

Role of Hg...Hg Interactions in Structure Stability of [HgX]⁻ (X = Cl, Br, I) Based Inorganic-Organic Hybrid Compounds

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Abstract: To analyze the metallophilic interactions in [HgX]⁻, (X = Cl, Br, I), series of inorganic-organic hybrid materials were analyzed through single crystal x-ray crystallographic techniques. It has been observed that few compounds HgCl1, HgCl2, HgCl3 and HgCl9 of mercuric chloride series validate the phenomenon of mercuriphilic interactions with minimum Hg...Hg distance of 3.831(1), 3.920(2), 3.810(3) and 3.984(1)Å respectively, whereas in mercuric bromide series, this phenomenon is predominant in the compounds of HgBr1, HgBr4, HgBr5, HgBr9 and HgBr11 with minimum Hg...Hg distance of 3.970(1), 3.860(1), 3.799(1), 3.884(1) and 3.873(1)Å respectively. Only three compounds in mercuric iodide series confirms the phenomenon of mercuriphilic interactions with Hg...Hg = 3.938(1) in HgI8, Hg...Hg = 4.011(1) in HgI11 and Hg...Hg = 3.649(2)Å in HgI13 where as the metallophilicity is missing in other remaining compounds of all the three series. The Hg-Cl bond distances experiential in the range of 2.346(7) to 2.852(5)Å and Cl-Hg-Cl bond angles in the range of 79.2 to 180°.

Keywords: Secondary interactions, Hg motifs, Mercuriphilic interactions, Inorganic-Organic hybrid materials, Metal-organic framework

Introduction

A hybrid of organic and inorganic is a combination of organic materials and inorganic materials¹ at the molecular level. In such hybrid materials, it is possible to expect very interesting characteristics that are not found in the organic polymer or the inorganic material independently. In this paper, we consider the organic-inorganic hybrid materials which are attracting much attention recently and describe the principles of their preparation, new methods of synthesis, and the possibilities that can be expected as materials². Metallophilic interactions are increasingly appreciated as a type of closed-shell interaction that can be used deliberately to form metal-metal contacts³. These interactions are observed between metals with d¹⁰ and d⁸ electron configurations⁴. Contacts between metals have particular potential in the field of molecular electronics⁵. Interactions between one or more metals with an open-shell

have distinct and different bonding consequences that can include covalent metal-metal bond formation⁶ as well as ferro or antiferro-magnetic coupling⁶⁻⁸. Hg...Hg interactions are designated as mercurophilic interactions and depicts an interesting phenomenon of $d^{10}...d^{10}$ metal contacts⁹⁻¹². As part of our research on secondary interactions in organic-inorganic hybrid materials¹¹, three series of compounds whose crystal structures have already been reported¹³⁻⁵⁶ have been selected based on $[HgX]^-$, (X = Cl, Br, I) anion for study of mercurophilic interactions through crystallography data.

Experimental

All the structures were pictorially simulated by using computer software through⁵⁷ cif-data files and geometry of metalophilic interactions as shown in Table 1. The HgCl1 crystal structure has been refined up to 0.051 with 1191 reflections and HgCl2 has R-factor of 0.046 for 3334 reflections. The reliability index of 0.028 has been achieved with 4421 reflections in HgCl3 whereas its value is 0.026 for 11417 reflections of HgCl4. The value of R-index is 0.040 for 2904 reflections of HgCl5 and in HgCl6 it is 0.034 for 1804 reflections. The well refined crystal structure of HgCl7 with refined parameter of 0.039 and 0.040 for HgCl8 shows the structure solution results with 2726 and 3928 $F > 2\sigma(F_o)$ reflections, respectively. HgCl9 and HgCl10 derivatives of the selected series have been refined up to 0.0529 and 0.0322 values, respectively.

Table 1. Hg...Hg contacts and torsion angle ($^{\circ}$) with symmetry codes in $[HgX]^-$, (X = Cl, Br, I) derivatives

Code	Hg...Hg bond distance (Å)	Torsion Angle[1,2,3,4] $^{\circ}$	Code	Hg...Hg bond distance (Å)	Torsion Angle[1,2,3,4] $^{\circ}$
HgCl1	Hg...Hg ⁱ = 3.831(1)	—————	HgBr14	Hg...Hg ^{xxxiii} = 5.019(1)	Br1-Hg1...Hg1 ^{xxxiii} -Br1 ^{xxxiii} = 180.00(2)
HgCl2	Hg...Hg = 3.920(2)	—————	HgBr15	Hg...Hg ^{xxxiv} = 4.505(1)	Br2-Hg1...Hg1 ^{xxxiv} -Br1 ^{xxxiv} = 34.38(3)
HgCl3	Hg...Hg ⁱⁱ = 3.810(3)	Cl(1)-Hg...Hg ⁱⁱ -Cl(2) ⁱⁱ = -99.67(3)	HgBr16	Hg...Hg ^{xxxv} = 6.562(1)	Br2-Hg1...Hg2 ^{xxxvi} -Br3 ^{xxxvi} = 93.99(2)
HgCl4	Hg...Hg ⁱⁱⁱ = 6.245(1)	Cl2-Hg...Hg ⁱⁱⁱ -Cl1 ⁱⁱⁱ = 76.24(1)	HgBr17	Hg...Hg ^{xxxvii} = 5.309(1)	Br1-Hg1...Hg1 ^{xxxvii} -Br2 ^{xxxvii} = 20.11(2)
HgCl5	Hg...Hg ^{iv} = 7.020(1)	Cl2-Hg...Hg ^{iv} -Cl1 ^{iv} = 92.36(1)	HgBr18	Hg...Hg ^{xxxviii} = 5.296(2)	Br1-Hg1...Hg1 ^{xxxviii} -Br1 ^{xxxviii} = 180.00(5)
HgCl6	Hg1...Hg2 ^v = 5.407(1)	Cl3-Hg2...Hg1 ^{vi} -Cl2 ^{vi} = -94.43(1)	HgI1	Hg...Hg ^{xxxix} = 8.892(2)	I1-Hg1...Hg1 ^{xi} -I2 ^{xi} = 102.82(1)
HgCl7	Hg1...Hg1 ^{vii} = 6.079(1)	Cl3-Hg1...Hg1 ^{vii} -Cl2 ^{vii} = 76.02(4)	HgI2	Hg...Hg ^{xli} = 9.511(6)	I2-Hg1...Hg2 ^{xlii} -I2 ^{xlii} = -57.13(3)

HgCl8	Hg...Hg ^{viii} = 6.302(2)	Cl1-Hg...Hg ^{viii} - Cl4 ^{viii} = 92.40(3)	HgI3	Hg...Hg ^{xlii} = 10.592(2)	I3-Hg...Hg ^{xlii} - I2 ^{xlii} = 87.46(1)
HgCl9	Hg1...Hg1 ^{ix} =3.984(1)	Cl11-Hg1...Hg1 ^{ix} - Hg1...Hg2 = Cl12 ^{ix} = 13.05(3)	HgI4	Hg...Hg ^{xliii} = 5.307(1)	I4-Hg...Hg ^{xliii} - I4 ^{xliii} = - 90.751(4)
HgCl10	Hg...Hg ^x = 8.320(1)	Cl1-Hg1...Hg1 ^{xi} - Cl3 ^{xi} = 72.14(1)	HgI5	Hg...Hg ^{xliv} = 6.774(1)	I1-Hg...Hg ^{xliv} - I1 ^{xliv} = -37.34(3)
HgBr1	Hg...Hg ^{xii} = 3.970(1)	Br1-Hg...Hg ^{xiii} - Br2 ^{xiii} = 92.91(7)	HgI6	Hg...Hg ^{xlv} = 4.381(3)	I1-Hg...Hg ^{xlv} - I2 ^{xlvi} = -68.14(1)
HgBr2	Hg...Hg ^{xiv} = 4.391(1)	Br-Hg...Hg ^{xiv} -Br ^{xiv} = -50.56(2)	HgI7	Hg...Hg ^{xlvii} = 4.374(1)	I2-Hg...Hg ^{xlvii} - I3 ^{xlviii} = 112.62(1)
HgBr3	Hg...Hg ^{xv} = 5.409(2)	Br1-Hg...Hg ^{xvi} - Br1 ^{xvi} = 161.16(3)	HgI8	Hg...Hg ^{xlix} = 4.357(2)	I2-Hg...Hg ^{xlix} -I2 ^l = 112.66(4)
HgBr4	Hg...Hg ^{xvii} = 3.860(1)	Br2-Hg1...Hg1 ^{xvii} - Br3 ^{xvii} = -91.24(5)	HgI9	Hg...Hg ^{li} = 4.384(2)	I2-Hg...Hg ^{lii} -I2 ^{liii} = 112.66(1)
HgBr5	Hg...Hg ^{xviii} = 3.799(1)	Br1-Hg1...Hg1 ^{xix} - Br3 ^{xix} = 90.00(4)	HgI10	Hg...Hg ^{liv} = 3.937(1)	I6-Hg1...Hg4-I1 = -93.453(4)
HgBr6	Hg...Hg ^{xx} = 4.277(1)	Br-Hg...Hg ^{xxi} -Br ^{xxii} = -96.52(4)	HgI11	Hg...Hg ^{lv} = 8.850(2)	I1-Hg1...Hg1 ^{lvi} - I1 ^{lvi} = 180.00(2)
HgBr7	Hg...Hg ^{xxiv} = 4.282(1)	_____	HgI12	Hg...Hg ^{lvii} = 9.402(1)	I2-Hg1...Hg1 ^{lvii} - I2 ^{lvii} = -97.79(3)
HgBr8	Hg...Hg ^{xxv} = 4.081(1)	Br1-Hg1...Hg1 ^{xxv} - Br2 ^{xxv} = 67.94(1)	HgI13	Hg...Hg ^{lviii} = 4.011(1)	I1-Hg1...Hg2 ^{lix} - I5 ^{lix} = -89.67(3)
HgBr9	Hg...Hg ^{xxvi} = 3.884(1)	Br1-Hg1...Hg1 ^{xxvi} - Br1 ^{xxvi} = 180.00(5)	HgI14	Hg...Hg ^{lx} = 7.332(1)	I1-Hg1...Hg1 ^{lx} - I1 ^{lx} = 180.00(1)
HgBr10	Hg...Hg ^{xxvii} = 4.052(1)	Br1-Hg1...Hg1 ^{xxvii} - Br1 ^{xxvii} = -88.420(3)	HgI15	Hg...Hg ^{lxi} = 3.649(2)	I3-Hg2A...Hg2 ^{lxi} - I5 ^{lxi} = 113.20(5)
HgBr11	Hg...Hg ^{xxviii} = 3.873(1)	Br3- Hg1...Hg1 ^{xxviii} - Br4 ^{xxviii} = -99.20(2)	HgI16	Hg...Hg ^{lxii} = 4.693(1)	I1-Hg1...Hg1 ^{lxii} - I2 ^{lxii} = 36.77(2)
HgBr12	Hg...Hg ^{xxix} = 6.765(3)	Br1-Hg1...Hg1 ^{xxx} - Br2 ^{xxx} = -84.47(5)	HgI17	Hg...Hg ^{lxiii} = 7.303(1)	I1-Hg1...Hg1 ^{lxiii} - I2 ^{lxiii} = - 110.76(2)
HgBr13	Hg...Hg ^{xxxii} = 7.807(1)	Br1-Hg1...Hg1 ^{xxxii} - Br2 ^{xxxii} = 94.45(3)	HgI18	Hg...Hg ^{lxiv} = 7.174(3)	I1-Hg1...Hg1 ^{lxv} - I2 ^{lxv} = 169.01(1)

Symmetry codes: (i) x, 1+y, -1+z (ii) 1-x, 1-y, 1-z (iii) -x, 1-y, -z (iv) -x, -0.5+y, -z (v) x, y, -1+z (vi) x, y, 1+z (vii) x, y, 1+z (viii) x, -1+y, z (ix) -x, -y, -z (x) 1+x, y, z (xi) -1+x, y, z (xii) 1-x, 0.5+y, 0.5-z (xiii) -x, -y, 1-z (xiv) 0.5+x, 1-y, z (xv) x, 2+y, z (xvi) 0.5-x, -0.5+y, 0.5-z (xvii) -x, 1-y, -z (xviii) 1-x, -y, -z (xix) 1-x, -y, z (xx) x, 1-y, 0.5+z (xxi) 0.5-x, -0.5+y, 0.5-z (xxii) x, 1+y, z (xxiv) x, 0.25-y, 0.25-z (xxv) 1.5-x, 0.5-y, 1-z (xxvi) 1-x, 2-y, 1-z (xxvii) 1-x, y, 0.5-z (xxviii) 1-x, -y, 2-z (xxix) 1.5-x, 1.5-y, 1-z (xxx) 0.5-x, 1.5-y, -z (xxxi) -0.5+x, 1.5-y, -0.5+z (xxxii) 1.5-x, y, -0.5+z (xxxiii) -x, 1-y, -z (xxxiv) 1-x, 1-y, 3-z (xxxv) 1+x, y, -1+z (xxxvi) 1+x, 1+y, -1+z (xxxvii) 1-x, 2-y, -z (xxxviii) x, 1+y, z (xxxix) 1+x, y, z (xl) -1+x, y, z (xli) 0.75-y, 0.25+x, 0.25+z (xlii) 1-x, 1-y, 1-z (xliii) 1-x, y, 0.5-z (xliv) -0.5-x, y, 0.5+z (xlv) -x, -y, -z (xlvi) -x, -0.5+y, -z (xlvii) 0.5-x, y, -z (xlviii) 0.25-y, 0.75-x, -0.25+z (xlix) 1-x, 0.5-y, z (l) 1-x, y, z (li) 0.5+x, -0.5+y, 0.5-z (lii) 1.5-x, 1.5-y, z (liii) 1.5-x, 0.5-y, z (liv) 1-x, 1-y, 1-z (lv) x, 1+y, z (lvi) x, -1+y, z (lvii) -0.5+x, 0.5-y, -0.5+z (lviii) 1-x, 1-y, 1-z (lix) x, 0.5-y, 0.5+z (lx) x, -1+y, z (lxi) 1-x, y, 0.5-z (lxii) 1-x, 1-y, 3-z (lxiii) x, -1+y, z (lxiv) x, -1+y, z (lxv) 0.5+x, 0.5+y, z

The HgBr1 crystal structure has been refined up to 0.049. The value of R- factor for HgBr2 and HgBr3 has been observed to be 0.033 and 0.060 with 4332 and 2658 reflections respectively. The reliability index of 0.032 has been achieved with 2650 reflections in HgBr4 whereas its value is 0.054 for 2115 reflections in HgBr5. The value of R- index is 0.034 for 1804 reflections in HgBr6 and in HgBr7 it is 0.043 for 2759 independent reflections. The well refined crystal structure of Hg8 with refined parameter of 0.042 and 0.032 for HgBr9 shows the structure solution results with 2737 and 6386 reflections, respectively. HgBr10 and HgBr11 derivatives of the selected series have been refined up to 0.029 and 0.032 values for 1361 and 1921 reflections. The cell measurements reflection value of 4420 and 6912 has been used to obtain the refine parameter of 0.053 and 0.026 for the compounds of HgBr12 and HgBr13, respectively. The cell measurement reflections of 1208 are used to refine the crystal structure of HgBr18 up to 0.042 with 2358 reflections.

The HgI1 crystal structure has been refined up to 0.070 with 3378 reflections. The value of R-factor for HgI2 and HgI3 has been observed to be 0.037 and 0.101 with 1351 and 3912 reflections respectively. The reliability index of 0.064 has been achieved with 4575 reflections in HgI4 whereas its value is 0.029 for 1428 reflections in HgI5. The value of R- index is 0.064 for 685 reflections in HgI6 and in HgI7 it is 0.065 for 585 independent reflections. The cell measurements reflection value of 8558 and 250 have been used to obtain the refine parameter of 0.021 and 0.094 for the compounds of HgI12 and HgI13 with refine number of reflections of 2149 and 4237 respectively. The value of R-index is 0.087 for 4420 reflections in HgI14 and in HgI15 it is 0.049 for 4351 independent reflections. Similarly, HgI16 crystal structure has been refined up to 0.022 with 3209 independent reflections.

Results and Discussion

[HgCl] Hybrid materials

The Hg...Hg distance in compound HgCl1 is calculated as 3.831(1) Å which shows that the structure is stabilized by metallophilic interactions apart from X-H...A and Cl...Cl secondary interactions^{10,12}. Similar pattern of mercurophilic interactions is observed in HgCl2 derivative with Hg...Hg distance of 3.920(2) Å. In HgCl3 derivative, Hg atom at symmetry position $x, 1+y, -1+z$ establish a close contact of 3.810(3)Å with another Hg atom at symmetry position $1-x, 1+y, 0.5-z$. The pictorial projection is plotted along *ac*-plane and 1D chain pattern of Hg...Hg contacts supported through Cl...Cl interactions [Cl2...Cl2 = 3.919Å]. When viewed HgCl3 along *b*-axis, the organic layers are held in between this zig-zag pattern of inorganic halides through N-H...Cl interactions, in which Cl1 and Cl2 are responsible for stabilizing the organic-inorganic moieties at symmetry positions $x, -y, -0.5+z$ and $1-x, -y, 1-z$ respectively. Cl2 at symmetry position $1-x, -y, 1-z$ acts as bifurcated hydrogen acceptors having bifurcated angle as 92.24(2)°. The organic moiety (Phenylpiperazinium) stacked within the inorganic layers is further stabilized by C-H... π interactions at $1.5-x, -0.5+y, 0.5-z$ where $H-\pi = 2.983(1)$ and $C-H... \pi = 133.8^\circ$. The inorganic part (*i.e.* trichloromercurate) of the hybrid materials stabilized through zig-zag pattern of secondary interactions and the organic part (*i.e.* phenylpiperazinium) is sandwiched between inorganic layers as shown in Figure 1 along *ac*-plane.

Similarly when HgCl4 is viewed along *b*-axis, Inorganic-organic moieties are observed to be held through N-H...Cl interactions where Cl1 acts as bifurcated hydrogen acceptors with bifurcated angle of 88.58(9)°. The 2D chain pattern of Hg...Hg interactions has been observed in HgCl9 [tetrameric dichloro (trimethylammonio-*p*-toluenesulfonamide) mercury (II)]. The Hg1 atom is in contact with Hg2 at $1-x, 0.5+y, 0.5-z$ with Hg...Hg distance of 4.008(1)Å

forms the dimer of tetrameric mercuric dichloride in 1D chain pattern along *bc*-plane. The dimers are further connected through Hg...Hg interaction at $1+x, 0.5-y, 0.5+z$ with bond distance of 3.984(1)Å. Dimer-Hg...Hg-Dimer type of interaction forms 2D chain pattern down *a*-axis as shown in Figure 2.

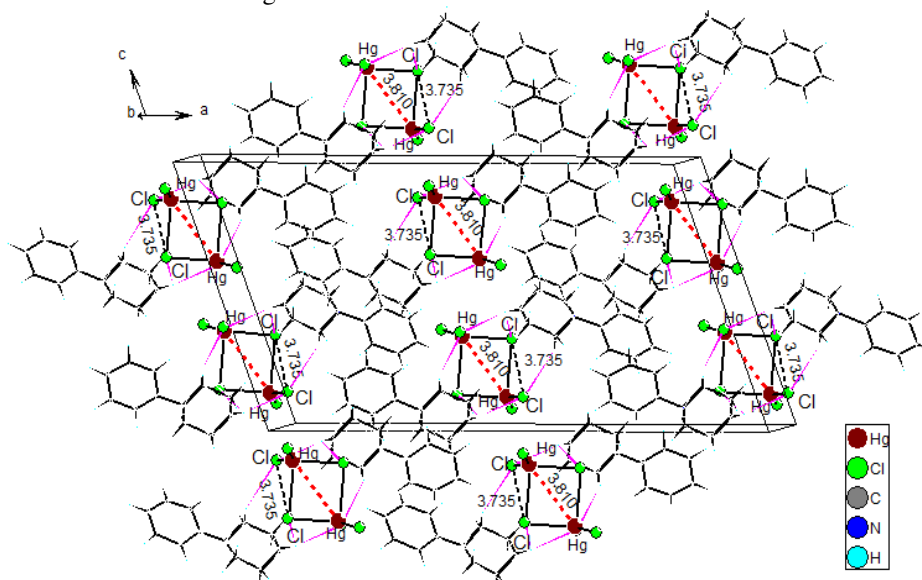


Figure 1. 1D chain pattern of Hg...Hg and Cl...Cl interactions in phenylpiperazinium trichloromercurate

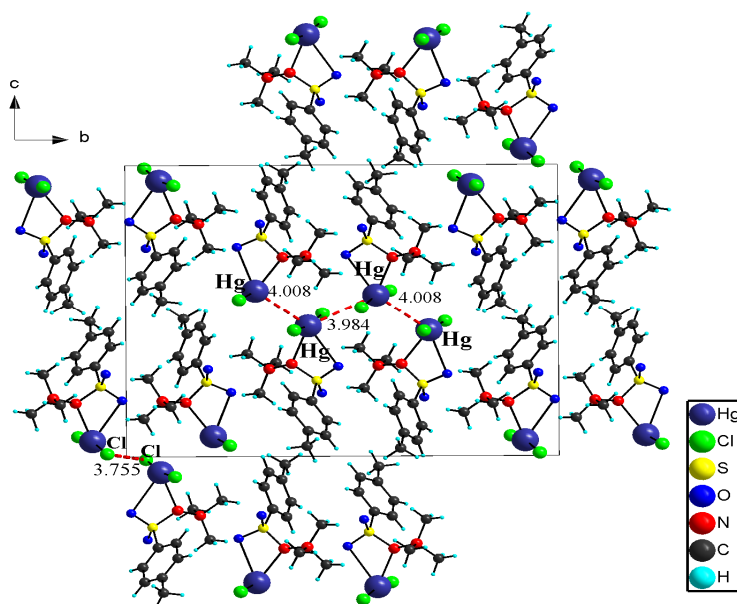


Figure 2. 2D Chain pattern of metallophilic Hg...Hg interactions in tetrameric dichloro (trimethylammonio-*p*-toluenesulfonamidate)mercury(II)

The crystal structure is further stabilized by X-H...A and Cl...Cl secondary interactions. The Hg...Hg bond distances for all other derivatives have been calculated for their minimum values and it has been observed that these distances are more than sum of van der Waals radii and hence cannot be considered as metallophilic interactions but these distances can play role in packing of mercuric chloride as in case of HgCl8 an anti-parallel arrangement of mercuric chloride through metal...metal contacts. The parallel chains of weak interactions along *ac*-plane are observed in HgCl10 and parallel layers of Hg...Hg contact [5.407(1)Å] in HgCl6 compound. Tetramer pattern of tetrachloromercurate through Hg...Hg contact can be drawn in HgCl4 along *ab*-plane. For HgCl5, the inorganic-organic moieties are held through N-H...Cl interactions along *b*-axis, in which Cl11 acts as bifurcated hydrogen acceptors with bifurcated angle of 113.94(1)°. But, in addition along *c*-axis, tide or wave form is observed with high tide for inorganic layers and low tide for organic layers. Similarly, for HgCl6 derivative, the inorganic-organic layers are better presented along *c*-axis and alternate parallel layers of organic moieties are held in between inorganic layers. N-H...Cl interactions play an important role in stabilizing the hybrid compound.

1D chain pattern of Hg...Hg contacts are seen in HgCl7 but not falls in the category of Hg...Hg interactions because of long distance of 6.079(1)Å and true picture of inorganic-organic hybrid material is presented in HgCl5 where 4-benzylpiperidinium is held in anti-parallel arrangement between the inorganic layers of tetrachloromercurate but the long distance of Hg...Hg contact [7.020(1)Å] demonstrate the lack of Hg...Hg interaction.

[HgBr] Hybrid materials

The Hg...Hg distance in compound HgBr1 is calculated as 3.970(1)Å which shows that the structure is stabilized by metallophilic interactions apart from X-H...A and Br...Br [minimum distance = 3.610(2)Å] secondary interactions^{10,19}. Mercury atom at symmetry position 1+x, 0.5-y and 0.5+z establish a close contact with Hg located at 1-x, 0.5+y and 0.5-z as shown in Figure 3. In HgBr2 compound, Hg...Hg contact is establish at -0.5+x, 1-y, z with minimum distance of 4.391(1)Å and the structure is further stabilized by weak Br...Br interactions. Hg atom at x, 1-y, -z is in close proximity with another Hg atom to establish Hg...Hg contact with distance of 3.860(1)Å and the structure is further stabilized by Br...Br interactions with minimum distance of 3.915(2)Å in compound HgBr4. The pictorial projection is plotted along *bc*-plane and organic moiety is presented in polyhedral. The head to head dimer pattern of Bis(tetraethylammonium)di- μ -bromo-bis(dibromomercury) is pictorially projected along *bc*-plane in which organic moiety is in polyhedral form as shown in Figure 4.

The 1D parallel layers of Hg...Hg interactions in bis(tetraethylammonium)octabromotri mercurate(II) (HgBr5) is paradigm of squash in of organic part within the chains of inorganic moiety of hybrid materials. Hg atom at symmetry position 1-x, 1-y, 1-z forms contact with another Hg atom at x, 1+y, 1+z with minimum distance of 3.799(1)Å. The structure is also stabilized by Br...Br interactions (d = 3.662(2)Å). In mercuric bromide derivatives HgBr6, HgBr7 and HgBr8, the close contacts of Hg...Hg are observed with symmetry positions of -x, 1+y, 1.5-z (Hg...Hg distance = 4.277(1)Å) in HgBr6; x, 0.25-y, 0.25-z (Hg...Hg distance = 4.282(1)Å) in HgBr7 and 1.5-x, 0.5-y, 1-z (Hg...Hg distance = 4.081(1)Å) in HgBr8 and these contacts are not comparable with their van der Waals radii. Hg...Hg interactions in poly[bromomercury(II)]-di-*m*-bromo- k^4 Br:Br-[bromomercury(II)]-*m*-1,4-bis(benzyl sulfanyl)butane- k^2 S:S'] (HgBr9) is established at 1-x, 2-y, 1-x symmetry position with minimum Hg...Hg distance of 3.884(1) Å. The metallophilic interaction in [*m*-1,2-bis(phenylsulfanyl)ethane- k^2 S:S']bis[dibromomercury(II)] (HgBr10) is confirmed because its Hg...Hg distance is 4.052(1)Å.

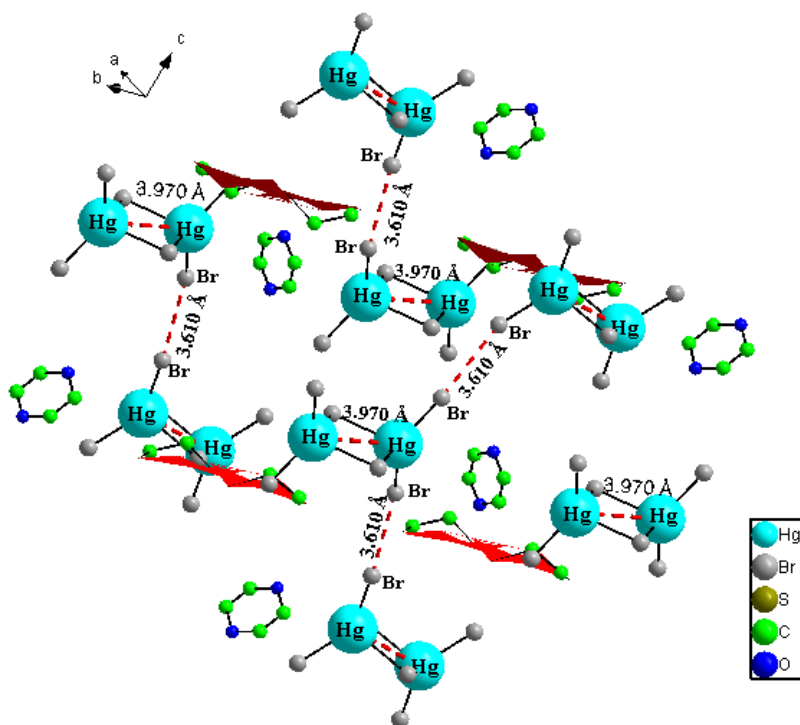


Figure 3. Hg...Hg and Br...Br interactions in HgBr1 derivatives

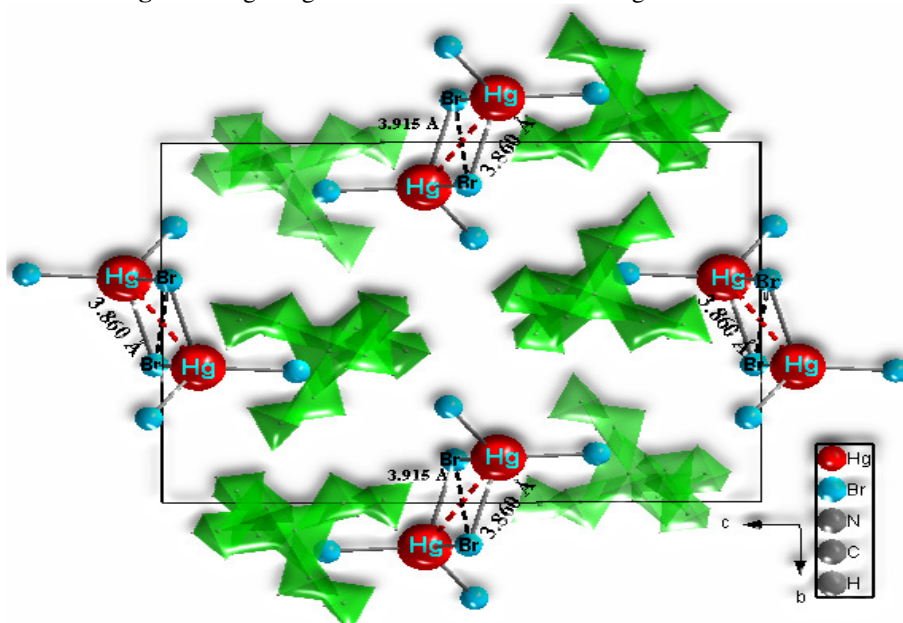


Figure 4. Dimer pattern of Bis(tetraethylammonium)di- μ -bromo-bis(dibromomercury) with metallic interaction at $-x, 1-y, -z$

In HgBr11 derivative of mercuric bromide, dimer pattern with head-to-tail configuration is observed with minimum Hg...Hg distance of 3.873(1)Å at symmetry position of 1-x, -y, 2-z. Dimer to dimer plane distance is calculated as 10.592(1)Å and 180.00(2)° value of Br-Hg...Hg-Br torsion angle shows that dimer pattern is planar at Hg...Hg contact. The minimum value of torsion angle (Br3-Hg...Hg-Br2) is 2.44(1)° for the compounds HgBr1 while the value of torsion angle is 180° for HgBr4, HgBr5, HgBr9, HgBr11, HgBr14 and HgBr18 derivatives of the selected series as given in Table 4.

[HgI] Hybrid materials

The Hg...Hg distance in compound HgI8(bis(tetrabutylammonium)decaiodotetra mercurate(II)) is calculated as 3.937(1)Å which shows that the structure is stabilized by mercuriphilic interactions apart from X-H...A and I...I secondary interactions. Similar pattern of mercuriphilic interactions is observed in HgI11 [Tris(1,10-phenanthroline) copper(II) di-*m*-iodo-bis(diiodomercurate) dimethylsulfoxide monohydrate] derivative with Hg...Hg distance of 4.011(1)Å. In HgI13 derivative, Hg atom at symmetry position x, 1+y, and z establishes a close contact of 3.649(2) Å with another Hg atom having 1-x, y and 0.5-z symmetry position and supported through I...I interactions (I...I=3.835(2)Å).

Conclusion

The Hg...Hg bond distances for all other derivatives of the selected series (HgCl, HgBr and HgI) have been calculated for their minimum values and it has been observed that these distances are more than sum of their van der Waals radii and hence cannot be considered as metallophilic interactions. Hence to understand the mechanism the structural studies have been made on HgCl₂, HgBr₂, HgI₂ systems. There is substantial congruence between the mercuriphilic pattern observed in the selected series of mercuric iodide based compounds and other metallophilic interactions. The packing views portray that Hg...Hg contacts have an advantage of versatility and flexibility of geometrical characteristics. Similar to other secondary interactions such as X-H...A and halogen...halogen, the mercuriphilic interactions could be a collective tool to design the new crystal structures.

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