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Hg…Hg Interactions in Mercuric Chloride Based Hybrid Materials

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Abstract

To study the secondary interactions in mercuric chloride based hybrid materials, a series of inorganic-organic compounds were analyzed crystallographically. It has been observed that few compounds [Hg1, Hg2, Hg3 and Hg9] validate the phenomenon of mercurophilic interactions with minimum Hg…Hg distance [3.831(1), 3.290(2), 3.810(1) and 3.984(1)Å] whereas the metallophilicity is missing in other compounds of the selected series. The novel entanglements of Hg motifs illustrate 1D and 2D chain pattern of mercurophilic and Cl…Cl interactions. 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. Mercurophilic interactions, Cl...Cl interactions, Hg motifs, 1D and 2D chain pattern, inorganic-organic hybrid materials.

Introduction

Metallophilicity is a name that indicates the affinity of two metal centers for one another. The metallophilic attraction is an almost new form of chemical bonding. Metallophilic interactions are increasingly appreciated as a type of closed-shell interaction that can be used deliberately to form metal-metal contacts (Pyykko 1997). The origin of this attraction seems to be dispersion effects, including their ionic terms (Runeberg *et al* 1999), influenced for heavy elements by relativistic effects (Pyykko *et al* 1997). These interactions are observed between metals with d^{10} and d^{8} electron configurations (Mendizabal and Pyykko 2004). Contacts between metals have particular potential in the field of molecular electronics (Cuniberti *et al* 2005). Interactions between one or more metals with an open-shell have distinct and different bonding consequences that can include covalent metal-metal bond formation (Cotton *et al* 2005) as well as ferro- or antiferro-magnetic coupling (Cotton *et al* 1999; West 1999). The phenomenon of two closed-shell metal centres approaching closer than sum of their van der Waals radii was termed as Metallophilicity (Pyykko 1997; 2004, Linda 2010). These interactions are understood to be a type of dispersion interaction between electron densities on larger and relatively reduced metal centers (Linda 2010). The energy of such bonding is on the order of hydrogen-bonding and can exert a significant influence on solid-state structures (Pyykko 2004).

Metallophilic interactions have strengths similar to typical hydrogen bonds (Pyykko 1997) and can lead to the generation of dimeric or polymeric structures, such as coinage metals with short M-M distances (Melnik and Parish 1986; Schmidbaur 1990; Housecroft 1992; Housecroft 1993; Imhof and Venanzi 1984). Pyykkö concludes that scalar relativistic effects cause these interactions to be stronger than what is to be expected by van der Waals interactions alone (Pyykko 1997). Mercury in particular became the subject of pertinent studies because Hg^{2+} has preference for low coordination number which is favourable for extra metal-metal bonding (Schmidbaur 2000). Hg…Hg interactions are designated as mercurophilic interactions and depicts an interesting phenomenon of $d^{10}…d^{10}$ metal contacts (King *et al* 2002; Bharara *et al* 2005; Vreshch *et al* 2012). The most promising criteria in defining mercurophilic interactions are bond length between two metal centres. This criteria must be modeled free of method error and remain systematic independent of system size to show strength is from metallophilic interactions. As part of our research on secondary interactions in organic-inorganic hybrid materials (Dinesh *et al* 2008), a series of ten compounds (Hg1 to Hg10) whose crystal structures were already reported (Ponnuswamy and Trotter 1984; Aharoni *et al* 1989; Zouari *et al* 1995; Spengler *et al* 1997a; Spengler *et al* 1997a; Spengler *et al* 1998a; Spengler *et al* 1998b; Amami *et al* 2002; Muir *et al* 2004 and Florke *et al* 2006) have been selected based on $[HgCl]^-$ anion for study of mercurophilic interactions through crystallography data.

2. Experimental Data

The experimental data for Hg1 to Hg10 compounds have been collected from Cambridge Structural Data Centre, U.K. and recycled by using Wingx software (Ferrugia 1999) for different types of secondary interactions. The recycled crystal structure data for all the compounds is presented in table 1. The Hg1 crystal structure was refined upto 0.051 with 1191 reflections and Hg2 has R-factor of 0.046 for 3334 reflections. The reliability index of 0.028 has been achieved with 4421 reflections in Hg3 whereas its value is 0.026 for 11417 reflections of Hg4. The value of R-index is 0.040 for 2904 reflections of Hg5 and in Hg6 it is 0.034 for 1804 reflections. The well refined crystal structure of Hg7 with refined parameter of 0.039 and 0.040 for Hg8 shows the structure solution results with 2726 and 3928 F > 2σ(Fo) reflections, respectively. Hg9 and Hg10 derivatives of the selected series were refined upto 0.0529 and 0.0322 values, respectively. The crystallographic data for Hg-centred bond distances and range of bond angles is given in table 2.

Table 1. Crystal structure data for Hg1 – Hg10 compounds.

Code	IUPAC name	Chemical Formula	Cell parameters	Space group	Crystal system	Reference
Hg1	Bis(triphenyl tellurium)di-μ-chloro-Bis(dichloromercurate)	$[Te(C_6H_5)_3^+]_2\ [Hg_2Cl_6^{2-}]$	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	Ponnu Swamy and Trotter 1984
Hg2	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	Aharoni *et al* 1989
Hg3	Phenylpiperazinium trichloromercurate	$C_{10}\ H_{14}\ Cl_3\ Hg\ N_2$	a=25.975(3) Å b=8.013(2) Å c=14.051(2) Å β=110.34(2)°	C 2/c	Mono clinic	Zouari *et al* 1995
Hg4	Bis(piperidinium) Tetrachloromercurate	$(C_5\ N\ H_{12})_2\ HgCl_4$	a=14.954(2) Å b=12.157(1) Å c=9.701(1) Å β=100.76(1)°	$P2_1/n$	Mono clinic	Spengler *et al* 1997(a)
Hg5	Bis-(4-benzylpiperidinium) Tetrachloromercurate	$[\ (C_6\ H_5)\ CH_2\ (C_5\ N\ H_{11})\ ]_2\ HgCl_4$	a=13.603(1) Å b=8.383(1) Å c=12.198(1) Å β=97.66(1)°	$P\ 2_1$	Mono clinic	Spengler *et al* 1997(b)
Hg6	1,3-Propanediammonium Tetrachloromercurate	$(NH_3\ C_3H_6\ NH_3)\ HgCl_4$	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	Spengler *et al* 1998
Hg7	Bis(1,2-ethanediammonium dichloride tetrachloromercurate	$[(NH_3\ C_2H_4\ NH_3)\ Cl]_2\ HgCl_4$	a=12.799(1) Å b=19.842(2) Å c=6.079(1) Å	P n m a	Ortho rhombic	Spengler *et al* 1998
Hg8	Bis(trimethylammonium) tetrachloromercurate(II)	$C_6\ H_{20}\ Cl_4\ Hg\ N_2$	a=18.741(2) Å b=6.302(2) Å c=13.069(3) Å γ=91.68(1)°	$P2_1/n$	Mono clinic	Amami *et al* 2002
Hg9	Tetrameric dichloro(trimethylammonio-p-toluenesulfonamidate) mercury(II)	$C_{40}\ H_{64}\ Cl_8\ Hg_4\ N_8\ O_8\ S_4$	a=7.994(1) Å b=21.634(2) Å c=17.296(1) Å β=93.32(0)°	$P\ 2_1/c$	Mono clinic	Muir *et al* 2004
Hg10	2,2-(propane-1,3-diyl)bis(1,1,3,3-tetramethylguanidinium) tetrachloromercurate	$C_{13}\ H_{32}\ Cl_4\ Hg\ N_6$	a=8.320(4) Å b=18.081(9) Å c=15.809(8) Å β=104.29(0)°	$P\ 2_1/c$	Mono clinic	Florke *et al* 2006

Table 2. Crystallographic data for Hg-centered bond distances (Å) and range of bond angles $(^{o})$

Code	IUPAC name	Hg-Cl bond distance(Å)	Cl-Hg-Cl bond angles $(^{o})$ range
Hg1	Bis(triphenyl tellurium)di-µ-chloro -Bis(dichloromercurate)	Hg-CI(I) = 2.350 (2) Hg-CI(2) = 2.684 (2) Hg-CI(2') = 2.717 (2) Hg-CI(3) = 2.350 (2)	89.6 - 141.3
Hg2	Chloro-n,n,n′,n′-tetramethylformamidinium-bis[dichloro mercury(II)]chloride	Hg-CI(I) = 2.312 (3) Hg-CI(2) = 2.331 (2) Hg-CI(3) = 2.926 (3) Hg-CI(4) = 2.983 (3) Hg-CI(5) = 3.278(3) Hg-CI(6) = 3.296 (3)	79.2 - 168.5
Hg3	Phenylpiperazinium trichloromercurate	Hg-Cl = 2.346(7) Hg-Cl2 = 2.365(7) Hg-Cl1 = 2.624(7) Hg-Cl1 = 2.852(5)	90.9 - 148.5
Hg4	Bis(piperidinium) Tetrachloromercurate	Hg-Cl1 = 2.515(2) Hg-Cl2 = 2.485(2) Hg-Cl3 = 2.431(3) Hg-Cl4 = 2.475(3)	99.3 - 114.9
Hg5	Bis-(4-benzylpiperidinium) Tetrachloromercurate	Hg-Cl3 = 2.424(3) Hg-Cl2 = 2.430(3) Hg-Cl4 = 2.450(3) Hg-Cl1 = 2.614(2)	99.2 - 115.8
Hg6	1,3-Propanediammonium Tetrachloromercurate	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)	88.4 - 180
Hg7	Bis(1,2-ethanediammonium dichloride tetrachloromercurate	Hg-Cl3 = 2.431(1) Hg-Cl4 = 2.474(1) Hg-Cl1 = 2.515(1) Hg-Cl1 = 2.484(1)	99.3 – 116.2
Hg8	Bis(trimethylammonium) tetrachloromercurate(II)	Hg-Cl1 = 2.604(4) Hg-Cl2 = 2.442(10) Hg-Cl3 = 2.430(7) Hg-Cl4 = 2.414(4)	101.4 – 117.5
Hg9	Tetrameric dichloro(trimethylammonio -p-toluenesulfonamidate) mercury(II)	Hg2-Cl2 = 2.325(6) Hg2-Cl2’ = 2.334(6) Hg1-Cl1 = 2.332(5) Hg2-Cl1’ = 2.340(5) Hg1-Cl2 = 3.089(6) Hg1-Cl2’ = 3.065(6)	84.3 – 167.6
Hg10	2,2-(propane-1,3-diyl)bis(1,1,3,3 -tetramethylguanidinium) tetrachloromercurate	Hg-Cl3 = 2.456(1) Hg-Cl2 = 2.502(1) Hg-Cl1 = 2.523(1) Hg-Cl4 = 2.533(1)	104.6 – 120.6

3. Results and discussion

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 Hg2, Hg6 and Hg9 shows the deviation from this linearity as presented in Figure 1. The Cl-Hg-Cl bond angles have wide range from minimum value of 99.3 to 114.9^{o} for molecule Hg4 and maximum range of 88.4 to 180^{o} for molecule Hg6 (Ponnuswamy and Trotter 1984; Aharoni *et al* 1989; Zouari *et al* 1995; Spengler *et al* 1997a; Spengler *et al* 1997a; Spengler *et al* 1998a; Spengler *et al* 1998b; Amami *et al* 2002; Muir *et al* 2004 and Florke *et al* 2006).

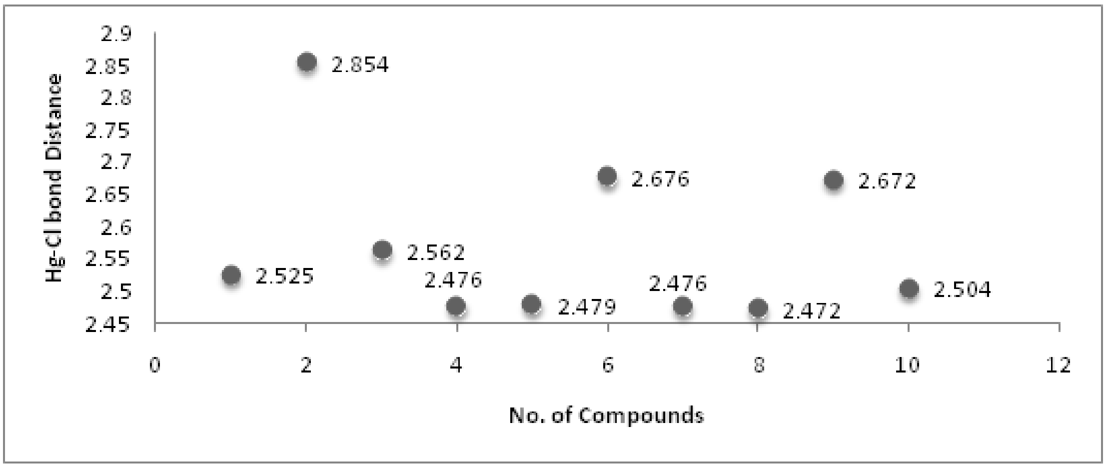


Figure 1. Graphical projection of Hg-Cl bond distances in Hg1-Hg10

The Cl…Cl and Hg…Hg bond distances with their symmetry positions are given in table 3.

Table 3. Cl…Cl and Hg…Hg contacts with symmetry positions.

Molecular Code	Cl…Cl bond distance (Å)	Hg…Hg bond distance (Å)	Symmetry Code
Hg1	Cl2…Cl2'= 3.807(4)	Hg…Hg$'$= 3.831(1)	
Hg2	Cl…Cl = 3.887(1)	Hg…Hg = 3.920(2)	
Hg3	Cl2…Cl2 = 3.919	Hg^{i}…Hg^{ii} = 3.810	x, 1+y, -1+z 1-x, 1+y, 0.5-z
Hg4	Cl4…Cl4 = 4.061(3)	Hg…Hg^{i} = 6.245(1)	-x, 1-y, -z
Hg5	Cl1…Cl3 = 4.471(4)	Hg…Hg^{i} = 7.021(7)	-x, 1.5+y, -z
Hg6	Cl2…Cl1 = 3.853(2) Cl1…Cl3 = 3.797(2) Cl2…Cl3 = 3.679(2)	Hg1^{i}…Hg2^{i} = 5.407(1)	x, -1+y, z -1+x, y, 1+z

Hg7	Cl3…Cl4 = 4.179(2) Cl2…Cl3 = 3.839(3) Cl4…Cl4 = 3.641(3)	Hg1^{i}…Hg2^{i}=6.979(1)	1+x, 1+y, 1+z x, 1+y, z
Hg8	Cl1…Cl3 = 3.852(9) Cl1…Cl2 = 4.053(10)	Hg…Hg^{i} = 6.302(2)	x, -1+y, z
Hg9	Cl1…Cl2 = 3.785(1) Cl1…Cl2 = 3.915(1) Cl1…Cl1 = 3.755(1) C11…C12 = 3.800(1)	Hg1…Hg2^{i} = 4.008(1) Hg1…Hg1^{ii} =3.984(1)	1-x, 0.5+y, 0.5-z 1+x, 0.5-y, 0.5+z
Hg10	Cl1…Cl3 = 5.908(2) Cl1…Cl3 = 5.169(2)	Hg…Hg^{i} = 8.320(1)	1+x, y, z

The Hg…Hg distance in compound Hg1 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 (Linda 2010; Vreshch *et al* 2012). Similar pattern of mercurophilic interactions is observed in Hg2 derivative with Hg…Hg distance of 3.920(2)Å. In Hg3 derivative, Hg atom at symmetry position x, 1+y, -1+z establish a close contact of 3.810Å 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]. 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 2 along ac plane.

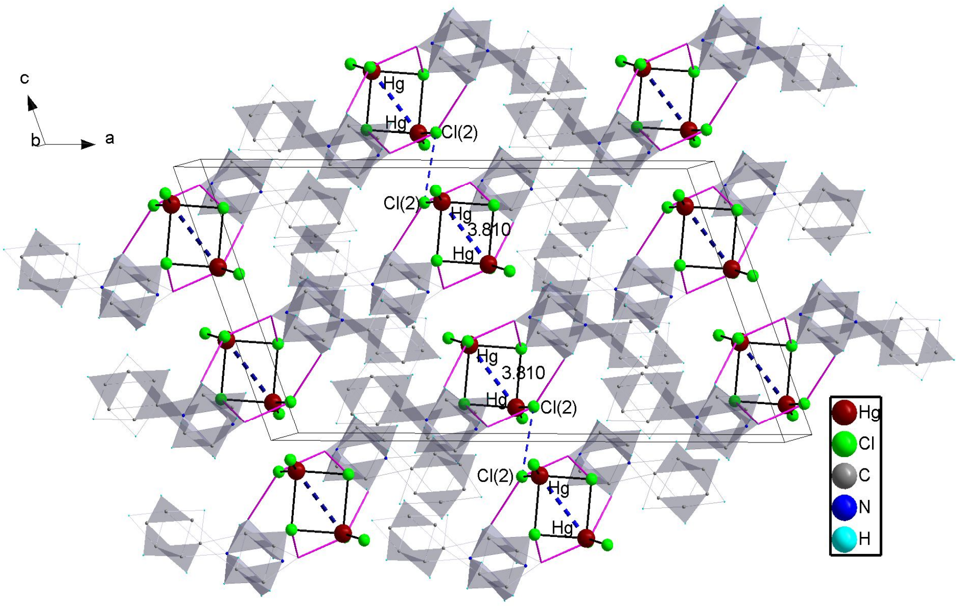


Figure 2. 1D chain pattern of Hg…Hg and Cl…Cl interactions in Phenylpiperazinium trichloromercurate.

The 2D chain pattern of Hg…Hg interactions has been observed in Hg9 [tetramercuric dichloro (trimethylammonio-pptoluenesulfonamide) 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 tetramercuric 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 3. The crystal structure is further stabilized by X-H…A and Cl…Cl secondary interactions.

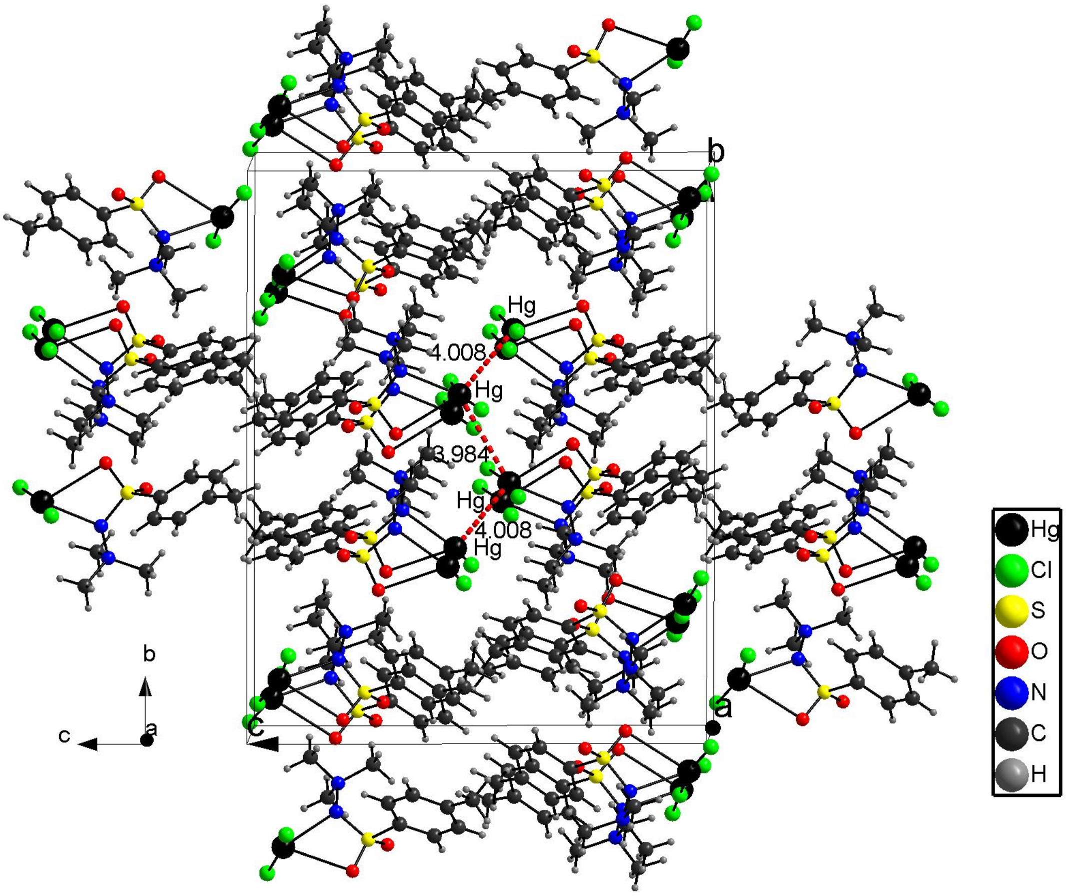
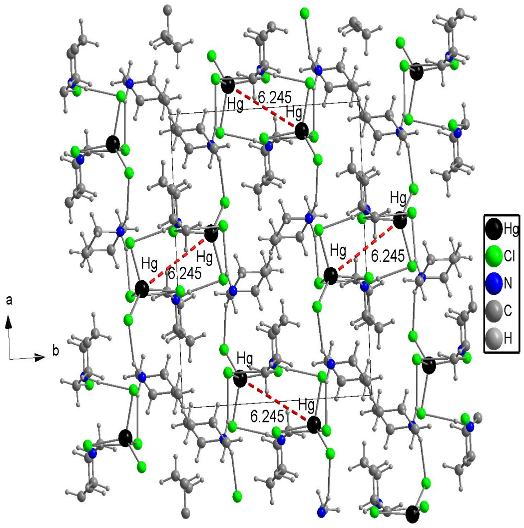
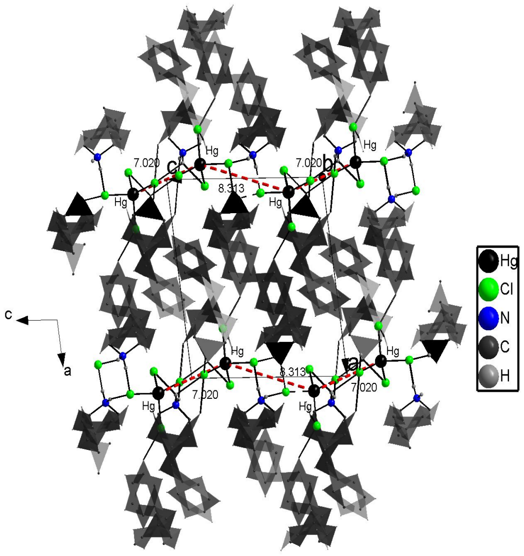


Figure 3. 2D chain pattern of metallophilic Hg…Hg interactions in Tetrameric dichloro (trimethylammonio-p- toluenesulfonamidate) mercury (II) .

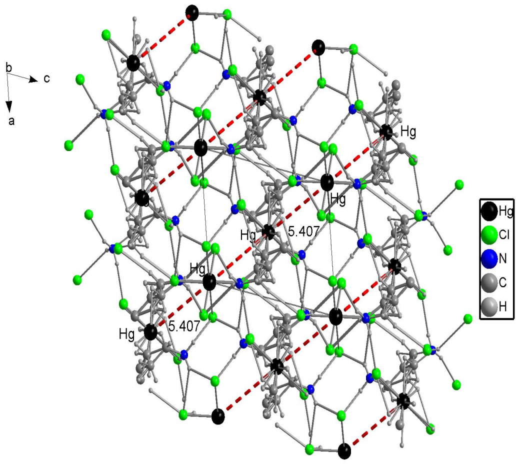
The Hg…Hg bond distances for all other derivatives have been calculated for their minimum values and it has been observed that these distances are more than van der Waals radii and hence cannot be considered as metallophilic interactions but these distances can play role in packing of mercuric chloride as in case of Hg8 an antiparallel arrangement of mercuric chloride through metal…metal contacts. The parallel chains of weak interactions along ac-plane are observed in Hg10 and parallel layers of Hg…Hg contact [5.407Å] in Hg6 compound. Tetramer pattern of tetrachloromercurate through Hg…Hg contact can be drawn in Hg4 along ab-plane. 1D chain pattern of Hg…Hg contacts are seen in Hg7 but not falls in the category of Hg…Hg interactions because of long distance of 6.979Å and true picture of inorganic-organic hybrid material is presented in Hg5 where 4-benzylpiperidinium is held in anti-parallel arrangement between the inorganic layers of tetrachloromercurate but the long distance of Hg…Hg contact [7.020Å] demonstrate the lack of Hg…Hg interaction as revealed in figure 4 (Pyykko 1997; King et al 2002; Pyykko 2004; Dinesh 2008; Linda 2010; Vreshch *et al* 2012).



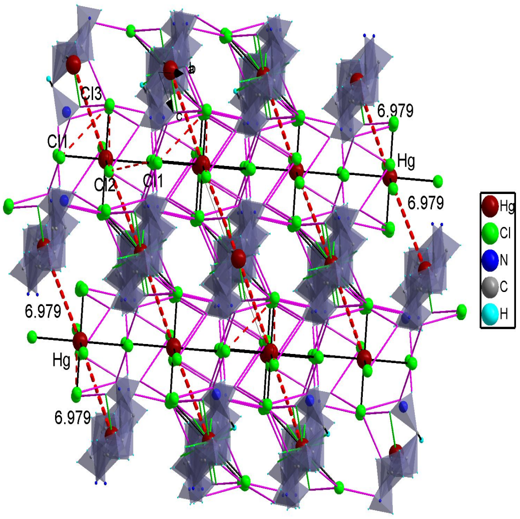
Hg4



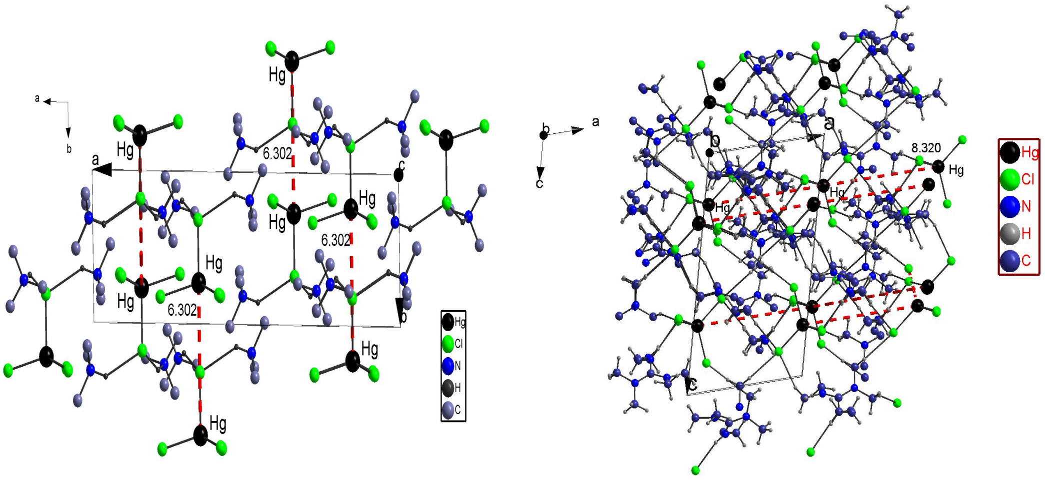
Hg5



Hg6



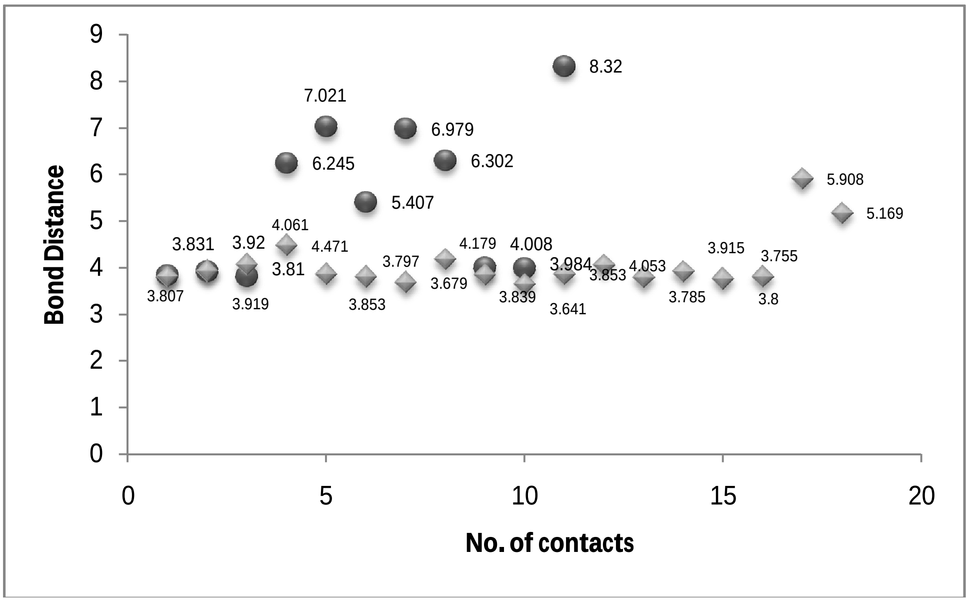
Hg7



Hg8 Hg10

Figure 4. Unit cell packing view of mercuric chloride based compounds with Hg…Hg contacts.

The scatter plot for Cl…Cl and Hg…Hg bond distances illustrate that most of the data points exist in the range of 3.5Å to 4.1Å 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 5.



4. Conclusions

There is substantial congruence between the mercurophilic pattern observed in the selected series of mercuric chloride 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 mercurophilic interactions could be a collective tool to design the new crystal structures.

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References

[1] Aharoni A, Kapon M and Reisner G M 1989 Acta Cryst. C45 40.
[2] Amami M, Smaolen S and Bensalah A 2002 Acta Cryst. E58 m416.
[3] Bharara M S, Bui T H, Parkin S and Atwood D A 2005 Dalton Trans. 3874.
[4] Cotton F A, Murillo C A and Walton R A 2005 Multiple Bonds between metal atoms, Springer Science, New York pp.818.
[5] Cotton F A, Wilkinson G, Murillo C A and Bochmann M 1999 Advanced inorganic chemistry, John Wiley & sons,New York pp.1355.
[6] Cuniberti G, Fagas G and Richter K 2005 Introducing Molecular Electronics, Springer New York p518.
[7] Dinesh J, Rademeyer M, Billing D G and Lemmerer A 2008 Acta Cryst E64 m1598.
[8] Farrugia L J 1999 J Appl Cryst 32 837.
[9] Florke U, Herres-Pawlis S, Heuwing A, Neuba A Seewald O and Henkel G 2006 Acta. Cryst. C62 m234.
[10] Housecroft C E 1992 Coord. Chem. Rev. 115 117.
[11] Housecroft C E 1993 Coord. Chem. Rev. 127 187.
[12] Imhof D and Venanzi L M 1994 Chem Soc Rev 23 185.
[13] King J B, Haneline M R, Tsunoda M and Gabbai F P 2002 J. Am. Chem. Soc. 124(32) 9350.
[14] Linda H D 2010 Dalton Transactions 39 3543.
[15] Melnik M and Parish R V 1986 Coord. Chem. Rev. 70 157
[16] Mendizabal F and Pyykko P 2004 Phys. Chem Chem Phys 6 900
[17] Muir K W, Morris D G and Chii C O 2004 Acta Cryst. E60 m60
[18] Ponnuswamy M N and Trotter J 1984 Acta Cryst. C40 1671
[19] Pyykko P 1997 Chem. Rev. 97 597
[20] Pyykko P 2004 Angew. Chem. Int. Ed Rev. 43 4412.
[21] Pyykko P, Runeberg N and Mendizabal F 1997 Chem. Eur. J. 3 1491
[22] Runeberg N, Schutz M and Werner H J 1999 J.Chem. Phys. 110 7210
[23] Schmidbaur H. 1990 Gold. Bull. 23 11.

[24] Schmidbaur H. 2000 Gold. Bull. 33(1) 3.
[25] Spengler R, Zouari F, BenSalah A and Burzlaff H 1997a Acta Cryst. C53 1407.
[26] Spengler R, Zouari F, BenSalah A and Burzlaff H 1997b Acta Cryst. C53 1566.
[27] Spengler R, Zouari R, Zimmermann H, BenSalah A and Burzlaff H 1998a Acta Cryst. C54 1628.
[28] Spengler R, Zouari R, Zimmermann H, BenSalah A and Burzlaff H 1998b Acta Cryst. C54 icu9800034.
[29] Vreshch V, Shen W, Nohra B, Yip S K, Yam V W, Lescop C and Rean R 2012 Chem. Euro. J. 18(2) 2012.
[30] West A R 1999 Basic Solid State Chemistry, John Wiley & Sons, New York pp.480.
[31] Zouari F, BenSalah A and Hovestreydt E R 1995 Acta Cryst. C51 1563.