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RESEARCH ARTICLE

Role of Halogen Interactions in Stabilizing Crystals of $[HgX]^-$ Based Hybrids

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Abstract: To analyze the halogen 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, HgCl6, HgCl7, HgCl8 and HgCl9 of mercuric chloride series validate the phenomenon of halogen interactions with Cl-Cl distance less than sum of their van der Waals radii, whereas in mercuric bromide series, this phenomenon is predominant in the compounds of HgBr1, HgBr4, HgBr5, HgBr8, HgBr9, HgBr10, HgBr11, HgBr13 and HgBr16 with Br-Br distance less than sum of their van der Waals radii. Only two compounds in mercuric iodide series HgI1 and HgI15 confirm the phenomenon of halogen interactions whereas these interactions are 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: Halogen interactions, Hg motifs, van der Waals radii, Inorganic-Organic hybrid materials, Metal-organic framework

Introduction

Crystal engineering is concerned with the construction of crystal structures of organic and metal organic species, using design principles that are derived from an understanding of the intermolecular interactions that prevail in molecular solids[1]. Ideally, the crystal to be designed has a specific function whether it is chemical reactivity of a desired kind, an optical, magnetic or electronic property, or still the ability to absorb within the crystal another small molecule[2-4]. To summarise, crystal engineering is the rational design of functional molecular solids. This subject has been in active investigation for around 30 years[5-14]. In the modern context, the concepts of crystal engineering are applicable to any kind of intermolecular assembly whether it is protein ligand recognition, the design of supramolecular polymers, systems for drug delivery or the study of organized media other than crystalline solids. Crystal engineering is accordingly of very wide scope and it has brought together investigators from many disciplines[15]. These include organic chemistry, inorganic chemistry, physical chemistry, x-ray crystallography, materials sciences and computational chemistry. The main aim of crystal engineering is to make particular crystal structures from particular molecules.

Inorganic-Organic hybrid materials

A hybrid of organic and inorganic is a combination of organic materials and inorganic materials[16] 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. For example, they can have features such as being flexible like a plastic but have excellent mechanical strength and thermal stability. Hybrid organic-inorganic materials in general represent the natural interface between two worlds of chemistry each with very significant contributions to the field of materials science and each with characteristic properties that result in distinct advantages and limitations[17].

Halogen···Halogen interactions

Although crystal engineering is still generally dominated by hydrogen bonding and metal–ligand interactions, halogen bonds have become increasingly studied and exploited, with a major renaissance over the last ten years. The first use of halogen bonding in liquid crystal formation has been reported by Coronado *et al*.,[18]. Before the discovery of halogen bonding, the approach for crystal engineering involved using halogen bonding, coordination chemistry and inter-ion interactions for the development of liquid-crystalline and solid-crystalline materials. Furthermore, halogen bonding is employed for the organization of radical cationic salts and fabrication of molecular conductors etc. Since the discovery of halogen bonding, new molecular assemblies exist[19]. The range of species capable of adopting halogen bonding interactions indicates a prevalent future for halogen bonds in crystal engineering. As a consequence of the spatially segregated regions of complementary electrostatic potential, interhalogen bonding is also observed with halogen groups acting as both nucelophiles and electrophiles. Desiraju *et al.,*[20] carried out systematic CSD search on the geometries of these contacts and deduced that the short X···X intermolecular distances arise from the specific attractive forces between the two halogen atoms in crystals and the non-spherical shape (polar flattening) of the halogen atoms was the consequence of this interaction. Price *et al*.,[21] showed that for X···X short distances especially chlorine–chlorine interactions could originate from anisotropic effects (non-spherical atomic charge distribution) between elliptically shaped chlorine atoms. The role of X···X contacts, appears to be important (irrespective of their cause) in determining supramolecular structures and it may be possible to exploit them directly in crystal engineering and for the design of supramolecular aggregates[22].

Experimental

All the structures were pictorially simulated by using Diamond software through[23] cif-data files and geometry of secondary interactions were analyzed as shown in Table 1-3. IR and Raman spectra tensors were calculated by using fractional co-ordinate obtained from single crystal XRD data as presented in Table 4. 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 $F > 2\sigma(Fo)$ reflections, respectively. HgCl9 and HgCl10 derivatives of the selected series have been refined up to 0.0529 and 0.0322 values, respectively.

Table 1. Crystal structure data for $[HgX]^-$, (X = Cl, Br, I) compounds

Code along with [Ref.]	IUPAC Name	Chemical Formula	Cell Parameters	Space group & Crystal System
HgCl1 [24]	Bis(triphenyl tellurium)di-μ-chloro-bis[(dichloromercurate(II)]	$[Te(C_6H_5)\ ^{3+}]_2\ [Hg_2Cl_6\,^{2-}]$	a = 9.090(6) Å b = 10.224(5) Å c = 10.820(5) Å α = 95.54(3)° β = 92.47(3)° γ = 99.48(3)°	P-1 *Triclinic*
HgCl2 [25]	Chloro-n,n,n′,n′-tetramethylformamidinium-bis[dichloro mercury(II)]chloride	$[C_5H_{12}ClN_2]^+[2HgCl_2.Cl]^-$	a = 10.840(3) Å b = 10.409(3) Å c = 7.422(2) Å α = 96.59(5)° β = 100.89(5)° γ = 107.53(5)°	P-1 *Triclinic*
HgCl3 [26]	Phenylpiperazinium trichloromercurate	$C_{10}H_{14}Cl_3HgN_2$	a = 25.975(3) Å b = 8.013(2) Å c = 14.051(2) Å β = 110.34(2)°	C2/c *Monoclinic*
HgCl4 [27]	Bis(piperidinium) Tetrachloromercurate	$(C_5NH_{12})_2HgCl_4$	a = 14.954(2) Å b = 12.157(1) Å c = 9.701(1) Å β = 100.76(1)°	$P2_1/n$ *Monoclinic*
HgCl5 [28]	Bis-(4-benzylpiperidinium) Tetrachloromercurate	$[(C_6H_5)CH_2(C_5NH_{11})]_2HgCl_4$	a = 13.603(1) Å b = 8.383(1) Å c = 12.198(1) Å β = 97.66(1)°	$P2_1$ *Monoclinic*
HgCl6 [29]	1,3-Propanediammonium Tetrachloromercurate	$(NH_3C_3H_6NH_3)HgCl_4$	a = 7.788(1) Å b = 7.796(1) Å c = 9.457(1) Å α = 68.11(1)° β = 72.90(1)° γ = 87.94(1)°	P-1 *Triclinic*
HgCl7 [30]	Bis(1,2ethanediammonium dichloride tetrachloromercurate	$[(NH_3C_2H_4NH_3)Cl]_2HgCl_4$	a = 12.799(1) Å b = 19.842(2) Å c = 6.079(1) Å α = β = γ = 90°	Pnma *Orthorhombic*
HgCl8 [31]	Bis(trimethylammonium)tetrachloromercurate(II)	$C_6H_{20}Cl_4HgN_2$	a = 18.741(2) Å b = 6.302(2) Å c = 13.069(3) Å γ = 91.68(1)°	$P2_1/n$ *Monoclinic*
HgCl9 [32]	Tetrameric dichloro(trimethylammonio-p-toluenesulfonamidate) mercury(II)	$C_{40}H_{64}Cl_8Hg_4N_8O_8S_4$	a = 7.994(1) Å b = 21.634(2) Å c = 17.296(1) Å β = 93.32(1)°	$P2_1/c$ *Monoclinic*
HgCl10 [33]	2,2-(propane-1,3-diyl)bis(1,1,3,3-tetramethylguanidinium) tetrachloromercurate	$C_{13}H_{32}Cl_4HgN_6$	a = 8.320(4) Å b = 18.081(9) Å c = 15.809(8) Å β = 104.29(0)°	$P2_1/c$ *Monoclinic*
HgBr1 [34]	$(BEDT\text{-}TTF)_4\ [Hg_2\ Br_6]$. THF	$C_{44}H_{40}Br_6Hg_2OS_{32}$	a = 17.080(2) Å b = 13.467(3) Å c = 15.991(4) Å β = 91.68(1)°	$P2_1/c$ *Monoclinic*

HgBr2 [35]	1-Bromomercurio-2-(2,5,8,11,14-pentaoxapentadecyl)benzene	$C_{16} H_{25}BrHgO_5$	a = 8.544(2) Å b = 13.164(1) Å c = 16.809(2) Å α = β = γ = 90°	$Pca2_1$ *Orthorhombic*
HgBr3 [36]	Aquabromo(6-carboxypyridine-2-carboxylato-O,N,O')mercury(II)	$C_7H_6BrHgNO_5$	a = 6.967(3) Å b = 9.068(3) Å c = 16.007(5) Å β = 91.05(3)°	$P2_1/n$ *Monoclinic*
HgBr4 [37]	Bis(tetraethylammonium)di-μ-bromo-bis[dibromomercury(II)]	$C_{16}H_{40}Br_6Hg_2N_2$	a = 9.115(2) Å b = 10.830(1) Å c = 16.140(4) Å β = 107.38(2)°	$P2_1/c$ *Monoclinic*
HgBr5 [38]	Bis(tetraethylammonium) octabromotrimercurate(II)	$C_{16}H_{40}Br_8Hg_3N_2$	a = 10.089(1) Å b = 10.089(1) Å c = 16.094(2) Å α = β = γ = 90°	$P4_2/m$ *Tetragonal*
HgBr6 [39]	Catena-(di-m-bromo(pyridine-3-carboxylato-O,O',N))mercury(II)	$[Hg Br(C_6H_4NO_2)]$	a = 14.202(1)Å b = 7.210(2)Å c = 15.368(3)Å β = 103.94(1)°	C2/c *Monoclinic*
HgBr7 [40]	(Pyrimidine-2-thionato-kS)(pyrimidinium-2-thionato-kS)mercury(II) tetrabromomercury(II)	$C_{16}H_{14}Br_4Hg_3N_8S_4$	a = 9.057(1) Å b = 17.200(1) Å c = 37.754(9) Å α = β = γ = 90°	Fddd *Orthorhombic*
HgBr8 [41]	[m2-1,4-Bis(ethylthio)butane-S,S']dibromomercury(II)	$C_4H_9Br_2HgS$	a = 10.019(2) Å b = 12.952(3) Å c = 14.798(3) Å β = 106.56(3)°	C2/c *Monoclinic*
HgBr9 [42]	Catena-Poly[[bromomercury(II)]-di-*m*-bromo-k4Br:Br-[bromomercury(II)]- m-1,4-bis(benzylsulfanyl) butane-k2S:S']	$C_9H_{11}Br_2HgS$	a = 7.847(2) Å b = 8.843(2) Å c = 9.639(2) Å α = 70.08(3)° β = 75.26(3)° γ = 88.53(3)°	P-1 *Triclinic*
HgBr10 [43]	[*m*-1,2-Bis(phenylsulfanyl)ethane-k2S:S']bis[dibromo mercury(II)]	$C_{14}H_{14}Br_4Hg_2S_2$	a = 22.033(1) Å b = 11.665(1) Å c = 8.076(1) Å β = 103.31(1)°	C2/c *Monoclinic*
HgBr11 [44]	Bis[(4-bromobenzoyl methyl)triphenylphosphonium] di-*m*-bromido-bis[dibromidomercurate (IV)]	$C_{52}H_{42}Br_8Hg_2O_2P_2$	a = 9.415(1) Å b = 21.885(1) Å c = 13.268(1) Å β = 100.79(1)°	$P2_1/n$ *Monoclinic*
HgBr12 [45]	Guanidinium tetrabromidomercurate(II)	$C_2H_{12}Br_4HgN_6$	a = 10.035(2) Å b = 11.164(2) Å c = 13.358(3) Å β = 111.67(3)°	C2/c *Monoclinic*
HgBr13 [46]	Bis(2,6-dibromopyridinium) tetrabromidomercurate(II) dihydrate	$C_{10}H_{12}Br_8HgN_2O_2$	a = 10.633(1) Å b = 13.514(1) Å c = 15.614(1) Å α = β = γ = 90°	Pccn *Orthorhombic*

HgBr14 [47]	[1,3-Bis(2-ethoxyphenyl)triazenido]bromidomercury(II)	$C_{16}H_{18}BrHgN_3O_2$	a = 10.234(1) Å b = 7.466(1) Å c = 22.412(1) Å β = 98.86(1)°	P2$_1$/n *Monoclinic*
HgBr15 [48]	Catena-poly[[[dibromidomercury (II)……………methanol monosolvate]	$C_{29}H_{28}Br_2HgN_4O_4$	a = 8.825(1) Å b = 12.967(2) Å c = 13.020(2) Å α = 95.75(1)° β = 99.10(1)° γ = 98.90(1)°	P-1 *Triclinic*
HgBr16 [49]	Dibromido(2,2’-dimethyl-4,4’-bi-1,3-thiazole-k2N,N’)mercury(II)	$C_8H_8Br_2HgN_2S_2$	a = 10.280(1) Å b = 11.160(1) Å c = 11.682(1) Å α = 88.45(1)° β = 85.33(1)° γ = 77.12(1)°	P-1 *Triclinic*
HgBr17 [50]	Dibromidobis(pyridine-3-carbonitrile-kN1)mercury(II)	$C_{12}H_8Br_2HgN_4$	a = 8.582(1) Å b = 9.407(1) Å c = 9.856(1) Å α = 81.93(1)° β = 71.43(1)° γ = 80.51(1)°	P-1 *Triclinic*
HgBr18 [51]	Dibromidobis{1-[4-(yridine-4-yl)phenyl]ethanone]mercury(II)	$C_{26}H_{22}Br_2HgN_2O_2$	a = 16.656(6) Å b = 5.296(2) Å c = 29.442(1) Å β = 102.45(1)°	C2/c *Monoclinic*
HgI1 [52]	$(BEDT\text{-}TTF)_4$ Hg_2 I_6 (I_8)	$C_{40}H_{32}Hg_2I_{14}S_{32}$	a = 8.892(1) Å b = 15.627(2) Å c = 17.840(2) Å α = 66.17(1)° β = 79.79(1)° γ = 85.81(1)°	P-1 *Triclinic*
HgI2 [53]	Bis(triethylsulfonium) Tetraiodomercurate(II)	$HgI_4S_2C_{12}H_{30}$	a = 13.903(1) Å b = 13.903(1) Å c = 25.963(3) Å α = β = γ = 90°	I4$_1$/a *Tetragonal*
HgI3 [54]	{3-[(1-Protonated-4-amino-2-methyl-5…….heptaiododimercurate dihydrate	$C_{24}H_{39}Hg_2I_7N_8O_4S_2$	a = 9.257(1) Å b = 10.947(3) Å c = 11.911(1) Å α = 96.86(1)° β = 109.00(1)° γ = 96.59(1)°	P-1 *Triclinic*
HgI4 [54]	{3-[(1-Protonated-4-amino-2-methyl-5…….dimethanol-monohydrate	$C_{26}H_{45}Hg_2I_7N_8O_5S_2$	a = 11.797(1) Å b = 19.238(2) Å c = 22.012(4) Å β = 98.57(1)°	C2/c *Monoclinic*
HgI5 [55]	Bis[iodo(1-methyl-1,3-imidazolium-2-thiolato-S)]mercury(II)	$C_8H_{12}HgI_2N_4S_2$	a = 11.543(2) Å b = 13.996(5) Å c = 9.918(1) Å α = β = γ = 90°	Pca2$_1$ *Orthorhombic*
HgI6 [56]	Diiodo-3,4,5,6-tetrahydropyrimidinium-2-thiolato mercury(II)	$C_4H_8HgI_2N_2S$	a = 12.826(2) b = 7.392(1) c = 11.447(2) α = β = γ = 90°	Pnma *Orthorhombic*

HgI7 [57]	Mercuric iodide	HgI_2	a = 12.393(2) Å b = 12.393(2) Å c = 24.889(1) Å α = β = γ = 90°	$I4_1/acd$ *Tetragonal*
HgI8 [57]	Mercuric iodide	HgI_2	a = 8.786(1) Å b = 8.786(1) Å c = 24.667(3) Å α = β = γ = 90°	$I4_1/amd$ *Tetragonal*
HgI9 [58]	Mercuric iodide	HgI_2	a = 8.786(1) Å b = 8.786(1) Å c = 12.334(3) Å α = β = γ = 90°	$P4_2/nmc$ *Tetragonal*
HgI10 [59]	Bis(tetrabutylammonium) decaiodotetramercurate(II)	$C_{32}H_{72}Hg_4I_{10}N_2$	a = 11.681(0) Å b = 15.770(0) Å c = 18.288(0) Å α = 114.33(0)° β = 104.18(0)° γ = 90.18(0)°	P-1 *Triclinic*
HgI11 [60]	Di-iodo-bis(*o*-chlorophenylbenzoylthiourea-kS)mercury(II)	$C_{28}H_{22}Cl_2HgI_2N_4O_2S_2$	a = 20.900(4) Å b = 8.850(2) Å c = 19.845(4) Å β = 118.26(3)°	C2/c *Monoclinic*
HgI12 [61]	Bis[4-trimethylammonio) phenyl] disulfidetetraiodo mercurate(II)	$C_{18}H_{26}HgI_4N_2S_2$	a = 10.497(1) Å b = 20.386(1) Å c = 13.226(1) Å β = 95.33(0)°	$P2_1/n$ *Monoclinic*
HgI13 [62]	Tris(1,10-phenanthroline)copper(II) di-*m*-iodo-bis(diiodomercurate) dimethyl sulfoxide monohydrate	$C_{38}H_{32}CuHg_2I_6N_6O_2S$	a = 12.663(1) Å b = 18.840(2) Å c = 20.138(2) Å β = 95.79(1)°	$P2_1/c$ *Monoclinic*
HgI14 [63]	Iodo-(picolinato-N,O)(picolinic acid-N,O)mercury(II)	$C_{12}H_9HgIN_2O_4$	a = 14.233(1) Å b = 7.332(4) Å c = 14.926(1) Å β = 109.03(1)°	C2/c *Monoclinic*
HgI15 [64]	Poly[n,n,n',n'-tetrakis[3-(methoxycarbonyl)propyl]ethylenediammonium [tetra-*m*-iodo-hexaiodotetramercurate]]	$C_{18}H_{34}Hg_4I_{10}N_2O_8$	a = 18.580(5) Å b = 16.805(4) Å c = 14.864(4) Å β = 100.63(0)°	C2/c *Monoclinic*
HgI16 [65]	Catena-poly[[[diiodidomercury(II)]-m-2,5-bis{5-methyl- 2-[(4-pyridyl)methoxy]phenyl}-1,3,4-oxadiazole] methanol monosolvate]	$C_{29}H_{28}HgI_2N_4O_4$	a = 9.046(3) Å b = 13.153(4) Å c = 13.213(4) Å α = 95.97(0)° β = 99.50(0)° γ = 97.27(0)°	P-1 *Triclinic*
HgI17 [66]	[1-(1H-Imidazo[4,5-f][1,10]phenanthrolin-2-yl)naphthalen-2-ol- k2N7, N8]diiodidomercury(II)	$C_{23}H_{14}HgI_2N_4O$	a = 14.427(1) Å b = 7.303(1) Å c = 21.134(2) Å β = 94.47(0)°	$P2_1/c$ *Monoclinic*
HgI18 [67]	Diiodido(1,10-phenanthroline-5,6-dione-k2N,N')mercury(II)	$C_{12}H_6HgI_2N_2O_2$	a = 11.794(3) Å b = 8.173(1) Å c = 15.398(3) Å β = 108.30(1)°	Cc *Monoclinic*

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 MoKα type of radiations having wavelength 0.71073 have been used to obtain the refine parameter for all the compounds of the selected series (HgBr1-HgBr18). The value of R-index is 0.030 for 3967 reflections in HgBr14 and in HgBr15 it is 0.104 for 4420 independent reflections. Similarly HgBr16 crystal structure has been refined up to 0.035 with 6912 reflections and HgBr17 has the R-factor of 0.033 for 3967 independent reflections. 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 well refined crystal structure of HgI8 with refined parameter of 0.096 and 0.054 for HgI9 shows the structure solution results with 11615 and 3734 reflections respectively. HgI10 and HgI11 derivatives of the selected series have been refined up to 0.048 and 0.085 values. 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

Halogen-Halogen Interactions

[HgCl]$^-$Hybrid materials

The bond lengths of Hg-Cl bond lies in an average range of 2.472 Å to 2.676 Å. The graphical projection of bond distances for these derivatives illustrate that most of the data points lie in between 2.45 to 2.55Å whereas the data points for HgCl2, HgCl6 and HgCl9 shows the deviation from this linearity as presented in Figure 1. The Cl-Hg-Cl bond angles have wide range from minimum value of 99.30 to 114.90^o for molecule HgCl4 and maximum range of 88.40 to 180^o for molecule HgCl6 as shown in Table 2.

The Graphical view for Cl…Cl bond distances illustrates that most of the data points exist in the range of 3.807Å to 3.949Å which corroborates that the crystal structures are stabilized by secondary interactions as this range is comparable with van der Waals radii as shown in Figure 2. The minimum value of torsion angle [Cl-Hg…Hg-Cl] is 4.12(1)^o for the compound HgCl6 having x, y, 1+z symmetry positions, while its maximum value is 76.02(4) for HgCl7as shown in Table 3.

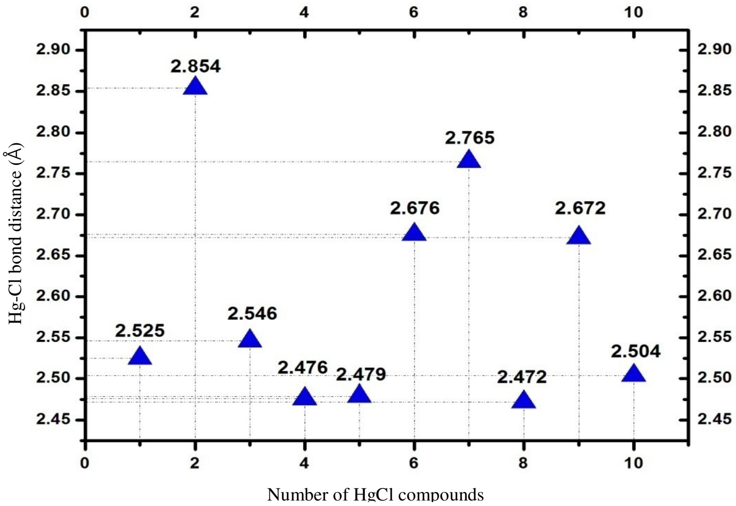

Figure 1. Scatter Plot of the average values of Hg-Cl bond distances

Table 2. Crystallographic data for Hg-centered bond distances (Å) and range of bond angles (°) in $[HgX]^-$, (X = Cl, Br, I)

Code	Hg-X bond distance(Å)	X-Hg-X (°) range	Code	Hg-X bond distance(Å)	X-Hg-X (°) range
HgCl1	Hg-Cl(1) = 2.350(2) Hg-Cl(3) = 2.350(2) Hg-Cl(2) = 2.684(2) Hg-Cl(2') = 2.717(2)	89.60 - 141.30	HgBr14	Hg1-Br1 = 2.401(1)	-
HgCl2	Hg-Cl(1) = 2.312(3) Hg-Cl(2) = 2.331(2) Hg-Cl(3) = 2.926(3) Hg-Cl(4) = 2.983(3) Hg-Cl(5) = 3.278(3) Hg-Cl(6) = 3.296(3)	79.20-168.50	HgBr15	Hg1-Br2 = 2.484(1) Hg1-Br1 = 2.491(1)	145.07
HgCl3	Hg-Cl3 = 2.346(1) Hg-Cl2 = 2.365(1) Hg-Cl1 = 2.624(1) Hg-Cl1 = 2.852(1)	90.90-148.50	HgBr16	Hg2-Br4 = 2.496(1) Hg1-Br1 = 2.497(1) Hg2-Br3 = 2.500(1) Hg1-Br2 = 2.521(1)	126.49-132.85
HgCl4	Hg-Cl3 = 2.431(3) Hg-Cl1 = 2.515(2) Hg-Cl2 = 2.485(2) Hg-Cl4 = 2.475(3)	99.30-114.90	HgBr17	Hg1-Br1 = 2.458(1) Hg1-Br2 = 2.474(1)	159.99
HgCl5	Hg-Cl3 = 2.424(3) Hg-Cl2 = 2.430(3) Hg-Cl4 = 2.450(3) Hg-Cl1 = 2.614(2)	99.20-115.80	HgBr18	Hg1-Br1 = 2.470(1)	147.81
HgCl6	Hg1-Cl4 = 2.397(2) Hg1-Cl2 = 2.821(2) Hg1-Cl1 = 2.839(2) Hg2-Cl3 = 2.528(2) Hg2-Cl2 = 2.701(2) Hg2-Cl1 = 2.775(2)	88.40-180.00	HgI1	Hg1-I1 = 2.669(3) Hg1-I3 = 2.674(3) Hg1-I2 = 2.845(3)	111.17-127.23

HgCl7	Hg1-Cl3 = 2.378(1) Hg1-Cl1 = 2.581(2) Hg1-Cl2 = 2.860(3) Hg1-Cl2 = 3.243(3)	84.69-169.81	HgI2	Hg1-I1 = 2.780(1) Hg2-I2 = 2.790(1)	107.74-112.98
HgCl8	Hg-Cl4 = 2.414(4) Hg-Cl2 = 2.442(1) Hg-Cl3 = 2.430(1) Hg-Cl1 = 2.604(4)	101.40-117.50	HgI3	Hg-I3 = 2.681(2) Hg-I4 = 2.736(1) Hg-I2 = 2.751(5) Hg-I2 = 2.840(2) Hg-I1 = 2.971(1)	97.90-122.90
HgCl9	Hg2-Cl21 =2.325(1) Hg1-Cl11=2.332(1) Hg2-Cl22=2.334(1) Hg1-Cl12=2.340(1) Hg1-Cl11=3.089(1) Hg2-Cl12=3.065(1) Hg1-Cl22=3.216(1)	84.30-167.60	HgI4	Hg-I3 = 2.696(1) Hg-I2 = 2.779(1) Hg-I4 = 2.785(1) Hg-I1 = 2.939(1)	98.15-121.62
HgCl10	Hg-Cl3 = 2.456(1) Hg-Cl2 = 2.502(1) Hg-Cl1 = 2.523(1) Hg-Cl4 = 2.533(1)	104.62-120.58	HgI5	Hg-I1 = 2.781(1) Hg-I2 = 2.800(1)	111.63
HgBr1	Hg-Br3 = 2.491(1) Hg-Br2 = 2.494(1) Hg-Br1 = 2.758(1) Hg-Br1 = 2.787(1)	88.59-132.88	HgI6	Hg-I1 = 2.687(1) Hg-I2 = 2.704(1)	123.06
HgBr2	Hg-Br = 2.443(1)	-	HgI7	Hg-I2 = 2.779(3) Hg-I3 = 2.789(1) Hg-I1 = 2.795(1)	103.22-112.77
HgBr3	Hg-Br = 2.412(1)	-	HgI8	Hg-I3 = 2.778(2) Hg-I2 = 2.793(2) Hg-I1 = 2.806(2)	103.76-112.56
HgBr4	Hg1-Br2 = 2.508(1) Hg1-Br1 = 2.532(1) Hg1-Br3 = 2.734(1) Hg1-Br1 = 2.736(1) Hg1-Br3 = 2.762(1)	90.82-122.15	HgI9	Hg-I3 = 2.785(3) Hg-I2 = 2.788(2) Hg-I1 = 2.801(3)	103.71-112.50
HgBr5	Hg2-Br4 = 2.388(1) Hg1-Br2 = 2.517(2) Hg1-Br3 = 2.533(2) Hg1-Br1 = 2.755(1)	92.84-180	HgI10	Hg3-I5 = 2.617(1) Hg1-I6 = 2.635(1) Hg1-I2 = 2.648(1) Hg1-I1 = 3.080(1) Hg1-I8 = 3.207(1) Hg2-I3 = 2.715(1) Hg2-I9 = 2.749(1) Hg2-I10 = 2.855(1) Hg2-I7 = 2.910(1) Hg3-I4 = 2.623(1) Hg3-I9 = 3.153(1) Hg3-I3 = 3.315(1) Hg4-I8 = 2.744(1) Hg4-I1 = 2.766(1) Hg4-I7 = 2.835(1) Hg4-I10 = 2.876(1)	86.82-149.08

HgBr6	Hg-Br = 2.647(1) Hg-Br = 2.653(1)	124.27	HgI11	Hg1-I1 = 2.658(1)	137.56
HgBr7	Hg2-Br = 2.602(1) Hg2-Br = 2.602(1) Hg2-Br = 2.602(1) Hg2-Br = 2.602(1)	106.26-113.39	HgI12	Hg1-I1 = 2.756(1) Hg1-I4 = 2.780(1) Hg1-I2 = 2.792(1) Hg1-I3 = 2.800(1)	104.33-119.65
HgBr8	Hg1-Br1 = 2.519(1) Hg1-Br2 = 2.565(1) Hg1-Br1 = 3.157(1) Hg1-Br2 = 3.212(1)	86.72-170.20	HgI13	Hg1-I2 = 2.690(1) Hg2-I4 = 2.691(1) Hg2-I3 = 2.697(1) Hg1-I1 = 2.730(1) Hg1-I5 = 2.902(1) Hg1-I6 = 2.915(1) Hg2-I5 = 2.925(1) Hg2-I6 = 2.950(1)	92.66-122.37
HgBr9	Hg1-Br1 = 2.515(1) Hg1-Br2 = 2.528(1) Hg1-Br1 = 2.965(1)	89.90-130.31	HgI14	Hg1-I1 = 2.605(4)	131.23
HgBr10	Hg1-Br2 = 2.440(1) Hg1-Br1 = 2.459(1)	158.41	HgI15	Hg2-I5 = 2.516(1) Hg1-I2 = 2.553(1) Hg1-I1 = 2.574(1) Hg1-I3 = 3.283(1) Hg1A-I2 = 2.570(1) Hg1A-I1 = 2.631(2) Hg1A-I4 = 3.110(2) Hg2-I3 = 2.883(1) Hg2-I4 = 2.883(1) Hg2-I3 = 3.086(1) Hg2A-I4 = 2.673(1) Hg2A-I3 = 2.794(4) Hg2A-I3 = 3.383(1)	85.20-163.60
HgBr11	Hg1-Br4 = 2.519(1) Hg1-Br2 = 2.543(1) Hg1-Br3 = 2.669(1) Hg1-Br3 = 2.792(1)	89.69-116.66	HgI16	Hg1-I2 = 2.644(1) Hg1-I1 = 2.648(1)	142.20
HgBr12	Hg1-Br2 = 2.559(1) Hg1-Br1 = 2.664(1)	101.62-121.74	HgI17	Hg1-I2 = 2.644(4) Hg1-I2 = 2.691(5)	135.01
HgBr13	Hg1-Br2 = 2.593(1) Hg1-Br1 = 2.622(1)	102.03-118.19	HgI18	Hg1-I1 = 2.664(4) Hg1-I2 = 2.674(4)	132.63

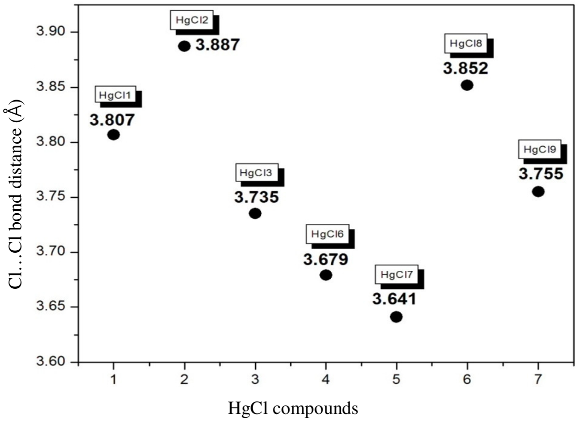

Figure 2. Scatter plot for Cl-Cl bond distances

Table 3. Halogen…Halogen bond distances (Å) and torsion angle (°) in $[HgX]^-$, (X = Cl, Br, I) compounds with symmetry positions

Code	X…X bond distance (Å)	Torsion Angle [1,2,3,4]°	Code	X…X bond distance (Å)	Torsion Angle [1,2,3,4]°
HgCl1	Cl2…Cl2 = 3.807(4)	-	HgBr14	Br1…Br1 = 4.921(1)	Hg1-Br1…Br1^{xix}-Hg1^{xix} = 180.00(2)
HgCl2	Cl…Cl = 3.887(1)	-	HgBr15	Br1…Br2 = 4.479(1)	Hg1-Br2…Br1^{xx}-Hg1^{xx} = 34.57(3)
HgCl3	Cl(1)…Cl(2) = 3.735(1) Cl(2)…Cl(2) = 3.919(1)	Hg-Cl(1)…Cl^{i}(2)-Hg^{i} = 79.95(2)	HgBr16	Br1…Br3 = 3.822(1)	Hg1-Br2…Br4^{xxi}-Hg2^{xxi} = 110.22(2)
HgCl4	Cl1…Cl2 = 4.245(4)	Hg-Cl4…Cl3-Hg^{ii} = -89.41(2)	HgBr17	Br1…Br1 = 4.186(1)	Hg1-Br1…Br1^{xii}-Hg1^{xxii} = -180.00(2)
HgCl5	Cl1…Cl2 = 4.470(5)	Hg-Cl1…Cl3^{iii}-Hg^{iii} = -123.04(2)	HgBr18	Br1-Br1 = 5.296(3)	Hg1-Br1…Br1^{xxiii}-Hg1^{xxiii} = 0.00(5)
HgCl6	Cl2…Cl3 = 3.679(2) Cl1…Cl3 = 3.797(2) Cl2…Cl1 = 3.853(2)	-	HgI1	I7…I7 = 2.737(4) I4…I5 = 2.821(3) I5…I6 = 2.979(3) I6…I7 = 3.421(3)	-
HgCl7	Cl4…Cl4 = 3.641(3) Cl2…Cl3 = 3.839(3)	-	HgI2	I1…I1 = 4.149(2)	Hg1-I1…I1^{xxiv}-Hg1^{xxv} = -180.00(1)
HgCl8	Cl1…Cl3 = 3.852(1)	Hg-Cl3…Cl1^{iv}-Hg^{iv} = 175.79(4)	HgI3	I2…I1 = 4.360(6)	-
HgCl9	Cl11…Cl11 = 3.755(1) Cl1…Cl2 = 3.785(1) Cl1…Cl2 = 3.800(1) Cl1…Cl2 = 3.915(1)	Hg1-Cl11…Cl11^{v}-Hg1^{v} = -180.00(3)	HgI4	I3…I3 = 4.215(2)	Hg-I3…I3^{xxvi}-Hg^{xxvi} = 68.17(2)
HgCl10	Cl3…Cl4 = 5.601(2)	Hg1-Cl4…Cl3^{vi}-Hg1^{vi} = -103.35(5)	HgI5	I1…I2 = 7.337(3)	Hg-I2…I1^{xxvii}-Hg^{xxvii} = -43.36(1)
HgBr1	Br2…Br3 = 3.610(2)	Hg-Br2…Br3^{vii}-Hg^{vii} = 121.58(1)	HgI6	I2…I2 = 4.492(1)	Hg-I2…I2^{xxviii}-Hg^{xxviii} = 179.18(1)
HgBr2	Br…Br = 4.356(1)	Hg-Br…Br^{viii}-Hg^{viii} = -51.14(2)	HgI7	I2…I2 = 4.134(2)	Hg-I2…I2^{xxix}-Hg^{xxix} = 67.55(1)
HgBr3	Br1…Br1 = 4.138(2)	Hg-Br1…Br1^{ix}-Hg^{ix} = -180.00(3)	HgI8	I1…I2 = 4.121(2)	Hg-I2…I1^{xxx}-Hg^{xxxi} = 67.48(4)
HgBr4	Br3…Br3 = 3.915(2)	Hg1-Br3…Br3^{x}-Hg1 = 180.00(5)	HgI9	I2…I3 = 4.137(2)	Hg-I2…I3^{xxxii}-Hg^{xxxiii} = 67.96(1)

HgBr5	Br1…Br4 = 3.662(2) Br1…Br1 = 3.992(2)	Hg-Br4…Br1^{xi}-Hg1^{xi} = 145.00(1)	HgI10	I3…I3 = 4.343(1)	Hg2-I3…I3^{xxxiv}-Hg2^{xxxiv} = -180.00(5)
HgBr6	Br…Br = 4.662(1)	Hg-Br…Br^{xii}-Hg^{xiii} = 2.45(5)	HgI11	I1…I1 = 5.667(2)	Hg1-I1…I1^{xxxv}-Hg1^{xxxv} = 180.00(3)
HgBr7	Br…Br = 5.817(2)	Hg2-Br…Br^{xiv}-Hg2^{xiv} = -61.76(7)	HgI12	I2…I4 = 6.459(1)	Hg1-I4…I2^{xxxvi}-Hg1^{xxxvi} = -164.47(2)
HgBr8	Br1…Br1 = 3.925(1)	Hg1-Br1…Br1^{xv}-Hg1^{xv} = 170.71(2)	HgI13	I5…I6 = 4.249(1)	Hg2-I5…I6-Hg1^{xxxvii} = -175.63(3)
HgBr9	Br1…Br1 = 3.891(2) Br1…Br2 = 3.982(2)	H1-Br1…Br1^{xvi}-Hg1^{xvi} = 180.00(5)	HgI14	I1…I1 = 7.332(1)	Hg1-I1…I1^{xxxviii}-Hg1^{xxxviii} = 180.00(1)
HgBr10	Br2…Br2 = 3.956(1)	Hg1-Br2…Br2^{xvii}-Hg1^{xvii} = -124.06(3)	HgI15	I1-I1 = 3.811(2)	Hg1-I1…I1^{xxxix}-Hg1A^{xxxix} = -156.65(1)
HgBr11	Br3…Br3 = 3.852(1)	Hg1-Br3…Br3^{xviii}-Hg1 = -180.00(2)	HgI16	I1…I2 = 4.594(1)	Hg1-I1…I2^{xl}-Hg1^{xl} = -37.52(2)
HgBr12	Br2…Br2 = 4.083(2)	-	HgI17	I1…I2 = 4.476(6)	Hg1-I2…I1^{xli}-Hg1^{xli} = -134.14(2)
HgBr13	Br1…Br3 = 3.396(1)	-	HgI18	I1…I2 = 4.197(5)	Hg1-I1…I2^{xlii}-Hg1^{xlii} = -176.07(2)

Symmetry codes: (i) x, 1-y, -0.5+z (ii) 0.5-x, 0.5+y, 0.5-z (iii) -x, 0.5+y, 1-z (iv) x, -1+y, z (v) -x, -y, -z (vi) -1+x, y, z (vii) x, 0.5-y, 0.5+z (viii) 0.5+x, 1-y, z (ix) -x, -y, 1-z (x) -x, 1-y, -z (xi) x, -y, 0.5-(xii) 1-x, y, 0.5-z (xiii) 0.5+x, -0.5+y, z (xiv) -0.25-x, -0.25-y, z (xv) 1-x, y, 0.5-z (xvi) 1-x, 2-y, 1-z (xvii) 1-x, y, 0.5-z (xviii) 1-x, -y, 2-z (xix) -1-x, 1-y, -z (xx) 1-x, 1-y, 3-z (xxi) 1-x, -y, 1-z (xxii) 1-x, 1-y, -z (xxiii) x, 1+y, z (xxiv) -x, -y, 1-z (xxv) x, -0.5+y, 1-z (xxvi) 2-x, y, 0.5-z (xxvii) 0.5+x, 1-y, z (xxviii) -x, 0.5+y, -z (xxix) -0.25+y, 0.25+x, 0.25-z (xxx) 1.5-x, y, 0.5-z (xxxi) 1.25-y, -0.25+x, 0.25+z (xxxii) 1-x, -0.5+y, 1-z (xxxiii) 0.5-x, y, 0.5+z (xxxiv) 1-x, 1-y, 1-z (xxxv) -x, 1-y, -z xxxvi) 1.5-x, 0.5+y, 1.5-z (xxxvii) x, 0.5-y. 0.5+z (xxxviii) x, -1+y, z (xxxix) 0.5-x, -0.5-y, 1-z (xl) 1-x, 1-y, 3-z (xli) x, 1+y, z (xlii) -0.5+x, -0.5+y, z

[HgBr]$^{-}$Hybrid materials

The bond lengths of Hg-Br bond lies in an average range of 2.401Å to 2.669Å. The graphical projection of bond distances for these derivatives illustrate that most of the data points lie in between 2.45 to 2.70Å whereas the data points for HgBr2, HgBr3, HgBr8 and HgBr14 shows the deviation from this linearity as presented in Figure 3. The Br-Hg-Br bond angles have wide range from minimum value of 126.49 to 132.85° for molecule HgBr16 and maximum range of 92.84 to 180° for molecule HgBr5 as described in Table 2.

The scatter plot for Br…Br bond distances as shown in Figure 4 illustrates that most of the data points exist in the range of 3.610Å to 3.922Å which shows that the crystal structures are stabilized by secondary interactions as this range is comparable with van der Waals radii. Among all these compounds showing Halogen…Halogen interactions, HgBr8 has the lowest value of 3.396Å.

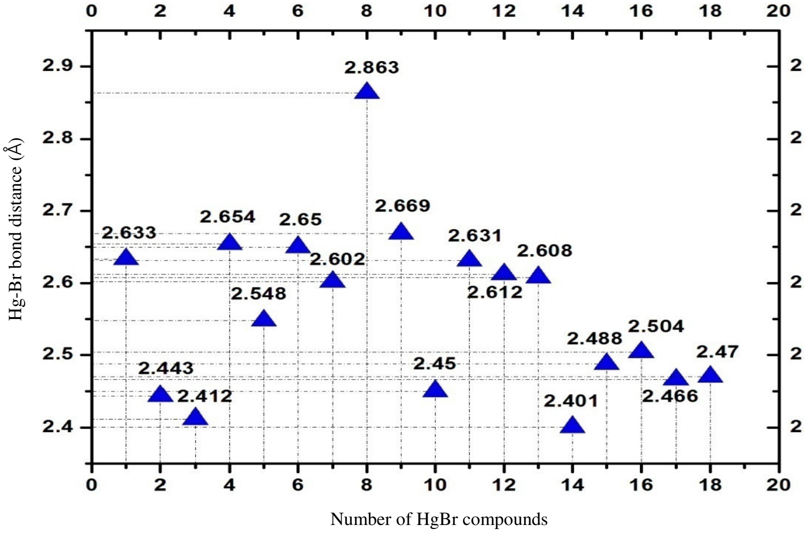

Figure 3. Scatter Plot of the average values of Hg-Br compounds

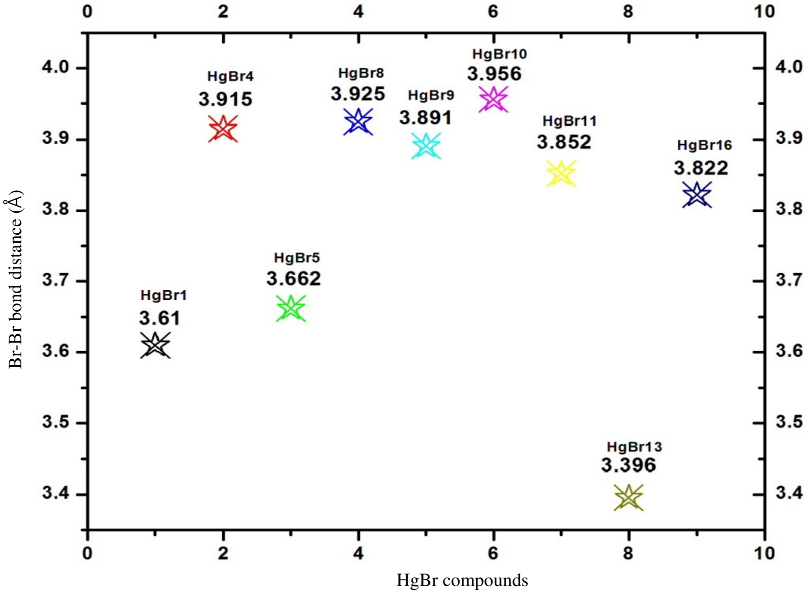

Figure 4. Scatter plot for Br-Br bond distances

[HgI]⁻ Hybrid materials

The bond lengths of Hg-I bond lies in an average range of 2.605Å to 2.785Å. The graphical projection of bond distances for these derivatives illustrate that most of the data points lie in between 2.65 to 2.80Å whereas the data points for HgI8, HgI12, HgI13, HgI14 and HgI15 shows the deviation from this linearity as presented in Figure 5. The I-Hg-I bond angles have wide range from minimum value of 107.74 to 112.98° for molecule HgI2 and maximum range of 85.20 to 163.60° for molecule HgI15 as shown in Table 2.

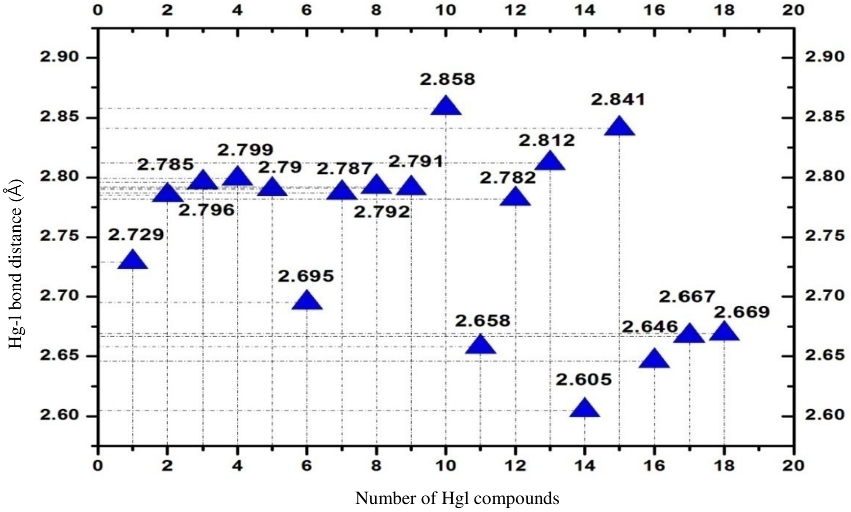

Figure 5. Scatter Plot of the average values of Hg-I bond distances.

While calculating the Halogen…Halogen Interactions based on HgI derivatives, it is found that only two derivatives *i.e*. HgI1 and HgI13 shows the minimum values of 3.420Å and 3.835Å respectively. All other compounds show its minimum values in the range of 4.121Å to 4.956Å which are not comparable with Van der Waals radii and hence cannot be fitted for Halogen…Halogen interactions (Table 3). The minimum value of torsion angle [I-Hg…Hg-I] is 2.15(3)° for the compound HgI11 at 1-x, 1-y, 1-z and x, 0.5-y, 0.5+z symmetry positions, while its maximum value is 180.00(1) for HgI12 with x, -1+y, z symmetry positions as given in Table 3.

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. 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-π = 2.983(1) and C-H…π = 133.8°. 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 6 along *ac*-plane.

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 7.

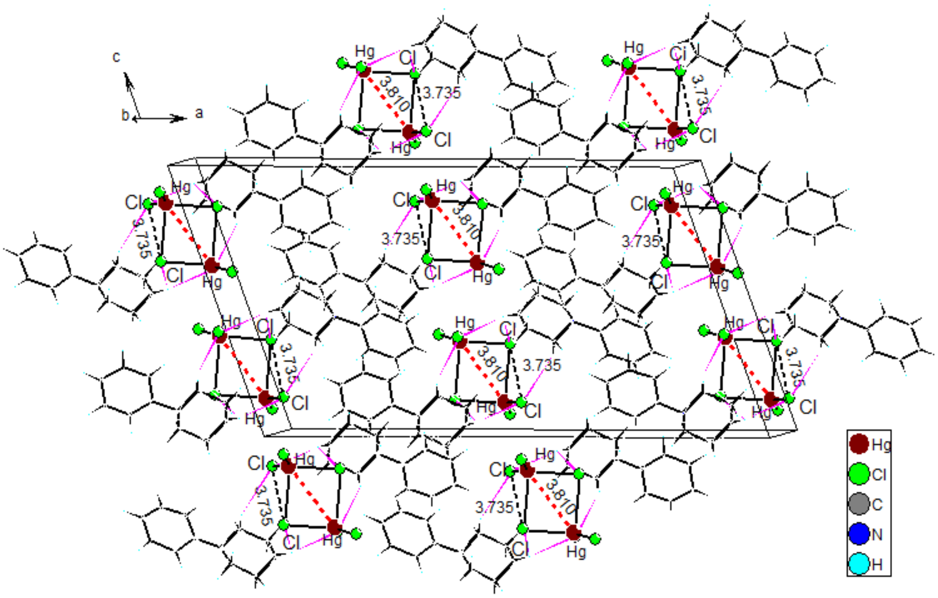

Figure 6. 1D chain pattern of Hg…Hg and Cl…Cl interactions in Phenylpiperazinium trichloromercurate

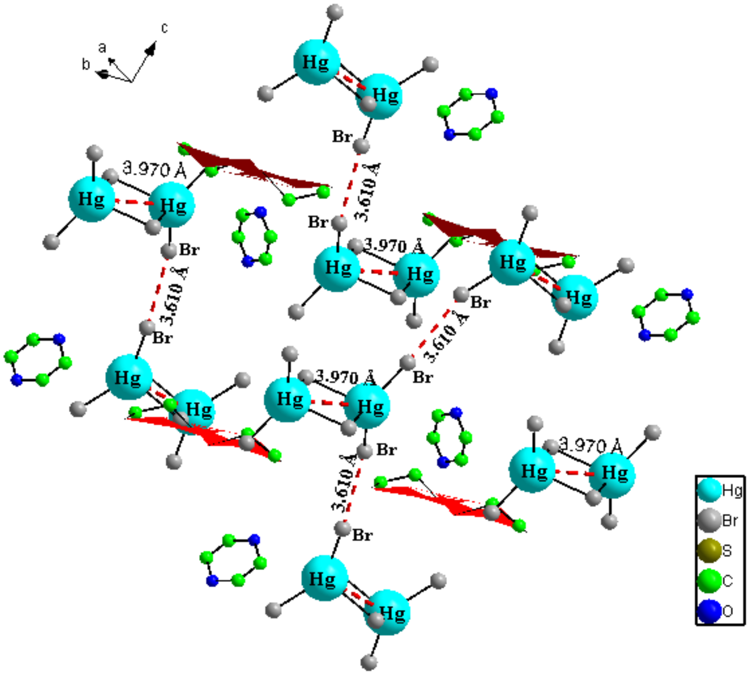

Figure 7. Hg…Hg and Br…Br interactions in HgBr1 derivatives

IR and Raman tensors

IR and Raman spectra tensors have been calculated by using fractional co-ordinate obtained from single crystal XRD data as presented in Table 4.

Table 4. Infra-Red and Raman spectra tensors for HgX derivatives

Compound	Active Mode Equation	Wykoff Positions	Infra-Red	Raman	Hyper-Raman
HgCl12	($\Gamma_{acoustic} = 3A_u$)	WP1 =[2i]	$A_u=1$	$A_g=1$	$A_u=1$
HgCl3	($\Gamma_{acoustic} = A_u + 2B_u$)	WP1 =[8f]	$A_u=1$ $B_u=1$	$A_g=1$ $B_g=1$	$A_u=1$ $B_u=1$
HgCl4	($\Gamma_{acoustic} = A_u + 2B_u$)	WP1 =[4e]	$A_u=1$ $B_u=1$	$A_g=1$ $B_g=1$	$A_u=1$ $B_u=1$
HgCl5	($\Gamma_{acoustic} = A + 2B$)	WP1 =[2a]	$A=1$ $B=1$	$A=1$ $B=1$	$A=1$ $B=1$
HgCl6	($\Gamma_{acoustic} = 3A_u$)	WP3 =[1a, 1h, 2i]	$A_u=3$	$A_g=1$	$A_u=3$
HgCl7	($\Gamma_{acoustic} = B_{1u} + B_{2u} + B_{3u}$)	WP2 =[4c, 8d]	$B_{1u}=2$ $B_{2u}=2$ $B_{3u}=2$	$A_g=2$ $B_{1g}=2$ $B_{2g}=2$ $B_{3g}=2$	$A_u=2$ $B_{1u}=2$ $B_{2u}=2$ $B_{3u}=2$
HgCl8,9,10& HgBr1	($\Gamma_{acoustic} = A_u + 2B_u$)	WP1 =[4e]	$A_u=1$ $B_u=1$	$A_g=1$ $B_g=1$	$A_u=1$ $B_u=1$
HgBr2	($\Gamma_{acoustic} = A_1 + B_1 + B_2$)	WP1 =[4a]	$A_1=1$ $B_1=1$ $B_2=1$	$A_1=1$ $A_2=1$ $B_1=1$ $B_2=1$	$A_1=1$ $B_1=1$ $B_2=1$
HgBr3,4	($\Gamma_{acoustic} = A_u + 2B_u$)	WP1 =[4e]	$A_u=1$ $B_u=1$	$A_g=1$ $B_g=1$	$A_u=1$ $B_u=1$
HgBr5	($\Gamma_{acoustic} = A_u + {}^1E_u + {}^2E_u$)	WP6 =[2c, 2e, 2f, 4i, 4j, 8k]	$A_u=6$ ${}^1E_u=6$ ${}^2E_u=6$	$A_g=3$ $B_g=5$ ${}^1E_g=5$ ${}^2E_g=5$	$A_u=6$ $B_u=4$ ${}^1E_u=6$ ${}^2E_u=6$
HgBr6	($\Gamma_{acoustic} = A_u + 2B_u$)	WP1 =[8f]	$A_u=1$ $B_u=1$	$A_g=1$ $B_g=1$	$A_u=1$ $B_u=1$
HgBr7	($\Gamma_{acoustic} = B_{1u} + B_{2u} + B_{3u}$)	WP3 =[16g, 32h, 8a]	$B_{1u}=3$ $B_{2u}=3$ $B_{3u}=3$	$A_g=2$ $B_{1g}=3$ $B_{2g}=3$ $B_{3g}=3$	$A_u=2$ $B_{1u}=3$ $B_{2u}=3$ $B_{3u}=3$
HgBr8	($\Gamma_{acoustic} = A_u + 2B_u$)	WP1 =[8f]	$A_u=1$ $B_u=1$	$A_g=1$ $B_g=1$	$A_u=1$ $B_u=1$
HgBr9	($\Gamma_{acoustic} = 3A_u$)	WP1 =[2i]	$A_u=1$	$A_g=1$	$A_u=1$
HgBr10	($\Gamma_{acoustic} = A_u + 2B_u$)	WP1 =[8f]	$A_u=1$ $B_u=1$	$A_g=1$ $B_g=1$	$A_u=1$ $B_u=1$
HgBr11	($\Gamma_{acoustic} = A_u + 2B_u$)	WP1 =[4e]	$A_u=1$ $B_u=1$	$A_g=1$ $B_g=1$	$A_u=1$ $B_u=1$
HgBr12	($\Gamma_{acoustic} = A_u + 2B_u$)	WP2 =[4e, 8f]	$A_u=2$ $B_u=2$	$A_g=2$ $B_g=2$	$A_u=2$ $B_u=2$
HgBr13	($\Gamma_{acoustic} = B_{1u} + B_{2u} + B_{3u}$)	WP2 =[4d, 8e]	$B_{1u}=2$ $B_{2u}=2$ $B_{3u}=2$	$A_g=2$ $B_{1g}=2$ $B_{2g}=2$ $B_{3g}=2$	$A_u=2$ $B_{1u}=2$ $B_{2u}=2$ $B_{3u}=2$
HgBr14	($\Gamma_{acoustic} = A_u + 2B_u$)	WP1 =[4e]	$A_u=1$ $B_u=1$	$A_g=1$ $B_g=1$	$A_u=1$ $B_u=1$
HgBr15,16,17	($\Gamma_{acoustic} = 3A_u$)	WP1 =[2i]	$A_u=1$	$A_g=1$	$A_u=1$

Contd…

HgBr18	($\Gamma_{acoustic} = A_u + 2B_u$)	WP2 =[4e, 8f]	A_u =2 B_u =2	A_g =2 B_g =2	A_u =2 B_u =2
HgI1	($\Gamma_{acoustic} = 3A_u$)	WP1 =[2i]	A_u =1	A_g=1	A_u =1
HgI2	($\Gamma_{acoustic} = A_u + {}^1E_u + {}^2E_u$)	WP3=[16f, 4a, 4b]	A_u =3 ${}^1E_u$ =3 ${}^2E_u$ =3	A_g=1 B_g =3 ${}^1E_g$ =3 ${}^2E_g$ =3	A_u =3 B_u =1 ${}^1E_u$ =3 ${}^2E_u$ =3
HgI3	($\Gamma_{acoustic} = 3A_u$)	WP2 =[1f, 2i]	A_u =2	A_g =1	A_u =2
HgI4	($\Gamma_{acoustic} = A_u + 2B_u$)	WP2 =[4e, 8f]	A_u =2 B_u =2	A_g =2 B_g =2	A_u =2 B_u =2
HgI5	($\Gamma_{acoustic} = A_1 + B_1 + B_2$)	WP1 =[4a]	A_1 =1 B_1 =1 B_2 =1	A_1 =1 A_2 =1 B_1 =1 B_2 =1	A_1 =1 A_2 =1 B_1 =1 B_2 =1
HgI6	($\Gamma_{acoustic} = B_{1u} + B_{2u} + B_{3u}$)	WP2 =[4c, 8d]	B_{1u} =2 B_{2u} =2 B_{3u} =2	A_g =1 B_{1g} =2 B_{2g} =2 B_{3g} =2	A_u =2 B_{1u} =2 B_{2u} =2 B_{3u} =2
HgI7	($\Gamma_{acoustic} = A_{2u} + E_u$)	WP3 =[16d, 16e, 32g]	A_{2u} =3 E_u =3	A_{1g} =3 B_{1g} =3 B_{2g} =3 E_g =3	A_{1u} =3 A_{2u} =3 B_{1u} =3 B_{2u} =3 E_u =3
HgI8	($\Gamma_{acoustic} = A_{2u} + E_u$)	WP3 =[16g, 16h, 8e]	A_{2u} =3 E_u =3	A_{1g} =3 B_{1g} =3 B_{2g} =3 E_g =3	A_{1u} =2 A_{2u} =3 B_{1u} =2 B_{2u} =3 E_u =3
HgI9	($\Gamma_{acoustic} = A_{2u} + E_u$)	WP4 =[4c, 4d, 8f, 8g]	A_{2u} =4 E_u =4	A_{1g} =4 B_{1g} =4 B_{2g} =2 E_g =4	A_{1u} =2 A_{2u} =4 B_{1u} =2 B_{2u} =4 E_u =4
HgI10	($\Gamma_{acoustic} = 3A_u$)	WP1 =[2i]	A_u =1	A_g=1	A_u =1
HgI11	($\Gamma_{acoustic} = A_u + 2B_u$)	WP2 =[4e, 8f]	A_u =2 B_u =2	A_g =2 B_g =2	A_u =2 B_u =2
HgI12,13	($\Gamma_{acoustic} = A_u + 2B_u$)	WP1 =[4e]	A_u =1 B_u =1	A_g =1 B_g =1	A_u =1 B_u =1
HgI14	($\Gamma_{acoustic} = A_u + 2B_u$)	WP2 =[4e, 8f]	A_u =2 B_u =2	A_g =2 B_g =2	A_u =2 B_u =2
HgI15	($\Gamma_{acoustic} = A_u + 2B_u$)	WP1 =[8f]	A_u =1 B_u =1	A_g=1 B_g =1	A_u =1 B_u =1
HgI16	($\Gamma_{acoustic} = 3A_u$)	WP1 =[2i]	A_u =1	A_g=1	A_u =1
HgI17	($\Gamma_{acoustic} = A_u + 2B_u$)	WP1 =[4e]	A_u =1 B_u =1	A_g =1 B_g =1	A_u =1 B_u =1
HgI18	($\Gamma_{acoustic} = 2A' + A''$)	WP1 =[4a]	A' =1 A'' =1	A' =1 A'' =1	A' =1 A'' =1

Conclusion

Due to the unique chemical nature of halogen bonding, this intermolecular interaction serves as an additional tool for the development of crystal engineering. The nature of intermolecular interactions between halogen atoms, X···X (X = Cl, Br, I), continues to be of topical interest because these interactions may be used as design elements in crystal engineering. Interactions between halogen atoms such as Cl···Cl, Br···Br and I···I are special cases of halogen bonding. It has become obviously clear that halogen…halogen interaction could very well be utilized as a design element in crystal engineering. On the basis of the short distances obtained between X---X, the halogen interactions are undoubtedly the vital forces responsible for stabilizing a crystal and definitely can play a pivoting role along with M---M and other non-covalent interactions in a crystal structure.

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