



# Structural-Stability Relationship in A Series of $[\text{ZnX}]^-$ Inorganic Organic Hybrid Materials

Research Article

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**Abstract.** To scrutinize the role the weak interactions in structure-stability of  $[\text{ZnX}]^-$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) based derivatives, three series of inorganic-organic hybrid materials were studied through single crystal X-ray crystallographic data obtained from IUCr in CIF format. The organic constituent of the hybrid compounds is holding the inorganic moiety through D-H...X interactions, where D is N, C or O of organic moiety acts as H-donor atom and X of inorganic component is Cl, Br I or F behaves as H-acceptor atom. The structural parameters such as the Zn-X bond distance lies in the range of 2.019(5) Å [ $\text{ZnF-3}$ ] to 2.730(4) Å [ $\text{ZnCl-1}$ ] and X-Zn-X bond angle has minimum value of  $82.35^\circ$  and maximum value of  $180^\circ$  for [ $\text{ZnF-3}$ ], were calculated. The maximum twist of X-Zn...Zn-X =  $179.8(3)^\circ$  at symmetry position of 0.5+x, 0.5-y, 0.5+z is observed in [ $\text{ZnBr-7}$ ] derivative.

**Keywords.** Non-covalent interactions; Structure stability; Hg motifs; Mercuriphilic interactions and 1D-2D structural parameters

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## 1. Introduction

Crystal engineering is the understanding of intermolecular interactions in the context of crystal packing and the utilization of such understanding in the design of new solids with desired physical and chemical properties [1]. It is a subject of great scope and application that has developed by a coming together of thought streams from many other subjects. During the last

30 years, it has attracted the attention and interest of a varied group of scientists, notably crystallographers and chemists [2]. A molecular crystal is a periodic assembly of molecules. This regular arrangement is held together by weak intermolecular interactions that are weaker than the intramolecular interactions that hold atoms together-covalent bonds. So, intermolecular interactions in crystals are also called non-covalent [3]. Indeed, the words “weak” and “strong” are quite subjective [4]. The strongest hydrogen bond, say the quasi-covalent symmetrical interaction in [HF<sub>2</sub>]<sup>-</sup> anion, is worth around 50 kcal mol<sup>-1</sup> while the weakest covalent bond, say the C–I bond, is worth only around 30 kcal mol<sup>-1</sup> [5]. Many interactions that could be important in the context of crystal packing lie in the lowest range of energies between 0.5 and 5 kcal mol<sup>-1</sup> [6]. Organic-inorganic hybrid materials do not represent only a creative alternative to design new materials and compounds for academic research, but their improved or unusual features allow the development of innovative industrial applications. Now a days, most of the hybrid materials that have already entered the market are synthesised and processed by using conventional soft chemistry based routes developed in the eighties.

Organic-inorganic hybrid materials are materials prepared by combining organic and inorganic building blocks [7]. The development of such materials, which have already found numerous applications, is one of the big achievements of sol-gel science [8]. The notion is to create materials with new combinations of properties by combining inorganic and organic building blocks on a molecular level [9]. Organic-inorganic hybrid 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 [10].

## 2. Experimental Details

All the structures were pictorially simulated by using Diamond software [11] through cif-data files and geometry of secondary interactions were analyzed as shown in Table 1 and 2.

In Table 1 compound code numbers are given to each cif-data files of ZnCl, ZnBr, ZnI and ZnF. Their IUPAC names are also mentioned in this table with their chemical formula, cell parameters (Å<sup>o</sup>), space group and crystal structure for the individual cif-data file, their refinement structure value is also mentioned in Table 1.

Crystallographic data for Zn-centered bond distances (Å) and range of bond angles (°) X-Zn-X in [ZnX]<sup>-</sup> (where X = Cl, Br, I, F) is also calculated in Table 2.

Different structural motifs were obtained within the organic moiety through  $\pi$ -interactions such as a C-H... $\pi$  interaction in ZnBr<sub>3</sub> with H91A atom at symmetry position 0.5-x, 1-y, 0.5+z in which  $\pi$  acts as acceptor of H91A atom at symmetry position 0.5-x, 1-y, 0.5+z of organic moiety of the metal-organic derivatives linking the organic components in 1D chain of C-H... $\pi$  interactions as shown in Figure 1.

**Table 1.** Crystal Structure Data for Zinc based metal-organic derivatives

Code with Ref.	Chemical Formula	IUPAC Name	Cell Parameters ( $\text{\AA}$ , $^\circ$ )	Crystal System Space group	Structure Refinement factor
ZnCl1 [12]	$C_{20}H_{49}Cl_6N_8O_{0.5}Zn_3$	1,4,8,11-tetraazacyclotetradecane(cyclam) with zinc(II) chloride	a=17.950(5), b=17.950(1), c=10.907(2) $\alpha = \beta = \gamma = 90$	Tetragonal  I -42d	0.047
ZnCl2 [13]	$C_6H_{24}Cl_2N_4O_3Zn$	Racemicchloro [tris(2-amino ethyl)amine] zinc(II)chloride trihydrate	a=15.556(3), b=7.682(2), c=12.384(2) $\beta = 96.80(2)$	Monoclinic  P2 <sub>1</sub> /a	0.040
ZnCl3 [14]	$C_{12}H_{32}Cl_4N_2Zn$	TetraethylammoniumTetramethyl ammoniumTetrachlorozincate(II)	a=13.087(2), b=13.087(2), c=11.793(1) $\alpha = \beta = \gamma = 90$	Tetragonal  P-42 <sub>1</sub> m	0.041
ZnCl4 [15]	$C_{37}H_{20}Cl_3N_2NaO_9Zn_2$	Zinc(II)Chloride-Methanol Complex of 2-[(1,3-Dihydro-1,3-dioxo-2H-inden-2-ylidene)	a=12.060(3), b=10.027(8), c=8.046(2) $\alpha = 76.36(5)$ , $\beta = 89.08(2)$ $\gamma = 66.09(4)$	Triclinic  P-1	0.048
ZnCl5 [16]	$C_{10}H_{24}Cl_2N_4O_4Zn$	Chloro(1,4,7,11-tetraazacyclotetradecane-N,N',N'',N''') zinc(II)Perchlorate	a=13.716(1), b=14.969(3), c=15.925(1) $\alpha = \beta = \gamma = 90$	Orthorhombic  Pcab	0.054
ZnCl6 [17]	$C_{12}H_{27}ClF_6N_3PZn$	Chloro(N,N',N''-trimethyl-1,5,9-triazacyclododecane- $\kappa^3N$ )zinc(II) Hexafluorophosphate	a=15.896(2), b=11.169(5), c=10.365(1) $\alpha = \beta = \gamma = 90$	Orthorhombic  Pna2 <sub>1</sub>	0.017
ZnCl7 [18]	$C_{11}H_{26}Cl_2N_4O_4Zn$	Chloro(1,4,8,12-tetraazacyclopentadeca $\kappa^4N$ )zinc(II) Perchlorate	a=9.850(7), b=15.118(1), c=11.957(8) $\beta = 95.83(1)$	Monoclinic  P2 <sub>1</sub> /n	0.063
ZnCl8 [19]	$Cl_4K_3NO_3Zn$	The double-anion salts $M_3$ $[ZnCl_4]NO_3$ ( $M = K^+$ and $NH_4^+$ )	a=9.256(3), b=9.726(3), c=12.073(3) $\alpha = \beta = \gamma = 90$	Orthorhombic  Pnma	0.044
ZnCl9 [20]	$C_4H_{14}Cl_2N_6S_2Zn$	Transition metal complexes with thiosemicarbazide-based ligands. XLIII.Chlorobis (3-methyl isothiosemicarbazide- $\kappa^2N^1, N^4$ ) zinc(II)chloride	a=9.402(2), b=10.121(3), c=13.710(3) $\alpha = \beta = \gamma = 90$	Orthorhombic  P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	0.065
ZnCl10 [21]	$C_6H_{14}ClNO_3Zn$	Redetermination of chloro (triethanolaminate)	a=7.401(9), b=8.016(6), c=8.291(1)	Triclinic	0.021

		zinc(II) at 150 K	$\alpha=89.41(1)$ , $\beta=77.54(1)$ , $\gamma=74.66(1)$	P-1	
ZnCl11 [22]	$C_{58}H_{48}Cl_2N_8$ $O_{10}Zn_2$	Bis[aquachlorobis(1,10-phenanthroline)zinc(II)] benzene-1,4-dioxyacetate dihydrate	$a=9.950(6)$ , $b=12.060(1)$ , $c=12.810(1)$ $\alpha=61.95(3)$ , $\beta=80.65(4)$ , $\gamma=73.92(3)$	Triclinic  P-1	0.042
ZnCl12 [23]	$C_{23}H_{23}Cl_2N_5$ $O_5Zn$	{N-[Bis(2-pyridyl)methyl]-N,N-bis(2-pyridyl)methylamine- $\kappa^5$ N}chloro zinc(II) perchlorate monohydrate	$a=14.635(7)$ , $b=12.476(5)$ , $c=15.314(7)$ $\beta=115.726(5)$	Monoclinic  P2 <sub>1</sub> /n	0.056
ZnCl13 [24]	$C_{12}H_{24}Cl_2N_6$ $S_3Zn$	Tris(allylthiourea-S)chloro zinc(II) chloride	$a=11.050(4)$ , $b=11.050(4)$ , $c=16.042(1)$ $\alpha=\beta=90$ , $\gamma=120(1)$	Trigonal  R3	0.037
ZnCl14 [25]	$C_{24}H_{18}ClN_5O$ $_4Zn$	Chlorobis(1,10-phenanthroline- $\kappa^2$ N,N')zinc(II) nitrate monohydrate	$a=9.661(1)$ , $b=11.102(2)$ , $c=12.000(2)$ , $\alpha=67.66(3)$ , $\beta=71.00(3)$ , $\gamma=71.65(3)$	Triclinic  P-1	0.038
ZnCl15 [26]	$C_{27}H_{25}Cl_2N_5$ $O_2Zn$	Aquachloridobis(1,10-phenanthroline- $\kappa^2$ N,N')zinc(II) chloride N,N-dimethyl formamidesolvate	$a=9.674(3)$ , $b=11.610(5)$ , $c=12.749(5)$ $\alpha=67.004(1)$ , $\beta=85.995(1)$ , $\gamma=80.025(1)$	Triclinic  P-1	0.033
ZnCl16 [27]	$C_5H_9ClNO_5P$ Zn	Furfurylammonium chloride zincophosphate	$a=12.759(4)$ , $b=9.634(2)$ , $c=8.629(2)$ $\beta=106.233(3)$	Monoclinic  P2 <sub>1</sub> /c	0.025
ZnCl17 [28]	$C_{12}H_{18}Cl_2N_6$ $O_2Zn$	Chlorido(pyridine-2-carboximidamide- $\kappa^2$ N <sup>1</sup> ,N <sup>2</sup> )zinc(II) chloride dihydrate	$a=7.166(1)$ , $b=9.712(1)$ , $c=13.233(3)$ $\alpha=92.225(3)$ , $\beta=96.138(3)$ , $\gamma=104.302(3)$	Triclinic  P-1	0.042
ZnCl18 [29]	$C_{36}H_{26}BiCl_5$ $N_6OZn$	Chloridobis(1,10-phenanthroline)zinc(II) tetrachloride(1,10-phenanthroline)bismuthate(III) monohydrate	$a=9.748(2)$ , $b=13.694(4)$ , $c=14.249(4)$ $\alpha=86.848(7)$ , $\beta=74.660(5)$ , $\gamma=80.692(7)$	Triclinic  P-1	0.024
ZnCl19 [30]	$C_{46}H_{37}ClN_6O$ $_5Zn$	zinc(II) coordination polymer incorporating [1,1'-biphenyl]-4,4'-dicarb	$a=8.936(2)$ , $b=9.781(2)$ , $c=22.382(5)$ $\alpha=86.696(2)$ ,	Triclinic	0.050

		oxylate and $N,N'$ -bis(pyridin-3-ylmethyl)-[1,1'-biphenyl]-4,4'-dicarboxamide ligands	$\beta=80.675(2)$ , $\gamma=89.888(2)$	P-1	
ZnCl20 [31]	$C_{26}H_{28}Cl_2F_4$ $N_{12}O_4Zn$	Poly[[ $\mu$ -chlorido- $\mu$ -[2-(2,4-difluorophenyl)-1,3-bis-(1,2,4-triazol-1-yl)propan-2-ol- $\kappa^2$ : $N^4:N^4$ ]-zinc] chloride dihydrate]	$a=10.231(6)$ , $b=11.812(6)$ , $c=14.359(9)$ $\alpha=91.191(7)$ , $\beta=107.481(5)$ , $\gamma=106.074(6)$	Triclinic	0.080
ZnBr1 [32]	$C_{12}H_{18}BrN_3$ OZn	{ $N$ -[3-(2-Aminoethylamino)propyl]salicylideneaminato- $O,N,N',N''$ } bromo zinc(II)	$a=19.951(6)$ , $b=7.170(2)$ , $c=19.761(8)$ $\alpha=\beta=\gamma=90$	Orthorhombic Pbna	0.048
ZnBr2 [33]	$C_6H_{16}Br_2N_2$ Zn	Dibromo( $N,N,N',N'$ -tetramethylethane-1,2-diamine) zinc(II)	$a=8.099(5)$ , $b=11.777(4)$ , $c=24.353(2)$ $\beta=99.473(3)$	Monoclinic $P2_1/n$	0.045
ZnBr3 [34]	$C_{21}H_{27}Br_2N_3$ $NiO_4Zn$	{[ $\mu$ - $N,N'$ -Bis(salicylidene)-1,3-propane diaminato]( $N,N$ -dimethylformamide)(methanol)nickel(II)} dibromozinc(II)	$a=10.530(1)$ , $b=14.418(1)$ , $c=16.333(1)$ $\alpha=\beta=\gamma=90$	Orthorhombic $P2_12_12_1$	0.036
ZnBr4 [35]	$C_{13}H_{23}Br_2N_3$ Zn	[( $S,S$ )- $N$ -(1-{6-[1-(Dimethylamino)ethyl]pyridin-2-yl}ethyl)- $N,N$ -dimethylamine- $\kappa^3N$ ] dibromozinc(II)	$a=9.968(2)$ , $b=11.508(2)$ , $c=15.491(4)$ $\beta=103.712(1)$	Monoclinic $P2_1$	0.051
ZnBr5 [36]	$C_{10}H_{18}Br_2N_2$ $O_2Zn$	catena-Poly [[dibromozinc(II)]- $\mu$ -( $R,R$ )-1,2-diacetamidocyclohexane]	$a=7.496(2)$ , $b=7.496(2)$ , $c=27.941(5)$ $\alpha=\beta=\gamma=90$	Tetragonal $P4_3$	0.030
ZnBr6 [37]	$C_{16}H_{12}Br_2N_4$ Zn	Dibromobis(phthalazine- $\kappa^2N^2$ ) zinc(II)	$a=7.366(1)$ , $b=8.297(1)$ , $c=14.414(2)$ $\alpha=85.66(1)$ , $\beta=75.23(1)$ , $\gamma=88.38(1)$	Triclinic P-1	0.054
ZnBr7 [38]	$C_4H_8Br_2O_2$ Zn	catena-Poly [dibromozinc(II)]-di- $\mu$ -1,4-dioxan- $\kappa^2O:O'$ ]	$a=7.133(2)$ , $b=12.038(4)$ , $c=9.831(3)$ $\beta=99.42(1)$	Monoclinic $P2_1/n$	0.041
ZnBr8 [39]	$C_{12}H_{14}Br_2N_2$ $O_4Zn$	Dibromobis(4-methoxypyridine $N$ -oxide- $\kappa^2O$ )zinc(II)	$a=7.178(2)$ , $b=8.501(2)$ , $c=14.108(3)$ $\alpha=78.294(3)$ , $\beta=76.293(3)$ ,	Triclinic	0.040

ZnBr9 [40]	$C_{12}H_{12}Br_2$ $N_2Zn$	catena- Poly[[dibromozinc (II)]- $\mu$ -1,2-bis(4- pyridyl)ethane]	$\gamma=83.317(4)$ a=5.593(6), b=8.860(1), c=14.043(1) $\alpha=90.206(2)$ , $\beta=96.662(2)$ , $\gamma=96.181(2)$	P-1 <i>Triclinic</i>	0.056
ZnBr10 [41]	$C_{13}H_{19}Br_3$ $N_2OZn$	Dibromo{4- bromo-2-[2- (diethylaminoethyl )iminomethyl] phenolato} zinc(II)	a=7.147(1), b=15.722(2), c=16.077(3) $\beta=101.768(2)$	<i>Monoclinic</i>  P2 <sub>1</sub> /c	0.053
ZnBr11 [42]	$[ZnBr_2(C_{12}$ $H_{17}BrN_2O)]$	Dibromo{4- bromo-2-[(3- dimethylaminopro pylimino)methyl]p henolato} zinc(II)	a=7.037(1), b=15.039(2), c=16.170(2) $\beta=92.041(3)$	<i>Monoclinic</i>  P2 <sub>1</sub> /n	0.079
ZnBr12 [43]	$C_{13}H_{18}Br_2Cl_2$ $N_2OZn$	Dibromo{2,4-dich loro-6-[2-(diethyla mino)ethyliminom ethyl] phenolato} zinc(II)	a=7.687(1), b=19.102(3), c=13.841(2) $\beta=118.452(3)$	<i>Monoclinic</i>  Pc	0.066
ZnBr13 [44]	$C_8H_8Br_2N_4Z$ n	Dibromobis(pyrida zine- $\mu$ N) zinc(II)	a=8.891(5), b=9.719(7), c=13.819(8) $\alpha=\beta=\gamma=90$	<i>Orthorhom bic</i>  P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	0.038
ZnBr14 [45]	$C_{11}H_{16}Br_2N_2$ OZn	Dibromo{2-[3- (methylamino)pro pyliminomethyl]ph enolato} zinc(II)	a=11.757(2), b=14.363(2), c=17.535(2) $\alpha=\beta=\gamma=90$	<i>Orthorhom bic</i>  Pbca	0.046
ZnBr15 [46]	$C_{10}H_{14}Br_2N_2$ OZn	Dibromo{2-[2- (methylamino)ethy liminomethyl]phen olato} zinc(II)	a=10.599(2), b=7.426(1), c=17.624(3) $\alpha=\beta=\gamma=90$	<i>Monoclinic</i>  P2 <sub>1</sub> /n	0.041
ZnBr16 [47]	$C_{29}H_{30}Br_2N_4$ $NiO_2Zn$	Dibromido-2 $\mu$ - <sup>2</sup> Br- bis(4-methyl pyridine-1 $\mu$ N){ $\mu$ - 2,2'-[propane-1,3- diylbis(nitrilometh ylidyne)]diphenola to-1 $\mu$ <sup>4</sup> O,N,N',O':2 $\mu$ <sup>2</sup> O,O'}nickel(II) zinc(II)	a=19.357(3), b=9.213(7), c=18.327(1) $\beta=114.382(1)$	<i>Monoclinic</i>  Cc	0.066
ZnBr17 [48]	$C_{11}H_{15}Br_2N_3$ O <sub>3</sub> Zn	Dibromo{2-[2- (ethylamino)ethyli minomethyl]-4- nitrophenolato} zinc(II)	a=11.714(2), b=11.683(2), c=13.070(2) $\beta=115.912(3)$	<i>Monoclinic</i>  P2 <sub>1</sub> /c	0.036
ZnBr18 [49]	$[(C_4H_9)_4N]_2[$ $ZnBr_4]$	Bis(tetra- <i>n</i> - butylammonium) tetrabromido zincate(II)	a=16.530(2), b=15.491(2), c=18.657(2) $\beta=116.13(1)$	<i>Monoclinic</i>  P2 <sub>1</sub> /n	0.049

ZnBr19 [50]	C <sub>12</sub> H <sub>16</sub> Br <sub>2</sub> Cl <sub>2</sub> N <sub>2</sub> OZn	Dibromido{2,4-dichloro-6-[3-(dimethylammonio)propyliminomethyl]phenolato}zinc(II)	a=8.235(1), b=14.573(2), c=29.099(3) α=β=γ=90	<i>Orthorhombic</i>  Pbca	0.050
ZnBr20 [51]	C <sub>13</sub> H <sub>19</sub> Br <sub>2</sub> Cl N <sub>2</sub> OZn	Dibromo{4-chloro-2-[(2-diethylaminoethylimino)methyl]phenolato}zinc(II)	a=14.920(1), b=8.962(1), c=13.092(2) β=92.600(1)	<i>Monoclinic</i>  P2 <sub>1</sub> /c	0.043
ZnBr21 [52]	[ZnBr <sub>2</sub> (C <sub>12</sub> H <sub>17</sub> ClN <sub>2</sub> O)]	Dibromido{4-chloro-2-[3-(dimethylamino)propyliminomethyl]phenolato}zinc(II)	a=7.103(1), b=14.851(2), c=16.058(2) β=91.886(2)	<i>Monoclinic</i>  P2 <sub>1</sub> /n	0.060
ZnBr22 [53]	[ZnBr <sub>2</sub> (C <sub>11</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>2</sub> ]	Dibromidobis(4-hydroxy-1,5-dimethyl-2-phenyl-3-pyrazolone)zinc(II)	a=9.824(3), b=9.824(3), c=26.120(3) α=β=γ=90	<i>Tetragonal</i>  P4 <sub>1</sub>	0.035
ZnBr23 [54]	[ZnBr <sub>2</sub> (C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> S)]	Dibromido(di-2-pyridyl sulfide- $\mu$ - <sup>2</sup> N,N')zinc(II)	a=11.038 (8), b=8.962 (5), c=13.157(1) β=91.663(9)	<i>Monoclinic</i>  P2 <sub>1</sub> /c	0.033
ZnBr24 [55]	C <sub>12</sub> H <sub>7</sub> D <sub>2</sub> Br <sub>2</sub> N <sub>3</sub> OZn	catena-Poly [[dibromidozinc(II)]- $\mu$ -3-(1H-benzimidazol-2-yl)[2,6- <sup>2</sup> H <sub>2</sub> ]pyridine N-oxide]	a=7.401 (5), b=15.017 (3), c=12.174(2) β=98.52(3)	<i>Monoclinic</i>  P2 <sub>1</sub> /n	0.033
ZnBr25 [56]	(C <sub>7</sub> H <sub>10</sub> N) <sub>2</sub> [ZnBr <sub>4</sub> ]	Bis(2,6-dimethylpyridinium)tetrabromidozincate(II)	a=17.237(2), b=9.075(17), c=13.730(1) α=β=γ=90	<i>Orthorhombic</i>  Pbcn	0.088
ZnBr26 [57]	C <sub>12</sub> H <sub>14</sub> Br <sub>2</sub> N <sub>2</sub> Zn	Dianilinedibromidozinc(II)	a=25.754(2), b=4.941(3), c=12.192(8) β=111.035(3)	<i>Monoclinic</i>  C2/c	0.024
ZnBr27 [58]	C <sub>12</sub> H <sub>28</sub> Br <sub>2</sub> N <sub>2</sub> SiZn	Dibromido[(tert-butylamino)dimethyl(piperidin-1-ylmethyl)silane- $\mu$ - <sup>2</sup> N,N']zinc(II)	a=12.028(4), b=10.651(3), c=14.563(5) β=109.752(4)	<i>Monoclinic</i>  P2 <sub>1</sub> /c	0.020
ZnBr28 [59]	[ZnBr <sub>2</sub> (C <sub>7</sub> H <sub>6</sub> N <sub>4</sub> )]	catena-Poly [[dibromidozinc(II)]- $\mu$ -4-(3-pyridyl)-4H-1,2,4-triazole]	a=6.787(6), b=18.769(1), c=8.643(7) β=101.316(1)	<i>Monoclinic</i>  P2 <sub>1</sub> /c	0.039
ZnBr29 [60]	C <sub>18</sub> H <sub>12</sub> Br <sub>2</sub> N <sub>2</sub> Zn	(2,2'-Biquinoline- $\mu$ - <sup>2</sup> N,N')dibromidozinc(II)	a=7.919(2), b=12.351(3), c=17.385(4) β=103.01(3)	<i>Monoclinic</i>  P2 <sub>1</sub> /n	0.070
ZnBr30 [61]	(C <sub>5</sub> H <sub>12</sub> NO) <sub>2</sub> [ZnBr <sub>4</sub> ]	Bis(4-methylmorpholin-4-ium)tetrabromido	a=7.500(1), b=20.925(4), c=12.670(3)	<i>Monoclinic</i>	0.047

		zincate(II)	$\beta=103.33(3)$	$P2_1/c$	
ZnBr31 [62]	$C_{12}H_{24}Br_2N_6$ $S_3Zn$	Tris(allylthiourea- $\kappa_S$ ) bromidozinc(II) bromide	$a=11.359(2)$ , $b=11.359(2)$ , $c=14.517(4)$ $\gamma=120.00(1)$	Trigonal  R3	0.019
ZnBr32 [63]	$C_{12}H_9Br_2N_3$ $O_2Zn$	Dibromido{2-[(4-nitrophenyl)imino methyl]pyridine- $\kappa^2N,N'$ }zinc(II)	$a=7.261(5)$ , $b=7.923(8)$ , $c=13.644(1)$ $\alpha=87.724(4)$ , $\beta=74.719(6)$ , $\gamma=82.007(6)$	Triclinic  P-1	0.056
ZnBr33 [64]	$(C_8H_{12}N)_2[ZnBr_4]$	Bis(2,4,6-trimethylpyridinium) tetra bromido zincate	$a=7.363(8)$ , $b=9.031(8)$ , $c=9.185(9)$ $\alpha=101.741(8)$ , $\beta=110.778(1)$ , $\gamma=96.321(8)$	Triclinic  P1	0.054
ZnBr34 [65]	$[ZnBr_2(C_5H_5N_3O)_2]$	Dibromidobis(pyrazine-2-carboxamide- $\kappa_N^4$ )zinc	$a=5.604(4)$ , $b=19.515(2)$ , $c=7.066(5)$ $\beta=106.835(5)$	Monoclinic  $P2_1/m$	0.046
ZnI1 [66]	$C_8H_{14}I_2N_2Zn$	Diiodobis(1-pyrroline) zinc(II)	$a=11.351(2)$ , $b=9.734(2)$ , $c=12.090(2)$ $\alpha=\beta=\gamma=90$	Orthorhombic  Pnma	0.034
ZnI2 [67]	$C_{16}H_{16}I_2N_4O_6Zn$	Diiodobis(nicotinamide- $N^1$ -acetate-O) zinc(II)	$a=14.059(9)$ , $b=7.650(4)$ , $c=18.656(9)$ $\alpha=\gamma=90$ , $\beta=93.60(6)$	Monoclinic  C2/c	0.021
ZnI3 [68]	$C_{23}H_{23}N_3O_2$ $Cu_2Zn$	{[ $\mu$ -Bis(salicylidene)-1,3-propane diaminato]-(3-methylpyridine) copper(II)} diiodozinc(II)	$a=8.903(1)$ , $b=10.017(1)$ , $c=16.709(1)$ $\alpha=73.58(2)$ , $\beta=74.84(3)$ , $\gamma=65.38(2)$	Triclinic  P-1	0.032
ZnI4 [69]	$C_{31}H_{34}I_2N_4Ni$ $O_2Zn$	{[ $\mu$ -Bis(salicylidene)-1,3-propane diaminato]-bis(3,5-dimethylpyridine)nickel(II)} diiodozinc(II)	$a=9.428(1)$ , $b=18.717(1)$ , $c=19.633(1)$ $\alpha=\gamma=90$ , $\beta=103.00(2)$	Monoclinic  $P2_1/c$	0.025
ZnI5 [70]	$C_{17}H_{16}CuI_2N_2O_2Zn$	{[ $\mu$ -Bis(salicylidene)-1,3-propanediaminato]-copper(II)} diiodozinc(II)	$a=13.821(9)$ , $b=9.373(1)$ , $c=15.308(1)$ $\alpha=\gamma=90$ , $\beta=92.14(2)$	Monoclinic  $P2_1/c$	0.040
ZnI6 [71]	$C_{23}H_{30}I_2N_4Ni$ $O_4Zn$	{[ $\mu$ -Bis(salicylidene)-1,3-propane diaminato]bis(N,N-dimethylformamide)nickel(II)} diiodozinc(II)	$a=10.602(1)$ , $b=15.321(1)$ , $c=18.269(1)$ $\alpha=\gamma=90$ , $\beta=98.73(1)$	Monoclinic  Cc	0.032

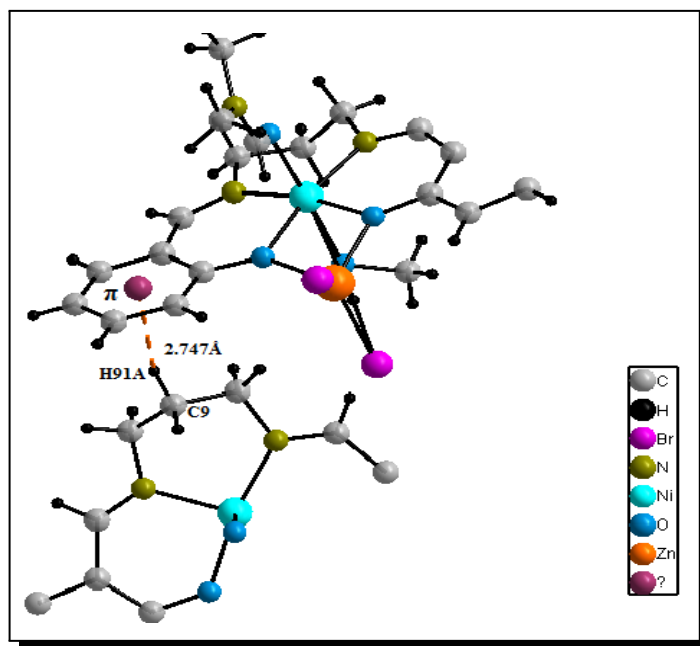


ZnI7 [72]	$[Zn(C_2H_8N_2)_3][CdI_4]I_2$	Bis[tris(ethylenedi-amine)zinc] tetraiodocadm-ate diiodide	a=14.803(2), b=14.803(2), c=16.991(4) $\alpha=\beta=\gamma=90$	Tetragonal  I-42d	0.027
ZnI8 [73]	$C_{44.85}H_{26.85}Cl_{2.55}I_4N_4$	[Tetrakis(4-iodophenyl)porphyrinato]zinc(II)	a=6.536(2), b=13.451(3), c=13.856(4) $\alpha=117.14(9)$ , $\beta=100.62(9)$ , $\gamma=92.73(8)$	Triclinic  P-1	0.047
ZnI9 [74]	$C_{26}H_{18}ClN_3O_2Zn$	catena-Poly[iodido(m <sub>3</sub> -4-{2-[3-(pyridin-4-yl)phenyl]-1 <i>H</i> -benzimidazol-1-ylmethyl}benzoato)zinc(II)]	a=12.925(3), b=10.175(2), c=17.334(4) $\alpha=\gamma=90$ , $\beta=104.80(4)$ ,	Monoclinic  P2 <sub>1</sub> /n	0.066
ZnF1 [75]	$[ZnCl(C_{12}H_{27}N_3)]PF_6$	Chloro(N,N',N''-trimethyl-1,5,9-triazacyclododecane- $\kappa^3N$ )zinc(II) Hexafluorophosphate	a=15.896(2), b=11.169(5), c=10.366(9) $\alpha=\beta=\gamma=90$	Orthorhombic  Pna2 <sub>1</sub>	0.017
ZnF2 [76]	$C_{20}H_{10}F_{12}N_2O_4Zn$	catena-Poly[[bis(hexafluoroacetato- $\kappa^2O,O'$ )zinc(II)]- $\mu$ -4,4'-bipyridine- $\kappa^2N:N'$ ]	a=8.061(4), b=8.061(4), c=36.648(3) $\alpha=\beta=\gamma=90$	Tetragonal  P4 <sub>3</sub> 2 <sub>1</sub> 2	0.048
ZnF3 [77]	$NaCdZn_2F_7$	Sodium cadmium dizinc heptafluoride (NaCdZn <sub>2</sub> F <sub>7</sub> )	a=10.347(3), b=10.347(3), c=10.347(3) $\alpha=\beta=\gamma=90$	Cubic  Fd-3m	0.032
ZnF4 [78]	$C_{34}H_{40}F_2N_4O_8Zn$	Diaquabis (N,N-diethylnicotinamide- $\kappa N$ )bis(4-fluorobenzoato- $\kappa O$ )zinc(II)	a=7.426(2), b=8.719(3), c=15.080(4) $\alpha=98.44(2)$ , $\beta=95.73(2)$ , $\gamma=112.94(3)$	Triclinic  P-1	0.050
ZnF5 [79]	$C_{26}H_{22}F_2N_4O_7Zn$	Bis(4-fluorobenzoato- $\kappa^2O,O'$ )bis(nicotinamide- $\kappa N^1$ ) zinc(II) monohydrate	a=8.236(2), b=12.371(2), c=14.897(3) $\alpha=113.18(3)$ , $\beta=99.02(6)$ , $\gamma=99.47(5)$	Triclinic  P-1	0.058
ZnF6 [80]	$[Zn(C_9H_7N_3)_2(H_2O)_4](CF_3SO_3)_2$	Tetraaquabis[5-(3-pyridyl- $\kappa N$ )pyrimidine] zinc(II)bis(trifluoromethanesulfonate)	a=9.360(4), b=17.198(3), c=9.686(5) $\beta=100.187(2)$	Monoclinic  P2 <sub>1</sub> /n	0.066
ZnF7 [81]	$C_{25}H_{27}Cl_3CrF_2N_5OZn$	trans-difluoridate trakis (pyridine- $\kappa N$ )chromium(III) trichlorido(pyridine- $\kappa N$ ) zincate monohydrate	a=9.136(7), b=12.852(3), c=13.607(3) $\alpha=103.69(3)$ , $\beta=105.07(3)$ , $\gamma=101.25(3)$	Triclinic  P-1	0.037

**Table 2.** Crystallographic data for Zn-centered bond distances (Å) and range of bond angles ( $^\circ$ ) in  $[ZnX]^-$  (where X = Cl, Br, I, F)

Code	Zn-X bond distance (Å)	X-Zn-X( $^\circ$ ) range
ZnCl1	Zn(1)-Cl(1)=2.730(4) Zn(2)-Cl(2A)=2.288(5)	108.83-177.51
ZnCl2	Zn-Cl(1)=2.355(8)	120.85
ZnCl3	Zn-Cl1=2.267(6) Zn-Cl2=2.266(6) Zn-Cl3=2.274(7)	108.5-112.9
ZnCl4	Zn-Cl1=2.205(2) Zn-Cl2=2.399(8)	119.31
ZnCl5	Zn-Cl1=2.273(8)	123.63
ZnCl6	Zn(1)-Cl(1)=2.201(4)	119.29
ZnCl7	Zn1-Cl1=2.284(1)	121.30
ZnCl8	Zn-Cl1=2.267(1) Zn-Cl2=2.278(1) Zn-Cl3=2.250(1)	106.79-110.63
ZnCl9	Zn1-Cl1=2.296(2)	122.50
ZnCl10	Zn1-Cl1=2.256(6)	112.50-114.98
ZnCl11	Zn1-Cl1=2.355(2)	121.02
ZnCl12	Zn(1)-Cl(1)=2.255(8)	120.63
ZnCl13	Zn1-Cl1=2.309(1)	119.52
ZnCl14	Zn1-Cl1=2.272(1)	121.35
ZnCl15	Zn1-Cl1=2.352(6)	118.63
ZnCl16	Zn(1)-Cl(1)=2.201(4)	123.25
ZnCl17	Zn1-Cl1=2.309(1)	121.12
ZnCl18	Zn1-Cl5=2.269(7)	120.35
ZnCl19	Zn1-Cl1=2.253(9)	119.64
ZnCl20	Zn1-Cl1=2.418(3) Zn1-Cl1=2.732(3)	82.44
ZnBr1	Zn-Br=2.481(1)	120.32
ZnBr2	Zn1-Br1=2.342(8) Zn1-Br2=2.358(8) Zn2-Br3=2.368(8) Zn2-Br4=2.352(8)	117.57-119.63
ZnBr3	Zn-Br1=2.336(2) Zn-Br2=2.363(2)	117.95
ZnBr4	Zn1A-Br1A=2.402(8) Zn1A-Br2A=2.440(8) Zn1B-Br1B=2.411(8) Zn1B-Br2B=2.450(9)	108.25
ZnBr5	Zn-Br1=2.342(1) Zn-Br2=2.349(1)	118.59
ZnBr6	Zn-Br2=2.359(1) Zn-Br1=2.359(1)	115.59
ZnBr7	Zn1-Br1=2.311(8) Zn1-Br2=2.317(8)	124.53
ZnBr8	Zn1-Br1=2.327(9) Zn1-Br2=2.356(1)	122.08
ZnBr9	Zn1-Br1=2.3634(7) Zn1-Br2=2.3778(7)	122.99
ZnBr10	Zn1-Br2=2.339(1) Zn1-Br3=2.452(1)	110.64
ZnBr11	Zn1-Br2=2.336(3) Zn1-Br3=2.391(3)	115.19
ZnBr12	Zn1-Br2=2.362(2) Zn1-Br1=2.398(2) Zn2-Br4=2.357(2) Zn2-Br3=2.365(2)	107.99-112.53
ZnBr13	Zn1-Br2=2.354(8) Zn1-Br1=2.373(8)	116.75
ZnBr14	Zn1-Br2=2.349(1) Zn1-Br1=2.396(9)	113.18
ZnBr15	Zn1-Br2=2.333(9)	117.10

ZnBr16	Zn1-Br1=2.396(8) Zn-Br1=2.400(1) Zn-Br2=2.372(3)	101.6
ZnBr17	Zn1-Br1=2.343(7) Zn1-Br2=2.383(8)	119.14
ZnBr18	Zn1-Br1=2.399(1) Zn1-Br2=2.401(1) Zn1-Br3=2.408(1) Zn1-Br4=2.416(1)	106.59 -112.84
ZnBr19	Zn1-Br1=2.367(1) Zn1-Br2=2.369(9)	112.64
ZnBr20	Zn1-Br1=2.357(1) Zn1-Br2=2.364(1)	114.41
ZnBr21	Zn1-Br1=2.335(1) Zn1-Br2=2.383(2)	115.39
ZnBr22	Zn1-Br2=2.350(1) Zn1-Br1=2.379(8)	111.94
ZnBr23	Zn1-Br2=2.350(6) Zn1-Br1=2.353(5)	118.38
ZnBr24	Zn1-Br2=2.357(7) Zn1-Br1=2.396(7)	114.22
ZnBr25	Zn1-Br1=2.400(2) Zn1-Br2=2.408(3)	108.14-115.15
ZnBr26	Zn1-Br1=2.385(3)	110.49
ZnBr27	Zn1-Br1=2.389(4) Zn1-Br2=2.362(3)	116.76
ZnBr28	Zn1-Br2=2.350(2) Zn1-Br1=2.388(2)	116.02
ZnBr29	Zn1-Br2=2.335(1) Zn1-Br1=2.350(1)	119.24
ZnBr30	Zn1-Br1=2.399(6) Zn1-Br2=2.400(1) Zn1-Br3=2.408(9) Zn1-Br4=2.425(9)	104.63-113.48
ZnBr31	Zn1-Br1=2.464(6)	120.32
ZnBr32	Zn1A-Br1=2.340(5) Zn1-Br1=2.343(1) Zn1-Br2=2.336(2) Zn1A-Br1=2.339(5)	64.77-113.75
ZnBr33	Zn1-Br2=2.390(2) Zn1-Br4=2.398(2) Zn1-Br1=2.427(2) Zn1-Br3=2.449(2)	107.09-112.48
ZnBr34	Zn1-Br1=2.328(1) Zn1-Br2=2.330(1)	126.45
ZnI1	Zn(1)-I(1)=2.557(8)	121.03
ZnI2	Zn-I=2.585(3)	104.29
ZnI3	Zn-I2=2.534(6) Zn-I1=2.538(8)	117.28
ZnI4	Zn-I2=2.541(5) Zn-I1=2.558(6)	116.94
ZnI5	Zn-I2=2.538(1) Zn-I1=2.541(1)	119.77
ZnI6	Zn-I2=2.530(9) Zn-I1=2.542(9)	117.51
ZnI9	Zn1-I1=2.527(1)	119.65
ZnF3	Zn-F2=2.020(5)	82.35-180



**Figure 1.** C-H... $\pi$  interaction in ZnBr<sub>3</sub> with H91A atom at symmetry position 0.5-x, 1-y, 0.5+z

### 3. Result and Discussions

The hydrogen bond geometry for ZnCl derivatives indicates that the acceptor bond length lies in the range of 1.78Å to 2.97Å and the donar-acceptor length exist in between 2.616Å to 3.910Å and H-centered D-A angle has values from 101° to 177°. Selected Hydrogen-Bonding Geometry (Å,°) in ZnBr derivatives. The hydrogen bond geometry for ZnBr derivatives indicates that the acceptor bond length lies in the range of 1.84Å to 3.08Å and the donar-acceptor length exist in between 2.732Å to 3.915Å and H-centered D-A angle has values from 82° to 179°.

Selected Hydrogen-Bonding Geometry (Å,°) in ZnI derivatives The hydrogen bond geometry for ZnI derivatives indicates that the acceptor bond length lies in the range of 2.22Å to 3.09Å and the donar-acceptor length exist in between 2.774Å to 3.904Å and H-centered D-A angle has values from 72° to 167°. Selected Hydrogen-Bonding Geometry (Å,°) in ZnF derivatives. The hydrogen bond geometry for ZnF derivatives indicates that the acceptor bond length lies in the range of 1.71Å to 2.92Å and donar-acceptor length exist in between 2.677Å to 3.771Å and H-centered D-A angle has values from 94° to 173° as shown in Table 3.

**Table 3.** Hydrogen bonding geometry of Zinc based hybrid materials

Zinc based hybrid material	Range H-A(Å)	Range X-A(Å)	Range X-H-A(°)
ZnCl <sub>2</sub>	1.78-2.97	2.616-3.910	101-177
ZnBr <sub>2</sub>	1.84-3.08	2.732-3.915	82-179
ZnI <sub>2</sub>	2.22-3.09	2.774-3.904	72-167
ZnF <sub>2</sub>	1.71-2.92	2.677-3.771	94-173

## 4. Conclusion

Weak interactions such as X-H...A, C-H... $\pi$ ,  $\pi$ ... $\pi$ , X...X and Metal...Metal were observed in [ZnX]<sup>2+</sup> based inorganic-organic hybrid materials.

Structure stability relationship of inorganic-organic hybrid material has been determined by

D-H...Cl = 1.78(Å) to 2.97(Å)

D-H...Br = 1.84(Å) to 3.08(Å)

D-H...I = 2.22(Å) to 3.09(Å) type of secondary interactions

Centroid to centroid interactions between the two organic moieties of hybrid materials has the range of 3.51(Å) to 3.88(Å) which is responsible for Luminescence properties of inorganic-organic hybrid materials such as in hybrid LED.

Zinc based hybrid materials are also used in junction diode of hybrid solar cells in which the stability of the hybrid structure is maintained by these weak interaction. Looking upon the industrial applications of hybrid material they are the future of nanotechnology due to combination of two different branches of solid state sciences such as organic and inorganic in which the properties of two different scientific worlds were clubbed together into single composite material.

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## Competing Interests

The author declares that he has no competing interests.

## Authors' Contributions

The author wrote, read and approved the final manuscript.

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