$[MX_6]^{3-}$ $[R]^{3+}$ Inorganic-Organic Hybrids: Study of Secondary Interactions

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ABSTRACT: *The two solid state branches i.e. inorganic and organic are clubbed together to form the hybrid composites which revolutionized the use of functional materials in today's energy deficit scientific community. The X-ray crystallographic data of a series of* $[MX_6]^{3-}$ $[R]^{3+}$ *based inorganic-organic hybrid materials have been obtained from IUCr-crystallographic open data base which has been simulated and modeled to design the probable X-H…A, X-H…π, π…π, M…M, H…H type of non- covalent interactions. The inorganic composites and organic moieties are held together through these non-covalent interactions to form the single hybrid composite and characteristics of these non-covalent interactions to form the different structural patterns such as 1D chain, 2D Dimmers, 3D Pattern, etc. have been analyzed through the observations of packing interactions along 100, 010 and 001 crystal planes. The different structural properties through these non-covalent interactions have been analyzed to predict the industrial applications of inorganic-organic hybrids.*

Key Words: *Inorganic-organic hybrids, secondary interactions, 1D Chain, 2D Dimmer, 3D Pattern*

I. Introduction

The research on inorganic organic hybrid materials has experienced a volatile growth with the development of flexible inorganic chemistry based process. Infact, "chimie douce" provided a low temperature processing soft artificial solutions and the flexibility of the colloidal state allowed for mixing of inorganic-organic composites at the nanometer scale practically any ratio to create the so called hybrid materials [1]. The tunable structural properties relationship can be achieved with the control of one composition over another composition to design the nano hybrid derivatives. The design of such hybrids has potential to tailor the properties such as mechanical, electronic, optical, thermal, etc. which have multifunctional applications [2]. Particularly the sphere of "Hybrid-optics" has been terribly productive not solely scientifically however additionally in terms of applications. However there are many hybrids based optical devices already available in the market [3]. The research of functional hybrid material has changed the today's need of designing of new materials with desired applications. The combination of inorganic and organic material into single hybrid composite can enhance their physical and chemical properties which meet with the required applications of today's technocratic society [4]. Since the inorganic metal halides have the mechanical properties whereas the organic moieties are known for their optical properties. Therefore the combination of these two derivatives together into single composite can make the better materials with energy storage applications such as absorption of light energy and conversion of it into the electrical energy which is the basic requirement to fabricate the photovoltaic energy storage devices [5].

II. RESEARCH METHODOLOGY

The X-ray crystallographic data of a series of $[MX_6]^{3-}$ $[R]^{3+}$ based inorganic-organic hybrid materials have been obtained from IUCr-COD, crystallographic open database, U.K. The XRD data were simulated and modeled to design the probable X-H…A, X-H…π, π…π, M…M, H…H type of secondary interactions by using Diamond software [6]. The tabulation of XRD data of twenty six derivatives of the selected hybrids present that most of the hybrid materials exist in monoclinic [i.e. 14 derivatives] whereas 7 exists in triclinic, four in orthorhombic and one in tetra clinic crystal system as presented in Table 1. The crystals structured were refined within the reliability factor of 0.021 to 0.192, as reported in the corresponding references.

Table 1: Crystal Structure Data for $[ZnX_6$, HgX_6, and $CdX_6]^{3-}$, (X = Cl, Br, I) Compounds.

S. No.	Code	Unit Cell	R-Factor	Reference
1	ZnCl12	a=14.635(7)Å, b=12.476(5)Å, c=15.314(7)Å, β=115.73(5)°	0.056	[7]
2	ZnCl18	a=9.748(2)Å, b=13.694(4)Å, c=14.249(4)Å,	0.024	[8]

		α=86.848(7)°, β=74.660(5)°,γ=80.692(7)°		
3	ZnI3	a=8.903(1)Å, b=10.017(1)Å, c=16.709(1)Å, α=73.58(2)°, β=74.84(3)°,γ=65.38(2)°	0.032	[9]
4	HgBr3	a = 6.967(3) Å, b = 9.068(3) Å, c=16.007(5) Å, β = 91.05(3)°	0.060	[10]
5	CdBr7	a = 15.567(1)Å, b = 15.567(1)Å, c = 6.778(1)Å, γ = 120.0^0	0.039	[11]
6	CdBr18	a = 7.889(4)Å, b = 10.519(3)Å, c = 18.712(2)Å, β = $97.69(3)^0$	0.063	[12]
7	CdCl1	a = 16.240(2)Å, b = 7.272(1)Å, c = 7.987(2)Å, β = 116.44(1)°	0.063	[13]
8	CdCl3	a= 33.131(3) Å, b = 7.792(1) Å, c = 7.256(1) Å, α=β=γ=90°	0.028	[14]
9	CdCl5	a = 7.336(1)Å, b = 7.401(2)Å, c = 10.408(4)Å, β = $93.34(2)^0$	0.055	[15]
10	CdCl10	a = 8.830(3)Å, b = 9.692(3)Å, c = 10.579(3)Å, α = 97.81(1)°, β = 111.19(1)°	0.024	[16]
11	CdCl11	a = 3.827(1)Å, b = 7.159(1)Å, c = 8.776(1)Å, α = $87.59(2)^0$, β = $82.73(2)^0$, γ = $75.64(2)^0$	0.027	[17]
12	CdCl13	a = 6.939(1)Å, b = 12.945(2)Å, c = 7.971(1)Å, α=β=γ=90°	0.032	[18]
13	CdCl16	a = 7.119(2)Å,b = 14.408(3)Å, c = 8.640(13)Å, β = $107.98(2)^0$	0.048	[19]
14	CdCl17	a = 17.552(1)Å, b = 9.317(1)Å, c = 7.171(4)Å, β = $110.86(2)^0$	0.025	[20]
15	CdCl23	a = 6.324(1)Å, b = 7.415(4)Å, c = 19.243(1)Å, α=β=γ=90^0	0.049	[21]
16	CdCl25	a = 7.870(1)Å, b = 8.845(1)Å, c = 11.081(1)Å, α = $106.72(4)^0$, β = $91.02(4)^0$, γ = 107.38(5)	0.024	[22]
17	CdCl30	a = 8.163(1)Å, b = 9.718(1)Å, c = 19.676(2)Å, α = $100.45(1)^0$, β = $92.23(1)^0$, γ = $106.27(1)^0$	0.033	[23]
18	CdCl31	a = 12.730(1)Å, b = 12.730(1)Å, c=19.543(2)Å, α=β=γ=90^0	0.052	[24]
19	CdCl39	a = 17.545(2)Å, b= 8.090(2)Å, c = 27.245(1)Å, β = $104.94(2)^0$	0.025	[25]
20	CdCl42	a = 19.770(1)Å, b=13.955(3)Å, c= 15.145(4)Å, β = 110.42(1)°	0.026	[26]
21	CdCl43	a = 9.049(2)Å, b = 9.732(2)Å, c = 10.668(3)Å, α = $71.52(2)^0$, β = $77.44(2)^0$, γ = $80.73(2)^0$	0.032	[27]
22	CdCl47	a = 26.272(1)Å, b= 8.877(2)Å, c = 14.453(3)Å, β = 115.46(3)°	0.037	[28]
23	CdCl51	a = 28.839(1)Å, b= 3.731(1)Å, c = 17.846(4)Å, β = 123.26(3)°	0.043	[29]
24	CdCl52	a = 15.145(2)Å, b=13.887(2)Å, c= 11.594(2)Å, β = 102.86(2)°	0.192	[30]
25	CdCl54	a = 7.726(1)Å, b = 7.223(1)Å, c = 12.761(1)Å, β = 95.48(2)°	0.021	[31]
26	CdCl59	a = 8.886(2)Å, b = 14.116(3)Å, c = 14.251(3)Å α = 87.92(3)°, β = 71.88(3)°, γ = 75.20(3)°	0.053	[32]

III. RESULTS AND DISCUSSION

The inorganic-organic hybrid derivatives are held together through non-covalent secondary interactions in single composite. These secondary interactions are holding together the inorganic metal halides and the organic phenyl moieties together in one composite structure. The X-H…A secondary interaction represent the X-H as a C-H or N-H functional group of organic moieties and A is the halide functional group of the inorganic component. The average value of secondary bond distance through hydrogen with the organic moiety and inorganic component [(H…A)Å] lies in the range of 1.81(1) Å to

2.99(2) Å with an angular attachment [(X-H…A)Å] within the range of 104.0(1)° to 177.0(1)°**.** The descriptions of these secondary interactions between the organic moiety and inorganic component have different structural patterns as explained by Desiraju and Co-Workers [33-34]. Fig. 1 represents the 2D dimmer pattern of hybrid material along a-axis held together through C-H…Br interaction.

The 1D chain pattern is observed in ZnCl12, CdBr7, CdBr18, CdCl1, CdCl3, CdCl5, CdCl16, CdCl17, CdCl23, CdCl25, CdCl30, CdCl31, CdCl42, CdCl51 and HgBr3 hybrid derivatives. 2DDimer pattern is observed in ZnCl18, CdCl47 and CdCl54 hybrid derivatives whereas the 3D pattern of X-H…A type of secondary interactions has been observed in CdCl10, CdCl11, CdCl13, CdCl39, CdCl43, CdCl52, CdCl59 and ZnI3 hybrid derivatives.

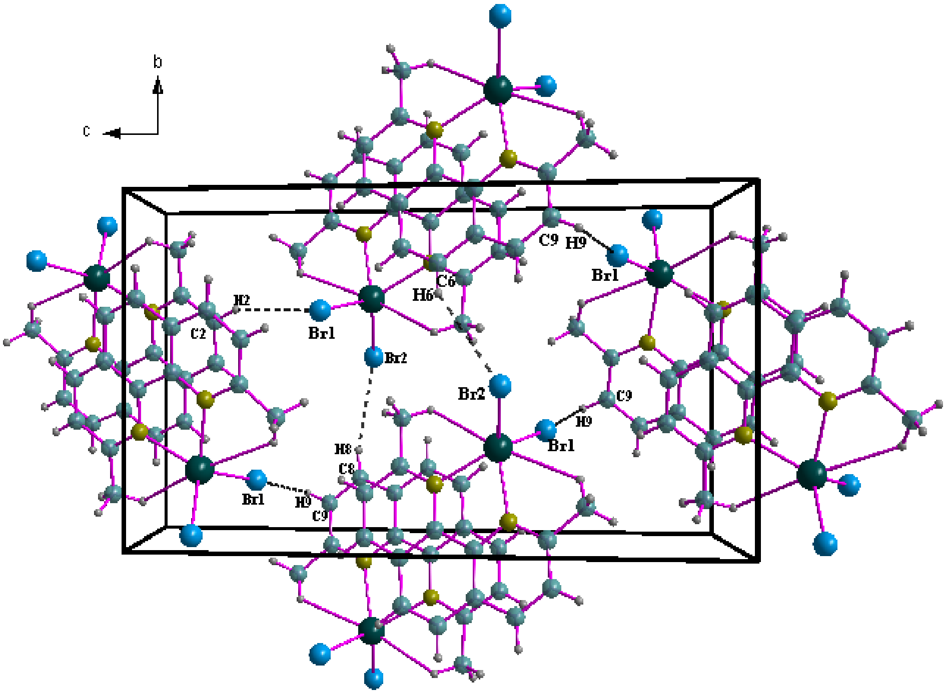

Figure 1: 2D pattern of inorganic organic hybrid material along a-axis held with C-H…Br interaction.

Table 2 Crystallographic data for d-θ is presented in this table.

Code	**X-H…A**		**Code**	**X-H…A**	
	(H…A)Å	**(X-H…A)°**		**(H…A)Å**	**(X-H…A)°**
CdBr7	2.74(1) 2.70(1)	151.0(1) 160.0(1)	CdCl42	1.88(1) 2.38(2)	136.8(1) 170.0(5)
CdBr18	2.98(1)	149.0(1)	CdCl43	2.92(3) 2.80(3) 2.83(3)	124.3(3) 147.3(3) 163.2(2)
CdCl10	2.60(1) 2.58(1) 2.45(1) 2.32(1)	157.0(1) 149.0(1) 156.0(1) 104.0(1)	CdCl47	2.39(1) 2.48(1) 1.98(1) 2.30(1) 2.74(1)	161.0(1) 156.0(1) 132.0(1) 141.0(1) 122.0(1)
CdCl11	1.87(5) 1.95(5) 2.57(6) 2.66(7) 2.46(8)	174.0(4) 165.0(5) 124.0(6) 138.0(6) 158.0(6)	CdCl51	1.90(4)	172.0(6)
CdCl13	2.53(1) 2.48(1) 2.69(1) 2.10(1) 2.54(1)	136.2(1) 157.4(1) 118.5(1) 127.4(1) 138.8(1)	CdCl52	2.98(1) 2.76(3) 2.93(4) 2.83(2) 2.99(3)	123.2(2) 117.1(3) 125.9(2) 109.1(2) 111.1(2)

CdCl16	2.05(1) 2.03(1) 2.46(1)	158.0(1) 166.0(1) 152.0(1)	CdCl54	2.60(1) 2.77(1)	154.0(1) 114.0(1)
CdCl17	2.83(1) 2.84(1)	171.0(1) 132.0(1)	CdCl59	2.38(1) 2.47(1) 2.54(1) 2.88(1) 2.38(1) 2.51(1) 2.93(1) 2.33(1) 2.37(1) 2.61(1) 2.75(1) 2.44(1) 2.40(1) 2.38(1) 2.55(1) 2.91(1)	176.0(1) 157.0(1) 148.0(1) 121.0(1) 176.0(1) 149.0(1) 123.0(1) 162.0(1) 172.0(1) 140.0(1) 127.0(1) 159.0(1) 167.0(1) 177.0(1) 143.0(1) 128.0(1)
CdCl23	1.97(1) 2.02(1)	167.0(1) 159.0(1)	HgBr3	1.81(1) 2.14(1) 1.99(1)	153.0(1) 157.0(1) 159.0(1)
CdCl25	2.99(2)	172.3(1)	ZnCl12	2.90(1) 2.60(1) 2.75(1) 2.71(1) 2.85(1) 2.80(1) 2.74(1) 2.62(1) 2.55(1) 2.92(1) 2.34(1)	165.0(1) 155.0(1) 169.0(1) 137.0(1) 167.0(1) 131.0(1) 147.0(1) 134.0(1) 151.0(1) 152.0(1) 177.0(1)
CdCl30	1.82(1) 2.01(1) 1.89(1) 1.92(1) 2.66(5) 2.54(5) 2.56(4) 2.50(4) 2.09(5)	172.2(1) 171.3(1) 168.9(1) 167.6(1) 137.0(4) 144.0(5) 169.0(4) 159.0(6) 172.0(6)	ZnCl18	2.82(1) 2.82(1) 2.80(1) 2.69(1) 2.80(1)	140.0(1) 147.0(1) 164.0(1) 159.0(1) 133.0(1)
CdCl31	2.12(1)	176.0(8)	ZnI3	2.81(1) 2.87(1)	111.0(1) 111.0(1)
CdCl39	2.56(1) 2.37(1) 2.31(1) 2.41(1) 2.31(1) 2.03(1) 2.54(1) 2.28(1) 2.34(1) 2.13(1)	138.0(1) 144.0(1) 169.3(1) 151.0(1) 161.8(1) 167.2(1) 156.9(1) 119.5(1) 150.2(1) 152.3(1)			

The centroid…centroid (π…π) Å distance lies in the range of 3.633(2) Å for CdBr18, 3.731(7) Å for CdCl51, 3.669(3) Å for ZnCl12 and 3.590(7) Å for ZnCl18 which explains the role of such type of secondary interactions within the organic moieties. The d-θ cut-off criterion for secondary interactions presents that the above mentioned π…π distances falls in the range of very weak secondary interactions and hence does not play a predominant role in structural motifs.

The metal…metal bond distance lies in the range of 3.514(1) Å to 3.876(4) Å which further shows the non-existence of such interactions in hybrids. The halogen…halogen bond distances lies in the range of 3.452(1) Å to 3.990(1) Å and as per the X…X cut-off criterion for bond distance, such type of secondary interactions does not play vital role in structural motifs.

IV. CONCLUSIONS

The research of inorganic organic hybrid materials is one of the most important areas of science and technology as such type of materials has advanced applications in energy storage devices. The combination of functional inorganic with the organic components made the hybrid materials to have wide range of industrial applications in materials science. The design the properties of these hybrids depends upon the secondary non-covalent interactions such as X-H…A, X-H…π, π…π, M…M and H…H which plays an important role in holding the two pure research areas (organic and inorganic) into single hybrid composite. It can be concluded that the d-θ cut-off range for non-covalent interactions in $[MX_6]^{3-}$ $[R]3^{+}$ type of hybrids exists in the range of 1.8 to 2.9 Å for hydrogen…acceptor distance and the donor…acceptor angle of 104 to 177°. The non-existence of π…π, X-H…π, M…M, H…H concludes that the organic layers are held together through the inorganic components only. The structural versatility of these hybrids may be concluded through their structural motifs. The present research study could be a tool to design the inorganic-organic functional hybrid materials with tailored properties.

V. References

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