beginning of the 20th century.[1]

Specifically, phosphorodithioates (or dithiophosphates), their corresponding acids, and metal complexes have been shown to have many commercial applications such as floatation reagents for the recovery of metals from their solutions, additives to lubricant oils, in pesticides, and in chemical warfare. More recently research has been conducted

Received 6 November 2008; accepted 11 January 2009.

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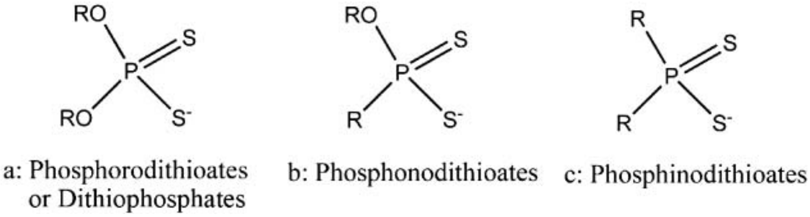

Scheme 1 Organodithio-derivatives of phosphorus.

on attempts to use these compounds to form of polymer–inorganic nanocomposites for biological and potential medicinal usage.[1–6]

In coordination chemistry, dithiophosphate ligands have versatile coordination modes towards metals. The complexes can be mono-, di-, or polynuclear, the choice being mainly determined by the ability of the ligands to perform terminal, bridging, or mixed structural functions.[6]

Also, these compounds are frequently supramolecular compounds, in which the molecular units are associated through secondary and/or dative bonds. This association is due to the tendency of the metal in the organometallic coordination center to increase its coordination number, and to the ability of the thio organophosphorus moieties to act as bridging ligands. The formation of supramolecular structures involves a process of self-organization, which goes beyond the simple packing of molecules in the crystal lattice.[7,8]

The organomercury derivatives of thio-sulfur ligands show the tendency to self-assemble in the solid state through secondary bonds and to form supramolecular structures, which can be either cyclic (or quasi-cyclic) dimers or polymeric arrays.[8,9] This feature can be seen in the case of phenylmercury diethyldithiophosphate [$PhHgS_2P(OEt)_2$] (dimer), methylmercury diphenyldithiophosphinate [$MeHgS_2PPh_2$] (dimer), phenylmercury diethyldithiophosphinate [$PhHgS_2PEt_2$] (polymer), and even methylmercury diphenylmonothiophosphinate [$MeHgS(O)PPh_2$] (polymer).[9]

In this article, we report the supramolecular structure of the dicyclopentyldithiophosphate mercury(II) complex polymer as determined by X-ray diffraction and compare with its diisopropyl analogue.[9]

RESULTS AND DISCUSSION

Spectral Data

The IR spectrum of the NH_4^+ dcpdtp was reported as 3285–3000, 2800–2750, 1421, 997, 680, 515 belonging to NH_4^+, CH_2 of cyclopentyl rings, C—O in P—O—C, P—O in P—O—C, P=S and P—S, respectively.[6]

In the IR spectrum of the synthesized complex, 2976–2896 for CH_2 of cyclopentyl rings, 1372 for C—O in P—O—C, 982 for P—O in P—O—C, 627 for P=S, 566 for P—S, 510 for Hg—S were seen. The shifts of P—S peaks and occurring of Hg—S peak indicated the sulfur atoms of the ligand bonded to metal atom.[6,7,9]

All IR data of the compound are in agreement with those of previously reported compounds. In the complex, due to the coordination of the mercury environment, the ν(P=S) bands shifted to lower and the ν(P—S) bands shifted to higher frequencies.[6,7,9]

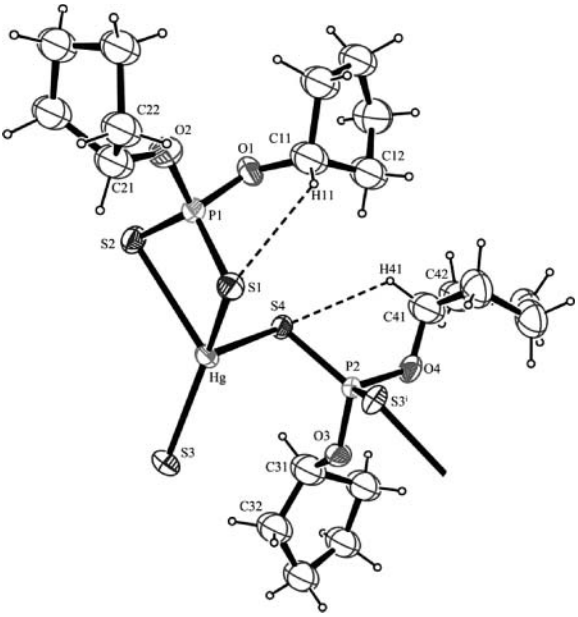

Figure 1 The monomeric unit and intramolecular hydrogen bonds of the title compound.

As expected in the UV-vis spectra of the diamagnetic complex, there is no band for the d-d transition, and the $n \rightarrow \pi^*$ transitions were seen at 260 and 272 nm, which were reported at 240 and 265 nm for NH_4^+ dcpdtp.

The Structure of the Monomeric Unit

Figure 1 is an ORTEP view (10% probability level) of the monomeric unit of the title compound, the cryptographic data are given in Table I, and selected bond lengths and angles are collected and compared with an analogue in Table II.

In the monomeric unit $[Hg(\mu\text{-}S_2P(OCp)_2)(S_2P(OCp)_2)]$ (Cp = cyclopentyl) moiety, one of the dithiophosphate ligands acts as a chelating ligand and bonds to the mercury atom by its two sulfur atoms, as the bond lengths are Hg—S1 = 2.475(4) and Hg—S2 = 2.854(5) Å. The other dithiophosphate ligand bonds to the mercury atom via one of the sulfur atoms (S4) (Hg—S4 = 2.645(3) Å), and the other sulfur atom (S3) is free to bond to the neighboring mercury atom, which is in the symmetry related (–x + 1/2, y – 1/2, –z + 1/2) monomeric unit (Hg-S3 = 2.406(5) Å) (Figure 1). So the second dithiophosphate ligand acts as a bridging ligand between the neighboring mercury atoms (Figures 1 and 2).

The monomeric units are arranged in order to give rise to an infinite polymeric structure along the direction of the b axis by the two-fold screw axis, so the monomeric unit goes at –x + 1/2, y – 1/2 + n, –z + 1/2, and x, y + n, z symmetries (n is integer) to compose a polymer (Figure 2; see also Scheme 2, which is available online in the Supplemental Materials).

The formation of the polymeric structure can be seen in the related analogue of the compound.[9] When the compared with the analogue structure of bis(isopropyl) dithiophosphatomercury(II),[9] bond lengths of the title compound are accordance in with the

Table I Crystal data and structure refinement for the compounds

Crystal Data	
Formula	C20 H36 Hg O4 P2 S4
Formula weight	731.26
Crystal system	Monoclinic
Space group	C2/c
a, b, c [Å]	34.481(2) 8.9238(5) 22.2950(14)
α, β, γ, [°]	90 123.232(4) 90
V [Å^3]	5738.3(6)
Z	8
d$_{calc}$ [g/cm^3]	1.693
F(000)	2896
Crystal Size [mm]	0.06 × 0.31 × 0.78
Data Collection	
Temperature (K)	296
Radiation [Å]	MoKα 0.71073
Absorbtion correction (μ, T$_{min}$-T$_{max}$)	Integration (5.79, 0.15–0.75)
Theta Min-Max [°]	1.8, 26.0
Dataset	–42:42; –10:11; –27:27
Tot., Uniq. Data, R$_{int}$	24806, 5614, 0.083
Observed data [I > 2.0 sigma(I)]	2521
Refinement	
N$_{ref}$, N$_{par}$	5614, 178
R, wR$_2$, S	0.0647, 0.1849, 1.01
$w = 1/[s^2(Fo^2) + (0.0865P)^2]$	where $P = (Fo^2 + 2Fc^2)/3$
Max. and Av. Shift/Error	0.09, 0.01
Min. and Max. R$_{esd}$. Dens. [e/Ang^3]	–1.01, 0.96

analog, which were reported as Hg—S1 = 2.482(2), Hg—S2 = 2.830(2), Hg—S3: 2.435(2), and Hg—S4 = 2.588(2) (Table II).

The geometry around the phosphorus atom is found as a distorted tetrahedral, as the P—S1, P—S2, P—O1, and P—O2 bond lengths are 2.012(6), 1.943(5), 1.578(14), and 1.539(18) Å, respectively. The selected geometric parameters are listed and compared with the analogue in Table II.

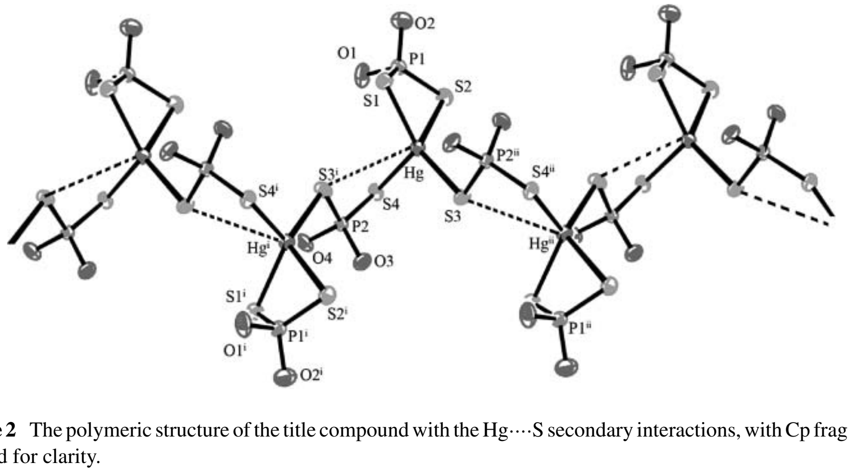

Figure 2 The polymeric structure of the title compound with the Hg···S secondary interactions, with Cp fragments omitted for clarity.

Table II Selected bond lengths and angles

	Title Compound	Related Compound*
Bond (Å)		
Hg—S1	2.475(4)	2.482(2)
Hg—S2	2.854(5)	2.830(2)
Hg—S3	2.406(5)	2.435(2)
Hg—S4	2.645(3)	2.588(2)
S1—P1	2.012(6)	2.007(3)
S2—P1	1.943(5)	1.976(3)
P2—S3^{i}	2.000(5)	2.012(3)
S4—P2	1.974(5)	1.984(3)
P1—O1	1.578(14)	1.579(6)
P1—O2	1.539(18)	1.578(6)
P2—O3	1.540(13)	1.559(5)
P2—O4	1.556(11)	1.573(6)
Angle (°)		
S1—Hg—S2	76.25(14)	77.48(7)
S1—Hg—S3	137.73(13)	132.64(7)
S1—Hg—S4	112.59(12)	115.08(7)
S2—Hg—S3	123.24(13)	90.58(7)
S2—Hg—S4	90.19(12)	121.17(8)
S3—Hg—S4	104.97(13)	108.23(7)
Hg—S1—P1	86.30(18)	79.53(7)
Hg1—S2—P1	77.6(2)	88.23(10)
Hg^{i}—S3^{i}—P2	100.6(2)	98.12(9)
Hg—S4—P2	99.27(17)	98.92(9)
S1—P1—S2	113.3(3)	113.73(13)
S1—P1—O1	112.1(6)	109.9(3)
S1—P1—O2	111.0(7)	105.7(2)
O1—P1—O2	98.8(9)	101.0(3)
S4—P2—O3	115.0(4)	105.7(2)
S4—P2—O4	111.3(5)	109.9(3)
S3^{i}—P2—S4	111.5(2)	111.7(2)
O3—P2—O4	102.5(6)	103.8(3)
S3^{i}—P2—O3	104.3(5)	105.6(2)
S3^{i}—P2—O4	111.7(4)	111.7(2)

Hydrogen Bond Geometry				
D—H····A	D—H (Å)	H····A (Å)	D·····A (Å)	D—H····A°
C11—H11····S1	0.9800	2.6500	3.27(3)	122.00
C41—H41····S4	0.9800	2.6400	3.24(3)	120.00
C42—H42a····S4^{ii}	0.97	2.96	3.89(3)	160.7

^{i}–x + 1/2, y – 1/2, –z + 1/2

^{ii}–x + 1/2, –y – 1/2, –z

*Bis(isopropyl)dithiophosphatomercury(II).[9]

Supramolecular Association

Intermolecular forces leading to supramolecular structures can be hydrogen bonds, donor–acceptor (Lewis acid–base type) interactions, or ionic interactions.[8]

The term secondary bond is described as "weak bonds between main group and metal atoms, longer than single covalent bonds, but shorter than van der Waals interatomic distances."[7,8] It is obvious from this definition that semi-bonding interactions can be identified only by crystal structure determinations with the aid of diffraction methods. Usually these bonds are not strong enough to survive in solution, but they can have spectacular effects in the building of a crystal structure.[8]

The title compound displays a supramolecular self-organization in the solid state through the additional Hg····S (3.517(4) Å) secondary interactions, based upon Hg····S3^{i} (i: –x + 1/2, y – 1/2+n, –z + 1/2 (n is integer) secondary interactions, with formation of chain-like polymeric arrays (Figure 2).[9]

If the secondary bonds are considered, the coordination number around the mercury atoms is five. The similar supramolecular association was reported in the analogue, as the additional secondary bond length was 3.413(2) Å (Table II).[9]

In addition to the interaction, there were found some weak intramolecular and intermolecular hydrogen bonds in the title compound. In the title compound, C11 and C41 atoms of Cp fragments act as hydrogen bond donors to S1 and S4 atoms of dithiophosphate to give intramolecular hydrogen bonds via its hydrogen atoms (Figure 1, Table II). Also, there is a weak intermolecular hydrogen bond between the H42a atom of C42 atom of a Cp part and S4 atom at –x + 1/2, –y – 1/2, –z. These hydrogen bonds form infinite polymeric chains that lie along the b axis and to each other along the c axis (Figure 3, which is available online in the Supplemental Materials).

EXPERIMENTAL

Materials and Measurements

Synthesis of the ligand ammonium dicyclopentyldithiophosphate (NH_4^+ dcpdtp) was described earlier.[6] FT-IR spectra (4000–200 cm^{-1}) were recorded on a Matson-1000 FT-IR spectrophotometer with samples prepared as KBr pellets. Magnetic susceptibilities were measured using a Sherwood scientific MX1 model Gouy magnetic balance at room temperature. UV-vis spectra were recorded with a Unicam UV2 UV-vis spectrometer in chloroform solutions. Elemental analysis for C, H, and S were performed using a Carlo Erba 1106 microanalyzer.

Crystallographic Analyses

The crystal data were collected using ω–2θ scan techniques on a Stoe IPDS-2 diffractometer with graphite-filtered Mo K_α radiation ($\lambda = 0.71073$ Å). Software program(s) used were as follows: for data collection and cell refinement: X-Area;[10] for data reduction: X-Red32[10]; to solve structure: Sir2004[11]; for refinement structure: ShelXL97[12]; for molecular graphics: OrtepIII[13]; to prepare material for publication: WinGX.[14] All H atoms were refined using a riding model.

Preparation of the Complex

While the analogues of the title compounds were synthesized by the reaction of dialkyldithiophosphoric acid with methyl or phenyl mercury acetate,[7,9] the complex was prepared by reacting aqueous solution of $HgCl_2$ (0.01 mol, 2.72 g) and the NH_4^+ dcpdtp (0.01 mol, 2.83 g).[6] The resulting white precipitate was filtered off, washed with water, and dried in air. The complex was recrystallized from an acetone-ethanol mixture (1:1). Yield 75%. $C_{20}H_{36}O_4P_2S_4Hg$: calcd. C, 32.85, H 4.96, S 17.54; found: C 32.90, H 5.34, S 17.12.

UV/vis ($CHCl_3$): $\lambda_{max} = 260, 272$ nm. FT-IR (KBr): $v = 2976–2896$ (CH_2), 1372 (C—O in P—O—C), 982 (P—O in P—O—C), 627 (P=S), 566 (P—S), 510 (Hg—S) cm^{-1}.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as the supplementary publication No. CCDC 679555. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

REFERENCES

1. I. P. Gray, H. L. Milton, A. M. Z. Slawin, and J. D. Woollins, *Dalton Trans.*, 3450 (2003).
2. Z. Li, J. Li, and S. Du, *J. Mol. Struct.*, **783,** 116 (2006).
3. F. Jian, H. Xiao, Y. Li, and K. Jiao, *J. Chem. Crystallogr.*, **33**(9)**,** 705 (2003).
4. W. Lei, Q. Hao, L. Lu, X. Yang, and X. Wang, *J. Chem. Crystallogr.*, **34**(6)**,** 387 (2004).
5. A. V. Ivanov, W. Forsling, M. Kritikos, O. N. Anzutkin, A. C. Larson, F. A. Zhukov, and Z. F. Yusupov, *Doklady Chem.*, **375**(1–3)**,** 236 (2000).
6. M. Taş, M. Yağan, H. Batı, B. Batı, and O. Büyükgüngör, *Indian J. Chem. Sec. A*, **47,** 37 (2008).
7. J. S. Casas, A. Castifieiras, I. Haiduc, A. Sanchez, J. Sordo, and E. M. Vazquez-Lopez, *Polyhedron*, **16**(5)**,** 781 (1997).
8. I. Haiduc, *Coord. Chem. Rev.*, **158,** 325 (1997).
9. J. S. Casas, E. E. Castellano, J. Ellena, I. Haiduc, A. Sanchez, and J. Sordo, *J. Chem. Crystallogr.*, **29**(7)**,** 831 (1999).
10. Stoe & Cie, X-Area (Version 1.18) and X-Red32 (Version 1.04), Stoe & Cie, Darmstadt, Germany (2002).
11. M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, and R. Spagna, *J. Appl. Crystallogr.*, **38,** 381 (2005).
12. M. Sheldrick, *SHELXL-97*, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany (1997).
13. C. K. Johnson and M. N. Burnett, *ORTEP-III (version 1.0.2)*, Rep. ORNL-6895, Oak Ridge National Laboratory, Oak Ridge, TN, USA (1996); Windows version: L. J. Farrugia, University of Glasgow, Glasgow, Scotland, U.K. (1997).
14. L. J. Farrugia, *J. Appl. Crystallogr.*, **32,** 837 (1999).