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Bang of Hydrogen Bonding on Covalent Bonds in $[HgX]^-$ (X = Cl, Br, I) Based Inorganic-Organic Hybrid Materials

KEYWORDS : Inorganic-organic hybrids, XRD structure analysis, hydrogen interactions, X-H…A bond range, X-Hg…X angle

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ABSTRACT *To understand the role of hydrogen interactions as compared to covalent bonds, series of mercuric halides based inorganic-organic hybrid derivatives have been selected and their single crystal X-Ray data were obtained from Cambridge Structure Data Centre, U.K. The structural data were simulated by using crystallographic software and the geometry of secondary interaction were analyzed for $HgCl_2$, $HgBr_2$, HgI_2 based inorganic-organic hybrid materials. The calculated average value of bond distance Hg…Cl = 2.64Å, Hg…Br = 2.63Å and Hg…I =2.75Å. The calculated average value for X-Hg…X bond angle = 108.3° for HgCl, 138.65° for HgBr and 109.95° for HgI. The detailed hydrogen bond analysis shows that strong-to-moderate hydrogen interactions exists in HgI, strong interactions in HgBr and weak hydrogen interactions in HgCl hybrid derivatives.*

INTRODUCTION

A hybrid material is a material that includes two moieties blended on the molecular scale. Commonly one of these compounds is inorganic and the other one organic in nature. Many natural materials consist of inorganic and organic building blocks distributed on the molecular or nanoscale. In most cases, the inorganic part provides mechanical strength and an overall structure to the natural objects while the organic part delivers bonding between the inorganic building blocks and/or the soft tissue. Typical examples of such materials are bone, or nacre (Kickelbick, 2007). Crystal engineering is the design and synthesis of molecular solid-state structures with desired properties, based on an understanding and exploitation of intermolecular interactions (Evans 2002). The secondary interaction mechanism between the organic and inorganic species is an important tool which is responsible to hold these two different moieties within a single crystal as single entity. Weak chemical interactions between the inorganic and organic entities leave some potential for dynamic phenomena in the final materials, meaning that over longer periods of time changes in the material, such as aggregation, phase separation or leaching of one of the components, can occur (Desiraju, 1989). To understand the mechanism of structural studies in hybrid materials, there is substantial congruence between the hydrogen-interactions and the covalent bonds, which is used as a collective tool to study the structural versatility and stability of materials.

EXPERIMENTAL

Analysis of secondary interactions is a part of our ongoing research on "Crystal engineering of hybrid materials (Dinesh et al., 2015) and to understand the role of hydrogen interactions as compared to covalent bonds, series of mercury based hybrid derivatives have been selected whose single crystal X-Ray data were obtained from Cambridge Structure Data Centre, U.K". The XRD data for all the derivatives were pictorially simulated by using Diamond software through cif-data files and geometry of secondary interactions were analyzed. 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 > 2σ(Fo) reflections, respectively. HgCl9 and HgCl10 derivatives of the selected series have been refined up to 0.0529 and 0.0322 values, respectively. The average values of bond distances and bond angles are presented in table 1(a) & 1(b), respectively.

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 HgBr8 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

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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. HgBr19 New has the R-factor of 0.035 for 5759 independent reflections. Similarly HgBr20 New crystal structure has been refined up to 0.025 with 942 reflections. The average values of bond distances and bond angles are presented in table 2(a) & 2(b), respectively.

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. The average values of bond distances and bond angles are presented in table 3(a) & 3(b), respectively.

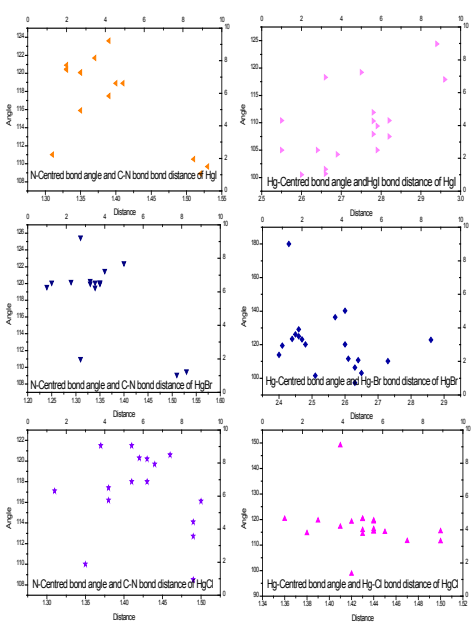

Figure 1: d-θ scatter plots for N and Hg centered bond distances and angles for $[HgX]^-$ based hybrids.

Table 1: Range of Hydrogen bond distances and angles in $[HgX]^-$ based hybrids

Hybrid based on	Range H---A(Å)	Range X---A(Å)	Range X-H---A(°)
HgCl	2.17-3.37	3.13-3.97	104-174°
HgBr	1.78-1.81	2.59-4.07	110-176°
HgI	1.59-3.29	2.45-3.94	113-172°

RESULTS AND DISCUSSION:

The calculated average value of Hg---Cl has 2.64Å bond distance, Hg---Br has 2.63Å bond distance and Hg---I has 2.75Å bond distance. The calculated average value HgCl in X-Hg---X has 108.30° bond angle, HgBr in X-Hg---X has 138.65° bond angle and HgI in X-Hg---X has 109.95° bond angle. In $[HgCl]^-$ based hybrid materials, the H-bond geometry depicts that H---A bond distance lies in the range of 2.17Å to 3.37Å and the X---A length exist in the range of 104° to 174°. H---A bond length has the range of 1.78Å to 1.81Å and donor-acceptor range of 2.59Å to 3.99Å and X-H---A angle exist in 110° to 176° for $[HgBr]^-$ based hybrid materials. In $[HgI]^-$ based hybrid materials, the range X---A, X---A and X-H---A are 1.59 to 3.32Å, 2.45 to 3.94Å and 113° to 172° respectively. The detailed H-bonding analysis concludes that the strong-to-moderate H-bonds exist in $[HgI]^-$, strong H-bonds in $[HgBr]^-$ and weak hydrogen interactions in $[HgCl]^-$ hybrid materials (Desiraju,2002, Braga, 2005). d-θ scatter plots for N-Centered in mercuric-iodide inorganic-organic hybrid derivatives shows that most of the data points lies in 1.32-1.42Å and 116-122° and for Hg-Centered data points this range is 2.6-2.83Å and 100-112° as shown in plot 1 and 2 of fig.1. d-θ scatter plots for N-Centered in mercuric-bromide inorganic-organic hybrid derivatives shows that most of the data points lies in 1.25-1.37Å and 118-122° and for Hg-Centered data points this range is 2.4-2.65Å and 100-125° as shown in plot 3 and 4 of fig.1. d-θ scatter plots for N-Centered in mercuric-Chloride inorganic-organic hybrid derivatives shows that most of the data points lies in 1.37-1.45Å and 116-121° and for Hg-Centered data points this range is 1.38-1.46Å and 110-120° as shown in plot 5 and 6 of fig.1.

CONCLUSION:

The mechanism of structure stability and its importance to design new hybrid materials of desired properties which can not be achieved by mono-type of materials can be analysed by geometrical characteristics of weak interactions such as H-bonds and their versatility and flexibility as compared to the covalent bonds. This experimental analysis concludes that role of H-bonds is predominant among all other secondary interactions and as par with covalent bonds to stabilize the crystal structure of a hybrid material which could be an important tool in crystal engineering. The detailed hydrogen bonding analysis concludes that the strong-to-moderate H-bonds exist in $[HgI]^-$, strong H-bonds in $[HgBr]^-$ and weak hydrogen interactions in $[HgCl]^-$ hybrid materials (Desiraju, 2002; Braga, 2005).

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