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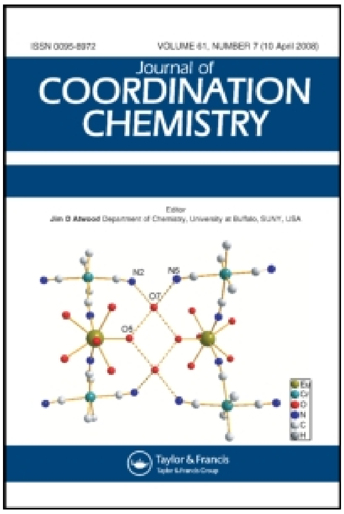

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The crystal structure of $(Ph_4P)_2[Hg_2(SPh)_6]$: Synthesis, characterization and structure supramolecularity

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X-ray analysis at ambient temperature has established the crystal structure of the monoclinic $(Ph_4P)_2[Hg_2(SPh)_6]$. It contains the bitetrahedral $[(PhS)_2Hg(\mu\text{-}SPh)_2Hg(SPh)_2]^{2-}$ anionic complex, in contrast to most mercury thiolate complexes, which contain the distorted-trigonal $[Hg(SPh)_3]^-$ species. The crystal supramolecularity was analysed in the context of the issue of Ph $\cdots$ Ph (phenyl $\cdots$ phenyl) supramolecular synthons and the relative energies of intraionic and interionic interactions. The crystal lattice is dominated by the Ph $\cdots$ Ph supramolecular synthons, containing parallel chains of Ph_4P^+ ions and stacks of $[Hg_2(SPh)_6]^{2-}$ ions. Each chain of cations contains alternating 6PE (sixfold phenyl embrace) and P4PE (parallel fourfold phenyl embrace) motifs, with a repeat distance. The canting of $[Hg_2(SPh)_6]^{2-}$ ions relative to their stack axis is correlated with the repeat length of the cation chains, with EF (edge-to-face) and OFF (offset-face-to-face) Ph $\cdots$ Ph interactions between Ph_4P^+ and $[Hg_2(SPh)_6]^{2-}$. The strength and directionality of these supramolecular synthons are evident in the calculated through-space energies ($-16.7\,kJ\,mol^{-1}$ per two Ph_4P^+ ions engaged in a P4PE and $-42.3\,kJ\,mol^{-1}$ per two Ph_4P^+ ions engaged in a 6PE).

Keywords: Mercury thiolates; Crystal structure; Supramolecular motifs; Phenyl $\cdots$ phenyl interactions; Phenyl embraces

1. Introduction

The crystal lattices of compounds containing phenyl groups are known to be dominated by supramolecular motifs that result from the attractive Ph $\cdots$ Ph intermolecular interactions [1]. Supramolecular motifs in the form of multiple phenyl embraces were characterized in crystal structures containing the Ph_4P^+ ion and relatives [2–5]. Recently, similar supramolecular motifs were recognized in the crystal structures of metal complexes containing aryl groups such as PPh_3 [6], 2,2′-bypyridine [7], 1,10-phenanthroline [8] and the crystal structures of sulphanes containing XPh_3 groups [9].

Mercury thiolate complexes are of interest [10, 11]; in biological systems, they show considerable variation in their coordination geometries, from four-coordinate

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tetrahedral to linear two-coordinate and trigonal three-coordinate [12, 13]. Homoliptic thiolato complexes of mercury have been investigated by X-ray crystallography, and most of these compounds are mononuclear $[Hg(SR)_3]^-$ with trigonal-planar or distorted trigonal-planar geometry [14–18]. The two exceptions to date are the complexes $(Et_4N)_2[Hg_2(SMe)_6]$ and $(Me_4N)_2[Hg_2(SPh)_6]$, which are dinuclear doubly bridging structures [19, 20]. On the contrary, Zn(II) and Cd(II) thiolate complexes of 1 : 3 molar ratio were found to prefer the dinuclear structure [21–23]. The size of the counter-cation may affect the formed geometries, where the larger cations contain the smaller anions, with the crystal influence completely ignored in these arylated compounds. However, this proved to be incorrect in the case of the Ph_4P^+ complex, for which the preparation, crystal structure, and crystal packing analysis are reported in this work.

2. Experimental

2.1. *Materials*

All materials were purchased from Aldrich and were used as received. Elemental analyses for C, H and S were carried out on a Perkin-Elmer % Analyser 2400 series (II) microanalyser. X-ray powder diffraction measurements were carried out on a Siemens D500 diffractometer setting with an unmonochromated CuK_α source radiation ($\lambda = 1.5418$ Å).

2.2. *Synthesis and crystallization*

The reactions were carried out under an atmosphere of nitrogen utilizing Schlenk techniques.

2.3. *Synthesis of $(Ph_4P)_2[Hg_2(SPh)_6]$*

A solution of $HgCl_2$ (3.0 g; 11 mmol) in 10 mL of MeOH was added to a well-stirred solution of PhSH (3.1 mL; 32.8 mmol) and Et_3N (4.7 mL; 32.8 mmol) in 20 mL of MeOH. To the resulting clear solution, Ph_4PBr (5.33 g; 12.7 mmol) in 10 mL of MeOH was added in portions, forming small amounts of white solid. The mixture was stirred until all the solid dissolved (*c.* 5 min). Upon standing undisturbed at RT, white solid was obtained, filtered, washed with small amounts of cold MeOH and dried *in vacuo*. The product was recrystallized from warm CH_3CN to give colourless crystals, one of which was used to collect the unit cell crystallographic data. Yield: 87%. Anal. Calcd for $Hg_2S_6P_2C_{84}H_{70}$: C, 58.15; H, 4.07; S, 11.09. Found: C, 57.96; H, 3.98; S, 11.11.

Several synthetic variants for the preparation of the salt are given below, and detailed experimental procedures are provided as supplementary material.

A solution of $HgCl_2$ (33 mmol) in 30 mL of MeOH was added to a stirred mixture of PhSH (91.9 mmol) and Et_3N (91.1 mmol) in 40 mL of MeOH. The resulting colourless solution was then treated with a solution of Ph_4PBr (38.2 mmol) in 20 mL of MeOH. After stirring for 5 min, the mixture was filtered, and the mother liquor was then allowed to stand undisturbed whereupon a white crystalline solid precipitated. The product was recrystallized from hot CH_3CN.

A stirred mixture of PhSH (5.3 mmol) and Et_3N (5.3 mmol) in 20 mL of CH_3CN was treated with solid Ph_4PBr (5.3 mmol) to yield a colourless solution. $HgCl_2$ (2.2 mmol) in 10 mL of EtOH was added in one portion, and the resulting mixture was allowed to stand undisturbed and then stored at $< 0°C$, whereupon colourless crystals were obtained, filtered, washed with cold CH_3CN, and dried *in vacuo*.

A suspension of $HgCl_2$ (0.92 mmol) in 90 mL of acetone was treated with a mixture of PhSH (2.1 mmol) and Et_3N (2.1 mmol) in 10 mL of acetone with stirring. To the resulting mixture, solid Ph_4PBr (1.0 mmol) was added with stirring until the entire solid dissolved. The clear colourless solution was kept undisturbed at RT for a few hours. The volume was then reduced to half under vacuum and left to stand overnight. The product formed was then collected, washed with acetone and dried *in vacuo* (RT 25°C).

It should be mentioned that powder diffraction measurements were performed for all the samples of $(Ph_4P)_2[Hg_2(SPh)_6]$, to confirm the bulk homogeneity of each crystallized sample. Moreover, the experimental powder diffraction measurements were compared with the calculated measurement from the structure determined crystallographically. These patterns were consistent, confirming the crystal form of the bulk for these solids.

2.4. *Crystal structure determination: solution and refinement of the structure*

Reflection data were measured with an Enraf-Nonius CAD-4 diffractometer in $\theta/2\theta$ scan mode using graphite-monochromated molybdenum radiation ($\lambda = 0.71017$ Å). Data were corrected for absorption [24]. The positions of all atoms in the asymmetric unit were determined by direct phasing (SIR92) [25] with hydrogen atoms included in calculated positions. Phenyl rings were modelled as rigid groups. One rigid group represented the four phenyl rings of the cation, while another was used for the anion rings. Each was allowed to refine, maintaining mm^2 symmetry. The thermal motion of each rigid group, along with its calculated hydrogen atoms, was refined as a TLX group (where T is the translation tensor, L is the libration tensor and X origin of libration). For the phenylthiolate groups, the S atom was included in the group thermal. The remaining atoms were refined anisotropically. Full details of the refinement [26] can be found in the supplementary information. Crystallographic details and crystal data obtained are in the supplementary materials, and selected bond lengths (Å) and angles (°) for $(Ph_4P)_2[Hg_2(SPh)_6]$ are listed in table 1.

2.5. *Crystal/Refinement data*

$(Ph_4P)_2[Hg_2(SPh)_6]$, $Hg_2S_6P_2C_{84}H_{70}$, $M_r = 1735.0$, monoclinic, space group $P2_1/c$, $a = 13.602(5)$, $b = 13.529(3)$, $c = 20.721(7)$ Å, $\beta = 106.13(2)$, $V = 3663(2)$ Å^3, $T = 21°C$, $Z = 2$, $D_{calc} = 1.57\ g\ cm^{-3}$, λ (Mo–Kα) $= 0.71073$ Å, $\mu = 4.434\ cm^{-1}$, $R = 0.032$, $wR = 0.036$.

Table 1. Experimental dimensions (Å, °) for the Hg_2S_6 cores of the $[Hg_2(SPh)_6]^{2-}$, in comparison with the core dimensions for similar compounds.

Parameter	$[PPh_4]_2[Hg_2(SPh)_6]$	$[NEt_4]_2[Hg_2(SPh)_6]^a$	$[NEt_4]_2[Hg_2(SMe)_6]^b$
Hg–^{t}S	2.454(2), 2.463(2)	2.442(2), 2.426(2) 2.439(2), 2.440(2)	2.473(2), 2.438(2)
Hg–^{b}S	2.660(2), 2.650(2)	2.645(2), 2.707(2) 2.695(2), 2.696(2)	2.629(2), 2.706(2)
^{t}S–Hg–^{t}S	116.2(1)	89.9(1), 89.1(1)	94.27(5)
^{b}S–Hg–^{b}S	89.4(1)	132.4(1),	121.87(7)
Hg–^{b}S–Hg	90.6(1)	91.2(1), 89.8(1)	85.73(5)
^{t}S–Hg–^{b}S	121.2(1), 100.8(1) 107.3(1), 119.5(1)	100.9(1), 103.8(1), 114.4(1), 109.1(1) 102.0(1), 106(1), 108.6(1), 107.8(1)	106.98(6), 116.09(7) 104.94(6), 108.68(7)

Note: ^{b}S and ^{t}S refer to the bridging and terminal thiolate ligands, respectively.
[a] From [19].
[b] From [20].

2.6. *Calculation of interionic energies*

The interionic potential for atoms with charges q_i, q_j separated by d_{ij} is given by equations (1) and (2) [1]

$$E_{ij} = e^a_{ij}[(d_{ij}/d^a_{ij})^{-12} - 2(d_{ij}/d^a_{ij})^{-6} = (q_i q_j)/(\varepsilon d_{ij}) \tag{1}$$

$$d^a_{ij} = r^a_l + r^a_j; \quad e^a_{ij} = (e^a_i e^a_j)^{0.5} \tag{2}$$

The dielectric permitivity, ε, was set to be distance dependent, as $\varepsilon = 2d_{ij}$. d^a_{ij} is the most negative (attractive) with e^a_{ij} magnitude. The relevant van der Waals parameters r^a (Å) and e^a_I (kJ mol^{-1}), respectively, were: H 1.62, 0.02; C 1.95, 0.08; P 2.10, 0.20; S 2.00, 0.20. The partial charges used for the coulombic energies were: $H^{+0.15}$, $C^{-0.1}$, $P^{+0.4}$ in Ph_4P^+; $Hg^{+0.4}$, $^{t}S^{-0.3}$, $^{b}S^{-0.2}$, $C^{0.0}$ (bonded to S), $C^{-0.12}$, $H^{+0.08}$ (in thiolates): assignment of these charges was informed by density functional calculations with Mulliken analysis, and by concepts of chemical periodicity. Tests showed that the coulombic energies in this compound are not strongly dependent on atom partial charges.

3. Results and discussion

3.1. *Molecular structure*

The asymmetric unit in the crystal structure of the title compound consists of one unit of $[Hg(SPh)_3]^-$ and one Ph_4P^+ ion. The anion is shown in figure 1 as centrosymmetric $[(PhS)_2Hg(\mu\text{-}SPh)_2Hg(SPh)_2]^{2-}$, with approximately tetrahedral coordination stereochemistry at Hg. It has an almost square core of Hg_2S_2 with angles very close to 90°. The S atoms of the bridging and terminal ligands are designated ^{b}S and ^{t}S, respectively, hereafter. The Hg–^{b}S bond distances are 2.611 Å, while the Hg–^{t}S bond distances are 2.477 and 2.478 Å. The core geometry parameters compared with other mercury thiolate compounds are given in table 1. These parameters suggest that the geometry around the metal is distorted from ideal tetrahedral geometry.

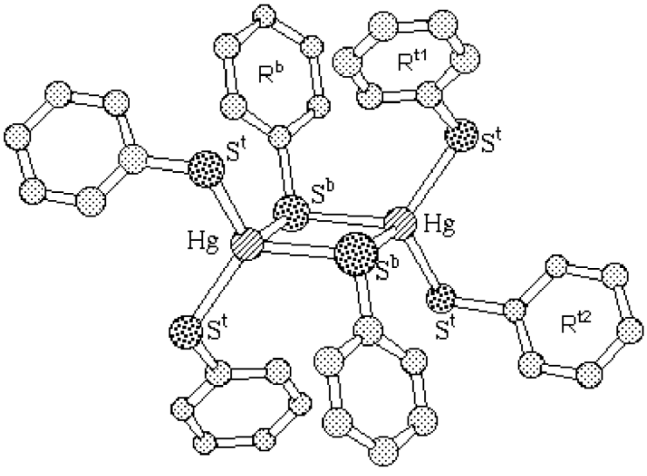

Figure 1. Molecular geometry of the $Hg_2(SPh)_6^{2-}$ anion crystallized with Ph_4P^+.

3.2. *Crystal supramolecularity*

3.2.1. Crystal packing. The overall crystal packing in the crystal structure shows stacks of anions with the cations zigzagging in the gaps between the anionic stacks forming a structure that can be described as columnar along the *a* axis, as illustrated in figure 2. The structure of $(Ph_4P)_2[Hg_2(SPh)_6]$ ($P2_1/c$) has stacks of anions along the *a* axis, with the centroids of the anions at $x = 0, 1, \ldots$, separated by $a = 12.36$ Å. Parallel to *a*, there are four stacks of anions along the *a* axis with a centroid separation of 13.6 Å from the central anion. Thus, each anion is surrounded by six anions with centroids separated by 12.36 Å (×2) and 13.6 Å (×4). The cationic molecules are arranged in four zigzags surrounding each stack of anions. Each anion is surrounded by eight cations, with anion-centroid to cation-P distances of 8.98 and 12.93 Å in the $z = 1/2$ region, 7.58 and 12.12 Å in the $y = 1/2$ region. The overall arrangement of anion and cation stacks occurs in an approximately fourfold array: four stacks of anions surround each chain of cations, and four chains of cations surround each stack of anions.

The Ph_4P^+ zigzag chains consist of two different phenyl embraces (figure 3), since each cation interacts with its two neighbours through one 6PE and one P4PE; comprising six and four phenyl rings involved in concerted $Ph \cdots Ph$ interactions, respectively. The $P \cdots P$ distance in the SPE is 6.25 Å, whereas the $P \cdots P$ distance in the PQPE is 8.02 Å.

3.2.2. Crystal packing energies. Having described the geometrical aspects of the packing, now the analysis will turn to the relevant crystal packing energies and interionic energies, which determine the crystal structures. The relationship between interionic interaction energy and distance is not simple, because the net van der Waals energies are generally a compromise between a smaller number of weakly repulsive shorter contacts and a larger number of weak dispersion attractions, and the attractive and repulsive electrostatic energies diminish slowly with distance [1]. The interionic energies

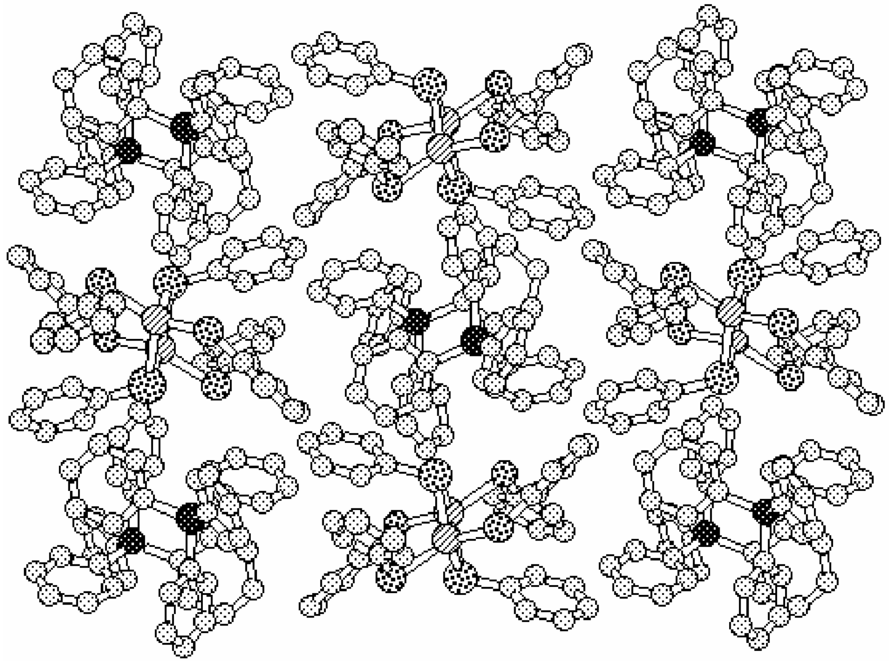

Figure 2. Representation of the crystal packing, projected along the *a*-axis.

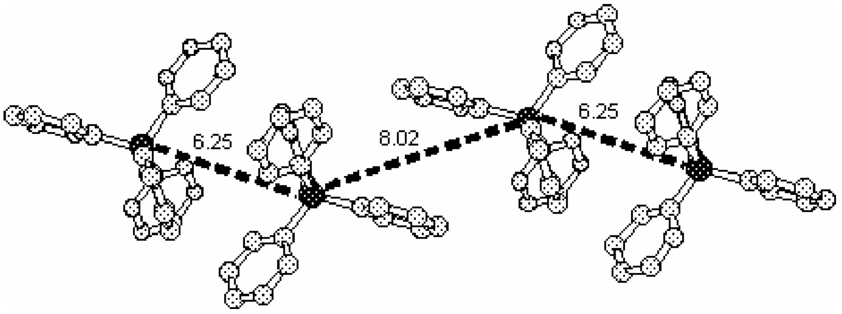

Figure 3. Zigzag chains of Ph_4P^+ cations showing alternating 6PE (P$\cdots$P distance 6.25 Å) and P4PE (P$\cdots$P distance is 8.02 Å); (P$\cdots$P$\cdots$P 144.5°).

are calculated using the summed atom–atom approximation and the vdW and Coulombic potentials described in the experimental section.

Table 2 presents calculated energies in the crystal structure. The interionic energies between $[Hg_2(SPh)_6]^{2-}$ ions along the stack (table 2A) and between stacks (table 2B) are very small and not repulsive. The embracing Ph_4P^+ cations are attractive as usual, with energies of -42.3 (6PE) and -16.7 (P4PE), (table 2C). Energies between contiguous Ph_4P^+ and $[Hg_2(SPh)_6]^{2-}$ ions (figure 4) are slightly more attractive, up to $-64.8\,\mathrm{kJ\,mol^{-1}}$ (table 2D). It is notable that the interionic attractions for $Ph_4P^+\cdots[Hg_2(SPh)_6]^{2-}$ are not very much larger than those for $Ph_4P^+\cdots Ph_4P^+$. This occurs because the net charges on the ions are widely dispersed, and the coulombic components of interionic energy are overshadowed by the van der Waals energies.

Table 2. Calculated interionic energies (kJ mol^{-1}) for $(Ph_4P)_2[Hg_2(SPh)_6]$.

	Interaction	Energy (kJ mol^{-1})
A	Between $[Hg_2(SPh)_6]^{2-}$ ions along the stack (per $[Hg_2(SPh)_6]^{2-}$ pair)	0.8
B	Between $[Hg_2(SPh)_6]^{2-}$ ions in adjacent stacks (per $[Hg_2(SPh)_6]^{2-}$ pair)	1.6 (12.4 Å)
		1.6 (12.4 Å) (identical)
C	Between Ph_4P^+ along cation chain (per Ph_4P^+ pair)	−42.3 for the 6PE (6.25 Å)
		−16.7 for the P4PE (8.02 Å)
D	Between anions and cations (per $[Hg_2(SPh)_6]^{2-}/Ph_4P^+$ unit)	−64.8 (7.58 Å)
		−56.9 (8.18 Å)
		−64.8 (8.97 Å)
		−22.6 (11.72 Å)
		−18.4 (12.12 Å)
		−17.6 (12.84 Å)
		−18.0 (12.93 Å)

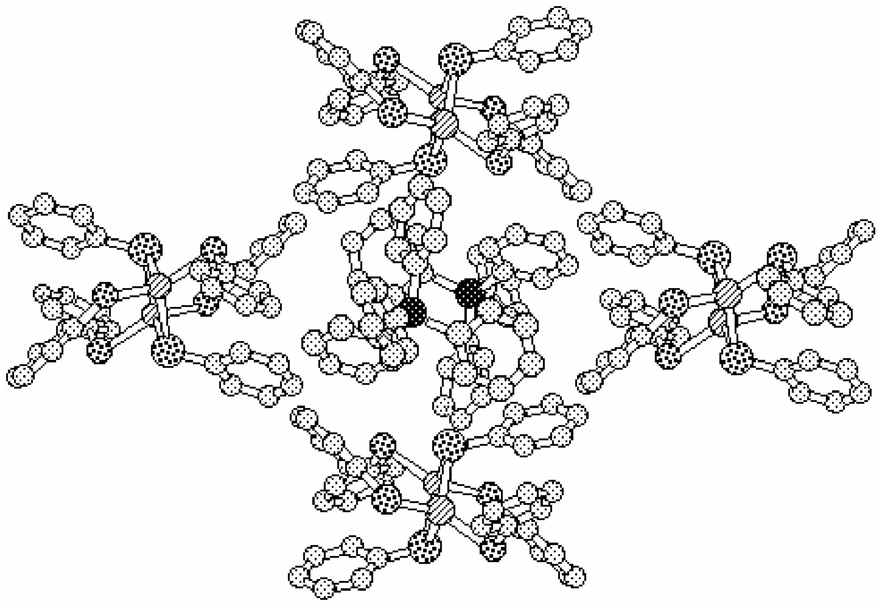

Figure 4. Single chain of cations (middle) surrounded by four stacks of anions in the structure, showing the unique phenyl rings orientation in the EF and OFF Ph ··· Ph interactions between anions.

Estimates of the lattice energy can be made by summation of components. As described in the crystal packing, the immediate surroundings of each $[Hg_2(SPh)_6]^{2-}$ are 2 $[Hg_2(SPh)_6]^{2-}$ along the stack, contributing negligible energy, and 14 Ph_4P^+ at centroid ··· P distances ranging from 5.6 to 12.9 Å (table 2D) contributing a total of −526.3 kJ mol^{-1}. The $Ph_4P^+ \cdots Ph_4P^+$ energies along the chains are −59.0 kJ mol^{-1} per repeating unit.

3.3. *Intra-$[Hg_2(SPh)_6]^{2-}$ energies*

The intraionic interaction energy for the molecular structure of the anion in the crystal structure (figure 1) was estimated to be −28.0 kJ mol^{-1}. These intraionic interactions are evident by the orientation of the phenyl rings, $R^b \cdots R^{t1}$, $R^b \cdots {}^aR^{t2}$ and the symmetry-related equivalents (by inversion operator; ${}^aR^b \cdots {}^aR^{t1}$ and ${}^aR^b \cdots R^{t2}$), where the interacting phenyl rings are oriented in an edge-to-face type arrangement (EF). This amount of energy for the intraionic interactions is an order of magnitude less than the interionic energy described for the crystal packing, clearly showing that the molecular geometry might be a consequence of crystal packing. This result is in good agreement with similar systems [21].

4. Conclusions

The crystal structure of the bitetrahedral anion $[Hg_2(SPh)_6]^{2-}$ has been characterized as the Ph_4P^+ salt. The crystal packing analysis shows that the packing is tight and phenyl rings have directed orientations allowing many EF and OFF interactions between Ph_4P^+ and $[Hg_2\,(SPh)_6]^{2-}$ leading to a tight crystal packing. The cation chains show a classical supramolecular motif of alternating 6PE and P4PE that are favourable energetically. The calculated interionic crystal packing energies are dominant, greater than the energies involved in the intraionic energies. These interactions that are favourable energetically would therefore add stability to the lattices of such compounds. This is evident in the isostructurality in different series of compounds such as the series $(Ph_4P)_2[M_2(SPh)_6]$; M = Cd, Zn and Mn [22,27].

The involvement of the phenyl rings of the anionic species with the cationic phenyl rings in these compounds with highly energetic interionic interactions is therefore a reason for these ring orientations to be determined by these interactions in the crystal structures in order to accommodate as many interactions as possible. Therefore, the distortion of M–S_4 core from T_d geometry [28–31] could be as a result of the crystal packing forces, especially Ph $\cdots$ Ph interionic interactions in these compounds. Otherwise, the suggested conformationally preferable interactions between the phenyl ortho protons and the thiolato sulphur atoms and/or the electronic influences within the anionic complexes represented in the π interactions of the sulphur $p\pi$ and the phenyl ring π orbitals as a reason for the distortion [28–31] would contribute at least about the same amount of stabilization energy as the Ph $\cdots$ Ph interactions. Thus, the Ph $\cdots$ Ph interactions would act as a molecular structure determination tool in compounds with highly phenylated surfaces.

Supplementary material available

The supplementary crystallographic data (CIF file) for the structure in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 251426. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Crystallographic data, in CIF format, are available for the crystal structure of the title compound. Alternative synthetic routes for the title compound are also available.

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