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Structure of inorganic–organic hybrid polymer assembled by mercury(II) iodide and sulfur-rich compound

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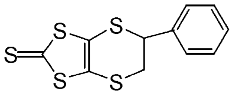
Abstract

The metal complex, $[Hg_2I_4(PEDT)]_\infty$ (**1**), PEDT = 4,5-(phenyl-ethylenedithio)-1,3-dithiole-2-thione, has been synthesized and characterized by single crystal X-ray diffraction. It is found to be an unusual organic–inorganic hybrid structure. The inorganic layer is composed of chains of Hg with bridging I, in one case doubly bridged and in the other singly, interconnected by further bridging I to complete the two dimensional connectivity. The organic layers contain pairs of centrosymmetrically related, and therefore head to tail, face to face molecules. Each molecule of such a pair participates in the formation of short S···S contacts with a molecule of a centrosymmetrically related neighboring molecule pair thus creating chains of molecules. The connectivity within the organic layer is completed by C–H···π contacts between the chains. Connectivity between the organic and inorganic layers is achieved by participation of the thione S in the coordination of one type of Hg.

Keywords: Mercury complexes; Molecular assembling; Dithiole; Thione; Crystal structure

1. Introduction

Sulfur-rich organic donor–acceptor compounds or radical salts are widely used as bricks in the crystal architecture of molecular materials. The S···S interaction or contact in these compounds is one of the most important contributors to their unique electronic properties [1,2]. It has been understood that intermolecular S···S interaction providing the pass way (band structure of the energy levels) of the electrons in the molecular conductor. Up to now great efforts have been made to design the molecular packing and to strengthen the S···S contacts by modifying the structure of the organic molecule itself, by changing the size of the counter ion and even the co-crystallized solvent molecules [3,4]. We are engaged in the synthesis of donor or acceptor compounds those are assembled by both metal coordination bonds and weak molecular interactions. In this context a series of polymeric complexes of 4,5-ethylenedithio-1,3-dithiole-2-thione (EDT = $C_5H_4S_5$) have been reported [5–8]. The metallic component in these complexes has been a metal ion (Ag^+) [5,6], a binuclear bridge (Hg_2Cl_4) [7] or a tetra-nuclear cluster (Cu_4I_4) [8]. In this paper a unique organic–inorganic hybrid compound is reported with the formula: $[Hg_2I_4(PEDT)]_\infty$ (**1**), PEDT = $C_{11}H_8S_5$, 4,5-(phenyl-ethylenedithio)-1,3-dithiole-2-thione, a derivative of EDT



PEDT=$C_{11}H_8S_5$

2. Experimental

Elemental analyses of C, H and N were performed using an EA1110 elemental analyzer. The IR spectra were recorded as KBr discs on a Nicolet Magma 550 FT-IR spectrometer. Electronic spectra are measured on a Shimadzu UV-240 spectrophotometer. The ligand, 4,5-(phenyl-ethylenedithio)-1,3-dithiole-2-thione (PEDT),

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was prepared according to the literature [9]. Acetonitrile and dichloromethane were dried by a standard method and distilled before use. The other chemicals were used as analytical pure reagents.

Synthesis of $[Hg_2I_4(PEDT)]_\infty$ (**1**). To an acetonitrile solution (5.0 ml) of HgI_2 (91 mg, 0.2 mmol) was added the ligand PEDT (30 mg, 0.1 mmol) in CH_2Cl_2 (5.0 ml). The mixed solution was stirred for 30 min at room temperature and then was filtered. The orange filtrate was evaporated and red precipitate obtained, which was washed with acetonitrile and finally dried in vacuum (yield 56%). Single crystals of **1** suitable for X-ray diffraction analysis were obtained by slow evaporation of the reaction filtrate. Elemental analysis calcd (%) for $C_{11}H_8S_5$ Hg_2I_4: C, 10.20; H, 0.77; found (%): C, 10.23; H, 0.87. IR (KBr, cm^{-1}): ν(C=C) 1447 ms, ν(C=S) 1011 vs, ν(Ph–H) 714, 694 ms. UV–vis (nm): L band 330, 410, CT band 430 sh.

Synthesis of $[Hg_2Cl_4(PEDT)_2]$ (**2**). To an acetonitrile solution (5.0 ml) of $HgCl_2$ (13.5 mg, 0.1 mmol) was added the ligand PEDT (15 mg, 0.05 mmol) in CH_2Cl_2 (5.0 ml). The mixed solution was stirred for 30 min at room temperature and then the orange filtrate was slowly evaporated. A red product was obtained which was washed with acetonitrile, and finally dried in vacuum (yield 60%). Elemental analysis calcd (%) for $C_{22}H_{16}S_{10}$ Hg_2Cl_4: C, 21.95; H, 1.52; found (%): C, 22.04; H, 1.45. IR (KBr, cm^{-1}): ν(C=C) 1451 ms, ν(C=S) 1022 vs, ν(Ph–H) 714, 694 ms. UV–vis (nm): L band 330, 410, CT band 430 sh.

X-ray crystallography. A crystal with dimension of $0.4 \times 0.3 \times 0.18$ mm^3 was mounted on a Siemens P4 diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). A total of 4619 reflections were collected using the omega scan technique [3952 unique, 2430 with $I > 2\sigma(I)$]. A psi-scan absorption correction was applied. The structure was solved by direct methods and refined using SHELXL-97 by full matrix least-squares. Final $R = 0.057$, $Rw = 0.130$, $[I > 2.00\sigma(I)]$ and $S = 0.90$. Other crystallographic data for $[Hg_2I_4(PEDT)]_\infty$: $C_{11}H_8Hg_2I_4S_5$, $M = 1209.25$, monoclinic, space group $P2_1/n$, $a = 16.388(3)$ Å, $b = 7.145(2)$ Å, $c = 19.161(4)$ Å, $\beta = 93.95(1)°$, $U = 2238.3(9)$ Å^3, $Z = 4$, D(calc.) = 3.589 g cm^{-3}, $T = 295(2)$ K, $F(000) = 2104$. The data of the maximal and minimal residual electron density are 1.967 and −2.187, respectively. Selected bond lengths and angles for complex **1** are listed in Table 1.

The asymmetric unit and atom labelling scheme are shown in Fig. 1. Atom pairs C(4A)/C(4B) and C(5A)/C(5B) are present due to disorder such that the ethylene bond is disordered over two orientations as C4A–C5A and C4B–C5B with occupancies of 0.61(2) and 0.39(2) for the major (A) and minor (B), (B not present in the figure) components, respectively.

Table 1
Selected bond lengths (Å) and angles (°) for complex **1**

Hg(1)–S(1)	2.567(4)	Hg(2)–I(1)	3.2836(18)
Hg(1)–I(1)	2.7003(13)	Hg(2)–I(3)	2.6466(16)
Hg(1)–I(2)	2.8335(16)	Hg(2)–I(3^{ii})	3.1557(16)
Hg(1)–I(2^{i})	2.8048(17)	Hg(2)–I(4)	2.5995(18)
Hg(2)–I(4^{iii})	3.5377(19)	S(1)–C(1)	1.699(17)
S(1)–Hg(1)–I(1)	113.10(11)	I(3)–Hg(2)–I(1)	96.25(5)
S(1)–Hg(1)–I(2)	105.06(11)	I(4)–Hg(2)–I(1)	91.86(5)
S(1)–Hg(1)–I(2^{i})	104.00(12)	I(3)–Hg(2)–I(1^{ii})	92.13(4)
I(1)–Hg(1)–I(2)	109.43(5)	I(4)–Hg(2)–I(3)	159.76(6)
I(1)–Hg(1)–I(2^{i})	115.71(5)	I(3)–Hg(2)–I(3^{ii})	93.03(4)
I(2)–Hg(1)–I(2^{i})	108.89(4)	I(4)–Hg(2)–I(3^{ii})	105.20(6)
Hg(1)–I(1)–Hg(2)	99.79(4)	I(4)–Hg(2)–I(4^{iii})	85.24(5)
Hg(1)–I(2)–Hg(1^{i})	104.48(5)	I(3)–Hg(2)–I(4^{iii})	88.14(5)
Hg(2)–I(3)–Hg(2^{ii})	86.97(4)	I(3^{ii})–Hg(2)–I(4^{iii})	83.75(5)
Hg(2)–I(4)–Hg(2^{ii})	94.76(5)	I(1)–Hg(2)–I(4^{iii})	174.15(5)
C(1)–S(1)–Hg(1)	105.4(6)		

Symmetry codes, i: 3/2 − x, 1/2 + y, 3/2 − z; ii: 1 − x, −y, 2 − z; iii: 1 − x, −1 − y, 2 − z.

3. Results and discussion

The complex **1** was synthesized by reacting the ligand with HgI_2 in a 2:1 mole ratio in 1:1 MeCN–CH_2Cl_2. The structure of $[Hg_2I_4(PEDT)]_\infty$ was revealed only by recourse to X-ray crystallography (see below). Instead of HgI_2, $HgCl_2$ was also used as starting material in synthesis. In this case, the chemical composition of the precipitated powder is quite different from **1**. A dinuclear complex $Hg_2Cl_4(PEDT)_2$ (**2**) is proposed although single crystals have not yet been obtained. An analog of **2** is $Hg_2Cl_4(EDT)_2$, in which both mercury atoms are four-coordinated and bridged to one another by two Hg–Cl–Hg bridges [7]. The C=C and C=S vibrations of the ligand in the IR spectra of both **1** and **2** (see experimental section) are shifted to lower frequencies in comparison with those of the free ligand (IR of PEDT: ν(C=C) 1485 ms, ν(C=S) 1060 vs, ν(Ph–H) 725, 698 ms, cm^{-1}).

Overall, as shown in Figs. 1 and 2, the inorganic (HgI_2) and organic (PEDT) components are coordinated via Hg–S bonds and confined to layers both parallel to (101) but, for the choice of origin used in the refinement of the structure,

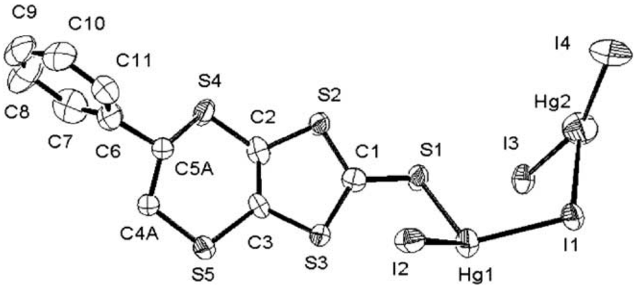

Fig. 1. ORTEP view of the asymmetric unit of $[Hg_2I_4(PEDT)]_\infty$ (**1**) showing the atom labelling scheme. Non-H atoms are shown as 50% probability displacement ellipsoids. H atoms and the lower occupancy C(4B) and C(5B) disordered atoms have been omitted for clarity.

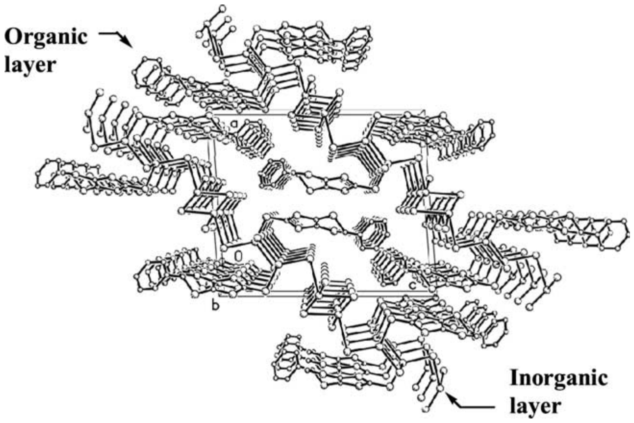

Fig. 2. The inorganic–organic hybrid structure showing the orientation and position of the layers relative to the unit cell.

passing through 1/2,0,0 (and 0,0,1/2) and 1,0,0 (and 0,0,1), respectively.

Two kinds of mercury centers are found within the inorganic layer (Figs. 1 and 3). Hg(1) is coordinated tetrahedrally by I(1), I(2), thiocarbonyl S(1) of the ligand and a neighboring $I(2^{i})$ forming an infinite zig-zag chain propagated in the direction of *b* by the operation of a crystallographic 2-fold screw axis. The Hg(1)–I distances fall in the comparatively narrow range 2.700(1)–2.834(2) Å and the Hg(1)–S(1) distance at 2.567(4) Å is longer than that [2.467(2) Å] of the EDT complex reported earlier [7]. In contrast Hg(2) has a highly distorted five coordinate environment with Hg–I now in the range 2.600(2)–3.538(2) Å. Despite this the angles at Hg(2) [see supplementary data] permit the coordination to be considered as square pyramidal with $I(3^{ii})$ at the apex. The atom pairs $I(3)/I(3^{ii})$ and $I(4)/I(4^{iii})$ each create centrosymmetric double bridges between pairs of Hg(2) atoms thus forming a doubly bridged chain propagated in the direction of *b*. All of the I atoms have a bridging function but the asymmetry of the Hg–I–Hg arrangements increases dramatically from I(2) [single bridge in the Hg(1) chains] < I(3) [like I(4), doubly bridging in the Hg(2) chains] < I(1) (bridging between chains) < I(4). The link provided by I(1) between the singly bridged Hg(1) chains and the doubly bridged Hg(2) chains creates 12 membered rings (Fig. 3).

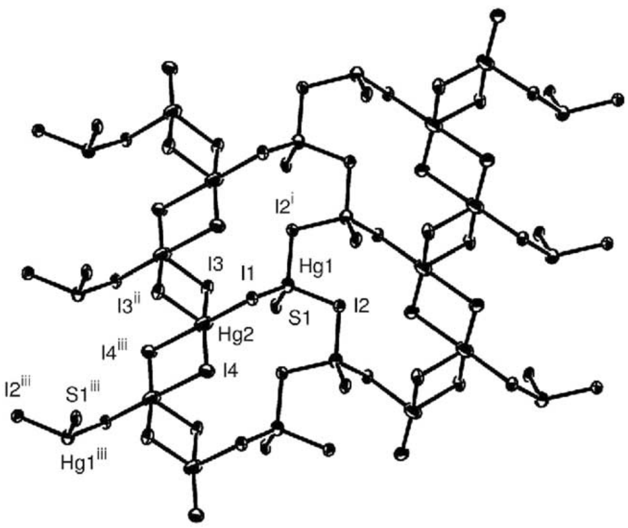

Fig. 3. Part of an inorganic layer viewed in projection on (101) in which the appropriate symmetry codes are included in the atom labels. Symmetry codes i: $3/2 - x$, $1/2 + y$, $3/2 - z$; ii: $1 - x$, $-y$, $2 - z$; iii: $1 - x$, $-1 - y$, $2 - z$.

As indicated above (Fig. 2) sulfur-rich organic molecules PEDT are found in between the inorganic layers just described. Within the organic layers (Fig. 4) the PEDT molecules are found in columns propagated in the direction of *b* (Fig. 2) and displaying two distinct forms of intermolecular contact both of which are constrained by the operation of a crystallographic center of symmetry. In the first of these the molecules are found in pairs head to tail and edge to edge such as to permit S···S contacts as $S(2)\cdots S(4^{iv})$ and $S(4)–S(4^{iv})$ of 3.582(6) and 3.607(1) Å, respectively, clearly less than the sum of van der Waals radii of two S atoms of 3.70 Å. In the second pairs of molecules are found, again head to tail, but now face to face with the five membered ring of one [C(1)/S(2)/C(2)/C(3)/S(3)] virtually completely superimposed on the six membered ring [S(4)/C(2)/C(3)/S(5)/C(5)/C(4)] of the other. The perpendicular distance between the planes of the molecules [planes defined by the six atoms C(2), C(3) and S(2) to S(5)] is found to be almost identical to the $S(2)\cdots S(5^{v})$ distance of 3.694(7) Å and consistent with S···S π stacking. The connectivity within the organic layer is completed by C–H···π interaction between neighboring columns of the form $C(10)–H(10)\cdots Cg^{vi}$ where Cg is the centroid of the phenyl ring with symmetry code $3/2 - x$, $y - 1/2$, $1/2 - z$ in which C(10)–H(10), $H(10)\cdots Cg^{vi}$, H_{perp} [the perpendicular distance of H(10) from the plane of the phenyl ring] and $C(10)\cdots Cg^{vi}$ are 0.93, 3.00, 3.00 and 3.816 Å, respectively, and γ [the angle between $H(10)\cdots Cg^{vi}$ and H_{perp}] and $C(10)–H(10)\cdots Cg^{vi}$ are 3.3 and 147°. The average deviation of the defining atoms from the plane of the phenyl ring is 0.016 Å while for the PEDT plane as defined above it is 0.011 Å rising to 0.25 Å with the inclusion of C(1) and S(1). The displacements of S(1), C(1), C(4A), C(4B), C(5A) and C(5B) from the PEDT plane as first defined are −0.323(19), −0.101(18), 0.33(3), 0.89(4), 1.02(2) and 0.24(3) Å, respectively. The dihedral angle between the phenyl ring and the PEDT plane as first defined is 76.2(5)°.

Since S···S contact is one of the most important factors which permits the sulfur-rich compounds to exhibit conductive or semi-conductive properties, the complex was doped by iodine and its conductivity was measured. Unfortunately, unlike other complexes we have reported [5–8,10], the doped compound is an insulator. The structural reason for this phenomenon is that the strong S···S contacts, below 3.60 Å, in this complex are not connected infinitely but only exist within pairs of the ligands.

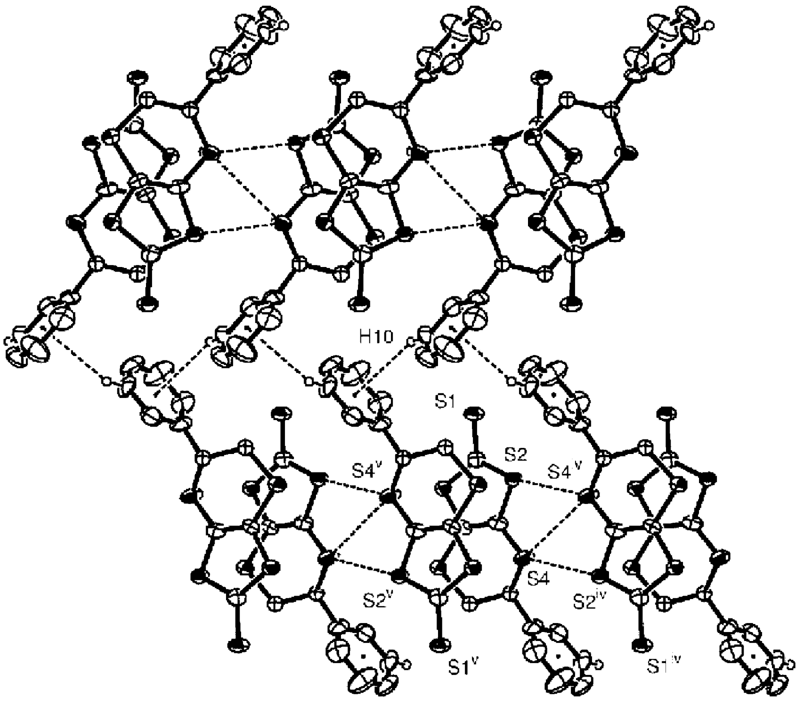

Fig. 4. Part of an organic layer. The representation is the same as in Fig. 1 except that the H atoms which participate in C–H···π contacts (dashed lines) are shown and only selected atoms are labelled. Dashed lines are also used to represent short S···S contacts (see text). Symmetry codes iv: $1 - x$, $-y - 1$, $1 - z$; v: $1 - x$, $-y$, $1 - z$.

The novel structure of **1** is very interesting in relation to the preparation of inorganic–organic hybrid materials. In sulfur-rich conductive materials, inorganic–organic layered materials attract most attention for their unique properties. Two kinds of layered sulfur-rich conductive compounds have been reported. One is inorganic–organic layered charge-transfer compounds, such as $(ET)_2Cu[N(CN)_2]Br$ [11] or $(ET)_2Cu[N(CN)_2]Cl$ [12] (ET = bis(ethylenedithio)tetrathiafulvalene), both notable as super-conductive materials. The other is layered inorganic–organic intercalation materials, such as FeOCl $(TTF)_{0.12}$ [13] (TTF = tetrathiafulvalene) and FeOCl $(ET)_{0.25}$ [14]. In both kinds of compounds, the orientation of the organic molecules or radicals in the organic layer is controlled by static and intermolecular forces. In compound **1**, however, the arrangement of the organic molecules is mainly controlled by the bonding between the organic molecules and the inorganic layer and the intermolecular contacts. Since the inter-layer molecular arrangement is very important for the properties of the materials, the preparation of sulfur-rich compounds, having direct coordination linkage between inorganic and organic moieties, is one of the challenges in the molecular assembly of functional materials.

In conclusion, a novel inorganic–organic hybrid compound with a sulfur-rich ligand has been characterized crystallographically. Despite the absence of good properties for this complex, the cooperation of coordination linkage and S···S interaction in structure arrangement is interesting and revelatory. By this strategy, new sulfur-rich compounds with diverse structures are expected through metal coordination assembly.

Acknowledgements

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References

[1] J.M. Williams, H.H. Wang, T.J. Emge, U. Geiser, M.A. Bano, P.C.W. Leung, K.D. Carlson, R.J. Thorm, A.J. Schultz, M. Whangbo, Prog. Inorg. Chem. 35 (1987) 1.
[2] P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R.A. Clark, A.E. Underhill, Coord. Chem. Rev. 110 (1991) 115.
[3] A.E. Pullen, R.-M. Olk, Coord. Chem. Rev. 188 (1999) 211.
[4] J.A. Schlurter, J.M. Williams, U. Geiser, H.H. Wang, A.M. Kini, M.E. Kelly, J.D. Dudek, Mol. Cryst. Liq. Cryst. 285 (1996) 43.
[5] J. Dai, M. Munakata, T. Kuroda-Sowa, Y. Suenaga, L.P. Wu, M. Yamamoto, Inorg. Chim. Acta 255 (1997) 163.

[6] J. Dai, T. Kuroda-Sowa, M. Munakata, M. Maekawa, Y. Suenaga, Y. Ohno, J. Chem. Soc., Dalton Trans. (1997) 2363.

[7] J. Dai, M. Munakata, G.Q. Bian, Q.F. Xu, T. Kuroda-Sowa, M. Maekawa, Polyhedron 17 (1998) 2267.

[8] J. Dai, M. Munakata, L.P. Wu, T. Kuroda-Sowa, Y. Suenaga, Inorg.Chim. Acta 258 (1997) 65.

[9] N. Svenstrup, J. Becher, Synthesis (1995) 215.

[10] J. Dai, M. Munakata, Y. Ohno, G.Q. Bian, Y. Suenaga, Inorg. Chim. Acta 285 (1999) 332.

[11] M. Kini, U. Geiser, H.H. Wang, K.D. Carlson, J.M. Williams, W.K. Kwok, K.G. Vandervoort, J.E. Thompson, D.L. Stupka, D. Jung, M.H. Wangbo, Inorg. Chem. 29 (1990) 2555.

[12] J.M. Williams, A.M. Kini, H.H. Wang, K.D. Carlson, U. Geiser, L.K. Montgomery, G.J. Pyrka, D.M. Watkins, J.M. Kommers, Inorg. Chem. 29 (1990) 3272.

[13] S.M. Kauzlarich, B.K. Teo, B.A. Averill, Inorg. Chem. 25 (1986) 1209.

[14] J.F. Bringley, J.M. Fabrwe, B.A. Averill, J. Am. Chem. Soc. 112 (1990) 4577.