

Metallophilicity in $[\text{CdBr}]^-$: A Case Study of Hybrid Materials

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Abstract- A series of inorganic–organic hybrid compounds were analyzed by using X-ray crystallographic techniques to study the secondary interactions in cadmium bromide based hybrid materials. The phenomenon of metallophilic interactions with minimum Cd...Cd distance [3.962(1), 3.389(3) and 3.924(1) Å] has been observed in Cd2, Cd7 and Cd11 compounds whereas the metallophilicity is missing in other compounds of the selected series. The novel entanglements of Cd motifs illustrate 1D and 2D chain pattern of metallophilic and Br...Br interactions. The Cd–Br bond distances exponential in the range of 2.505(1) to 2.924(1)Å and Br–Cd–Br bond angles in the range of 83.45(3) to 180°. The minimum value of Torsion angle is $-3.647(3)^\circ$ for the compound Cd10, when Cd atoms are taken in the centre while its minimum value is calculated as $28.211(1)^\circ$ for the compound Cd1, when Br atoms are taken in the centre.

Index Terms- Metallophilic interactions, inorganic-organic hybrid materials, Br...Br interactions, Cd motifs, 1D and 2D chain pattern.

I. INTRODUCTION

Students beginning their studies of structural science today are typically introduced to bonding partitioned between covalent and ionic extremes, supplemented by weaker intermolecular forces. Subsequently, they will learn about metallic bonding, the “sea of electrons” present in delocalized systems and perhaps read a little about cluster bonding. Yet to be incorporated into standard textbooks is the phenomenon of metallophilicity, a name that indicates the affinity of two metal centers for one another. The metallophilic attraction is an almost new form of chemical bonding and consists of dispersion. First described in detail based on the close Au...Au contacts in several Au(I) derivatives,[1] the phenomenon of two closed shell metal centers approaching closer than the sum of their van der Waals radii was termed aurophilicity,[2] and now the word metallophilicity is used in a general sense for many metals. These interactions are understood to be a type of dispersion interaction between electron densities on larger and relatively reduced metal centers [3, 4]. The energy of such bonding is on the order of hydrogen-bonding and can therefore exert a significant influence on solid-state structures [3]. One of the most interesting aspects of metallophilic bonding is that it can overcome electrostatic repulsion between cations or anions and bring together groups of like charge.

In recent years, the design and synthesis of metal-organic frameworks (MOF) based on the assembly of suitable and rigid building blocks have attracted great attention [5-10]. The design of polymeric coinage d^{10} metal complexes with fascinating structures has also received much attention [11-15], indicating in some studies that direct metal-metal interactions are among the most important factors for the manifestation of such structures. Between closed-shell species, no strong attractions are expected and, in fact, two closed-shell metal cations will normally repel each other. However, in the case of some coordination compounds, metal-metal attractions are present. Metallophilic interactions can lead to the generation of dimeric or polymeric structures, such as coinage metals with short M-M distances [16-20]. The most promising criteria in defining metallophilic 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 a part of our research on secondary interactions in inorganic-organic hybrid materials [21-23], a series of eighteen compounds (Cd1 to Cd18) whose crystal structures were reported [24-41] have been selected based on $[\text{CdBr}]^-$ anion for study of metallophilic interactions through crystallography data.

II. EXPERIMENTAL DATA

The experimental data for Cadmium Bromide based compounds [Cd1-Cd18] have been collected from Cambridge Structural Data Centre, U.K. and recycled by using WINGX software [42] for different types of secondary interactions. The recycled crystal structure data for all the compounds is presented in **Table 1**. The Cd1 crystal structure was refined upto 0.0420 for 1934 observed reflections. The value of R- factor for Cd2 and Cd3 has been observed to be 0.036 and 0.058 with 887 and 1401 reflections respectively. The reliability index of 0.034 has been achieved with 2673 reflections in Cd4 whereas its value is 0.0177 for 1127 reflections in Cd5. The value of R- index is 0.0610 for 2427 reflections in Cd6 and in Cd7 it is 0.0389 for 1137 observed reflections. The well refined crystal structure of Cd8 with refined parameter of 0.0290 and 0.0199 for Cd9 shows the structure solution results with 1494 and 1535 reflections, respectively. Cd10 and Cd11 derivatives of the selected series were refined upto 0.0407 and 0.0168 values for 3769 and 330 reflections. The cell measurements reflection value of 961 and 3328 has been used to obtain the refine parameter of 0.0286 and 0.0353 for the compounds of Cd12 and Cd13, respectively. The MoK α type of radiations having wavelength 0.71073 have been

used to obtain the refine parameter for all the compounds of the selected series (Cd1-Cd18). By the use of such radiations the value of R-index is 0.0212 for 2114 reflections in Cd14 and in Cd15 it is 0.0488 for 2877 independent reflections. Similarly Cd16 crystal structure has been refined upto 0.0235 with 2098 reflections and Cd17 has the R-factor of 0.0333 for 2348 independent reflections. The cell measurement reflections of 25

are used to refine the crystal structure of Cd18 upto 0.0628 with 2986 reflections. The crystallographic data for Cd—Centered bond distances and range of bond angles is given in **Table 2**.

TABLE-1: Crystal Structure Data for [CdBr] based inorganic-organic hybrid compounds.

Molecular Code	IUPAC Name	Chemical Formula	Cell Parameters	Space Group	Crystal System	Ref.
Cd1	Catena-[Cd{m-S(CH ₂) ₃ NHMe ₂ }Br ₂]	C ₅ H ₁₃ Br ₂ CdNS	a = 9.993(2) Å b = 6.824(1) Å c = 16.398(2) Å β = 96.0(1)°	P2 ₁ /n	Monoclinic	[24]
Cd2	Catena-Poly[Bis(3-methyl-4-nitropyridine N-oxide-O) cadmium-μ-bromo]	C ₁₂ H ₁₂ Br ₂ CdN ₄ O ₆	a = 15.743(5) Å b = 57.010(3) Å c = 3.962(1) Å	Fdd	Orthorhombic	[25]
Cd3	Bis(tetraethylammonium) tetrabromocadmiate	C ₁₆ H ₄₀ Br ₄ CdN ₂	a = 13.453(1) Å b = 13.453(1) Å c = 14.395(1) Å α = β = γ = 90.0°	P-4 ₂ m	Tetragonal	[26]
Cd4	Tetrabromocadmiate(II)Dafone (4,5-Diazafluoren-9-one)	C ₂₂ H ₁₈ Br ₄ CdN ₄ O ₄	a = 9.776(2) Å b = 10.740(2) Å c = 15.135(3) Å α = 71.69(2)° β = 87.93(2)° γ = 63.48(2)°	P-1	Triclinic	[27]
Cd5	Bis(thiourea)cadmium bromide	C ₂ H ₈ CdBr ₂ N ₄ S ₂	a = 13.052(2) Å b = 5.989(2) Å c = 13.542(3) Å α = β = γ = 90.0°	Pnam	Orthorhombic	[28]
Cd6	Bis-(4-amino-2(1H)-pyridinone)dibromocadmium(II)	C ₈ H ₁₀ Br ₂ CdN ₆ O ₂	a = 7.874(2) Å b = 12.624(3) Å c = 7.117(3) Å α = 105.87(4)° β = 92.67(3)° γ = 87.93(3)°	P-1	Triclinic	[29]
Cd7	Diethylammonium heptabromidedicadmium(II)	C ₁₂ H ₃₆ Br ₇ Cd ₂ N ₃	a = 15.567(1) Å b = 15.567(1) Å c = 6.778(1) Å γ = 120.0°	P-3	Trigonal	[30]
Cd8	Strontium hexabromodicadmiate(II)octahydrate	SrCd ₂ Br ₆ 8H ₂ O	a = 25.247(2) Å b = 4.083(1) Å c = 8.764(2) Å α = β = γ = 90.0°	P2 ₁ 2 ₁ 2	Orthorhombic	[31]
Cd9	Dibromobis(pyridinium-2-thiolato-kS)cadmium(II)	[CdBr ₂ (C ₅ H ₅ NS) ₂]	a = 13.050(3) Å b = 28.521(1) Å c = 8.065(2) Å α = β = γ = 90.0°	Fdd2	Orthorhombic	[32]
Cd10	Bis(tetra-n-butylammonium) tetrabromocadmiate(II) toluene disolvate	(C ₁₆ H ₃₆ N) ₂ [CdBr ₄] ₂ C ₇ H ₈	a = 15.154(1) Å b = 15.154(1) Å c = 23.382(2) Å α = β = γ = 90.0°	I-4 ₂ d	Tetragonal	[33]
Cd11	Poly[di-m2-bromido-m2-4,4'-bipyridine-	[CdBr ₂ (C ₁₀ H ₈ N ₂)]	a = 11.787(3) Å b = 12.554(3) Å	Cmmm	Orthorhombic	[34]

	cadmium(II)]		$c = 3.924(1)\text{\AA}$ $\alpha = \beta = \gamma = 90.0^\circ$			
Cd12	Catena-Poly[[1,10-phenanthroline-k2N,N']cadmate(II)]-di-m-bromido]	[CdBr2(C12H8N2)]	$a = 16.778(1)\text{\AA}$ $b = 10.759(1)\text{\AA}$ $c = 7.421(3)\text{\AA}$ $\beta = 108.66(4)^\circ$	C_2/c	Monoclinic	[35]
Cd13	Diaquadibromidobis[3-dimethylamino-1-(4-pyridyl-kN)prop-2-en-1-one]cadmium(II)	[CdBr2(C10H12N2O)2(H2O)2]	$a = 21.362(3)\text{\AA}$ $b = 8.436(1)\text{\AA}$ $c = 14.637(2)\text{\AA}$ $\beta = 114.46(3)^\circ$	C_2/c	Monoclinic	[36]
Cd14	Dibromidobis(N,N,N',N'-tetramethylthiourea-kS)cadmium(II)	[CdBr2(C5H12N2S)2]	$a = 18.613(2)\text{\AA}$ $b = 10.069(1)\text{\AA}$ $c = 13.460(1)\text{\AA}$ $\beta = 130.834(1)^\circ$	C_2/c	Monoclinic	[37]
Cd15	Di-m-bromido-bis[bromido(1-carboxymethyl-4-aza-1-azoniabicyclo[2.2.2]octane-kN4)(nitrito-k2O,O')cadmium(II)] dehydrate	[Cd2Br4(C8H15N2O2)2(NO2)2]2H2O	$a = 8.779(2)\text{\AA}$ $b = 13.374(3)\text{\AA}$ $c = 13.113(3)\text{\AA}$ $\beta = 101.99(3)^\circ$	$P2_1/n$	Monoclinic	[38]
Cd16	Poly[dibromidobis[m-1-(pyridin-4-ylmethyl)-1H-1,2,4-triazole-k2N:N']cadmium]	[CdBr2(C8H8N4)2]	$a = 7.780(1)\text{\AA}$ $b = 16.730(2)\text{\AA}$ $c = 8.468(1)\text{\AA}$ $\beta = 114.41(5)^\circ$	$P2_1/c$	Monoclinic	[39]
Cd17	Dibromido[(1R,2R,N1S)-N-(pyridin-2-ylmethyl)cyclohexane-1,2-diamine-k3N,N',N'']cadmium	[CdBr2(C12H19N3)]	$a = 8.715(2)\text{\AA}$ $b = 9.198(2)\text{\AA}$ $c = 19.759(4)\text{\AA}$ $\alpha = \beta = \gamma = 90.0^\circ$	$P2_12_12_1$	Orthorhombic	[40]
Cd18	Dibromido(2,9-dimethyl-1,10-phenanthroline-k2N,N')cadmium	[CdBr2(C14H12N2)]	$a = 7.889(4)\text{\AA}$ $b = 10.519(3)\text{\AA}$ $c = 18.712(2)\text{\AA}$ $\beta = 97.69(3)^\circ$	$P2_1/c$	Monoclinic	[41]

III. RESULTS AND DISCUSSION

The Br—Cd—Br bond angles have wide range from minimum value of $108.83(2)$ to $109.79(1)^\circ$ for Cd8 and maximum range of $86.79(2)$ to 180.0° for the derivatives Cd7 [Table 2]. The bond lengths of Cd—Br bond lies in an average range of 2.509\AA to 2.791\AA [22-39]. The Cd...Cd distance in Compound Cd2 is calculated as $3.962(1)\text{\AA}$ which shows that the structure is stabilized by metalphilic interactions apart from X—H...A and Br...Br secondary interactions [43,17] and it is seen in this compound [Cd2] that the minimum value of Br...Br bond distances comes out to be $3.810(2)\text{\AA}$ and $3.962(3)\text{\AA}$ as shown in Figure 1.

In Cd7 derivative of the selected series, one of the Cd atom having symmetry position $(x, y, 1+z)$ establishes a close contact of $3.389(3)\text{\AA}$ with another Cd atom. The pictorial presentation is plotted along ac -plane and 1D chain pattern of Cd...Cd contacts supported through Br...Br interactions [Br...Br = $3.827(1)\text{\AA}$] as shown in Figure 3. The inorganic part (i.e. heptabromidedicadmium) of the hybrid materials [Cd7] stabilized through zig-zag pattern of secondary interactions and

the organic part (i.e. Diethylammonium) are sandwiched between inorganic layers along ac -plane. The Scattering plot of Cd—Br bond distance is shown in Figure 2 in which the highest value of 2.785\AA is shown by the Compound Cd11.

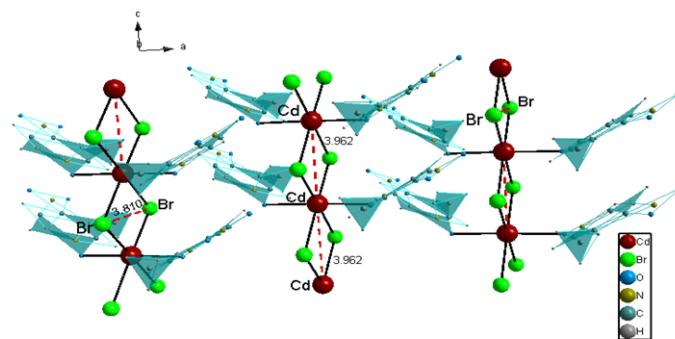


FIGURE-1: Cd...Cd Interactions in Catena-Poly [Bis(3-methyl-4-nitropyridine N-oxide-O) cadmium- μ -bromo].

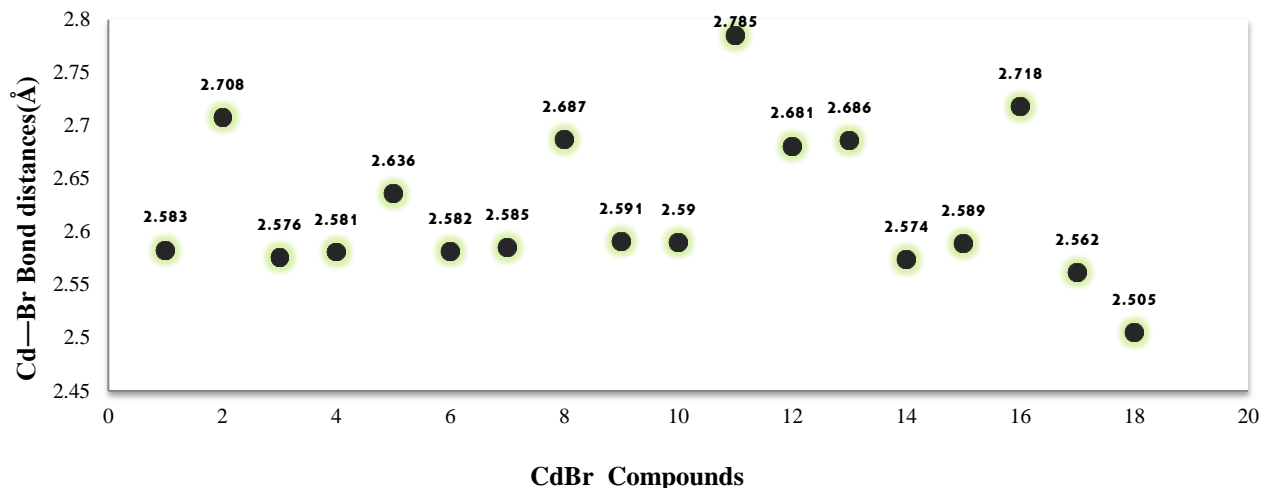


FIGURE-2: Scatter plot of Cd—Br bond distances (Å).

TABLE-2: Crystallographic data for Cd-centered bond distances (Å) and range of bond angles (°).

Code	Cd—Br bond distance(Å)	Br—Cd—Br Angle range(°)
Cd1	Cd—Br1 = 2.583(2) Cd—Br2 = 2.640(1)	105.86(1)—105.86(1)
Cd2	Cd—Br = 2.708(1) Cd—Br = 2.790(1)	86.14(5)—178.35(1)
Cd3	Cd—Br2 = 2.576(3) Cd—Br1 = 2.582(3) Cd—Br3 = 2.587(4)	108.00(1)—112.10(1)
Cd4	Cd—Br3 = 2.581(1) Cd—Br1 = 2.584(1)	103.70(1)—117.20(1)
Cd5	Cd—Br2 = 2.636(2) Cd—Br1 = 2.674(4)	102.48(1)—102.48(1)
Cd6	Cd—Br3 = 2.582(2) Cd—Br2 = 2.592(1)	104.24(1)—104.24(1)
Cd7	Cd1—Br2 = 2.585(1) Cd1—Br1 = 2.628(2) Cd2—Br3 = 2.785(1) Cd3—Br3 = 2.784(1)	86.79(2)—180.0
Cd8	Cd—Br1 = 2.687(1) Cd—Br2 = 2.722(1) Cd—Br2 = 2.760(1) Cd—Br3 = 2.773(1) Cd—Br3 = 2.854(1) Cd—Br3 = 2.924(1)	83.45(3)—174.12(3)
Cd9	Cd—Br = 2.591(1)	114.77(3)—114.77(3)
Cd10	Cd1—Br2 = 2.590(4)	108.83(2)—109.79(1)
Cd11	Cd1—Br1 = 2.785(1)	89.57(2)—180.0
Cd12	Cd1—Br1 = 2.681(1) Cd1—Br1 = 2.900(1)	87.15(2)—176.93(2)
Cd13	Cd1—Br1 = 2.686(1)	180.00(2)—180.00(2)
Cd14	Cd1—Br1 = 2.574(3)	114.68(2)—114.68(2)
Cd15	Cd1—Br2 = 2.589(1) Cd1—Br1 = 2.635(1)	89.13(3)—109.31(3)

Cd16	Cd1—Br1 = 2.718(4)	180.00—180.00
Cd17	Cd1—Br2 = 2.562(1) Cd1—Br1 = 2.605(1)	121.01(3)—121.01(3)
Cd18	Cd1—Br2 = 2.505(1) Cd1—Br1 = 2.512(1)	113.59(4)—113.59(4)

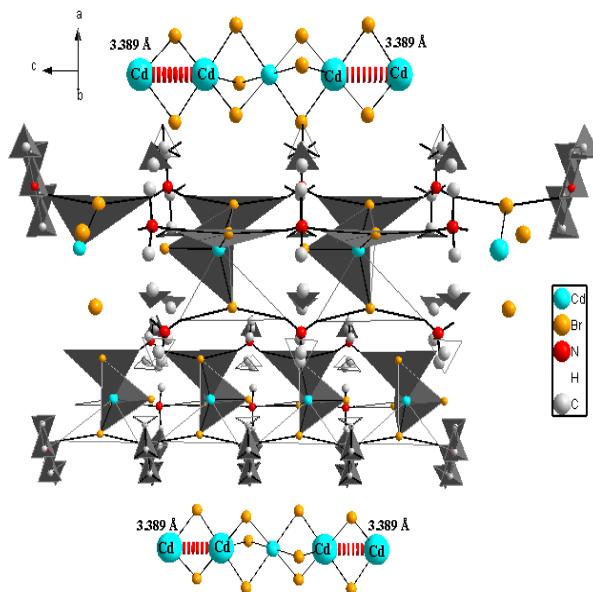


FIGURE-3: Metallophilic [Cd...Cd] Interactions in Diethylammonium heptabromidedicadmium(II)[Cd7] at (x, y, 1+z).

TABLE-3: Br...Br and Cd...Cd contacts with Symmetry positions.

Code	Br...Br Distances(Å)	Cd...Cd Distances(Å)
Cd1	Br1—Br2 = 4.168(2)	Cd—Cd ⁱ = 4.075(1)
Cd2	Br—Br = 3.810(2) Br—Br = 3.962(3)	Cd—Cd ⁱⁱ = 3.962(1)
Cd3	Br1—Br2 = 4.174(4)	Cd—Cd ⁱⁱⁱ = 9.385(2)
Cd4	Br1—Br2 = 4.078(2) Br4—Br3 = 4.089(2) Br1—Br4 = 4.420(2)	Cd—Cd ^{iv} = 8.860(2)
Cd5	Br1—Br2 = 4.149(4)	Cd—Cd ^v = 5.989(3)
Cd6	Br2—Br3 = 4.084(2) Br2—Br3 = 4.254(2)	Cd1—Cd1 ^{vi} = 7.117(3)
Cd7	Br3—Br3 = 3.827(1) Br3—Br3 = 4.044(1)	Cd2—Cd3^{vii} = 3.389(3)
Cd8	Br1—Br3 = 3.944(1) Br1—Br2 = 3.968(1)	Cd—Cd ^v = 4.083(1)
Cd9	Br—Br = 4.365(1) Br—Br = 4.920(1)	Cd—Cd ^{viii} = 7.671(1)
Cd10	Br2—Br2 = 4.213(1) Br2—Br2 = 4.238(1) Br2—Br2 = 6.442(1)	Cd1—Cd1 ^{ix} = 9.570(4)
Cd11	Br1—Br1 = 3.924(1)	Cd1—Cd1^x = 3.924(1)
Cd12	Br1—Br1 = 3.850(1) Br1—Br1 = 4.111(1)	Cd1—Cd1 ^x = 4.047(2)
Cd13	Br1—Br1 = 5.371(1)	Cd1—Cd1 ^{xi} = 7.319(1)
Cd14	Br1—Br1 = 4.333(1) Br1—Br1 = 4.953(1)	Cd1—Cd1 ^{xiii} = 7.130(1)
Cd15	Br1—Br1 = 3.978(2)	Cd1—Cd1 ^{xiii} = 4.037(1)
Cd16	Br1—Br1 = 4.757(1) Br1—Br1 = 4.942(1)	Cd1—Cd1 ^{iv} = 7.780(1)
Cd17	Br1—Br2 = 4.498(1) Br1—Br2 = 4.812(1)	Cd1—Cd1 ^{xiv} = 6.530(1)
Cd18	Br1—Br2 = 4.198(2)	Cd1—Cd1 ^x = 7.210(2)

Symmetry Codes: (i) 0.5-x, 0.5+y, 0.5-z; (ii) x, 1+y, z; (iii) 1-x, y, 1-z; (iv) 1+x, y, z; (v) x, -1+y, z; (vi) x, y, -1+z; (vii) x, y, 1+z; (viii) -0.5+x, y, 0.5+z; (ix) x, 0.5-y, 0.25-z; (x) 1-x, 1-y, 1-z; (xi) 1-x, y, 1.5-z; (xii) 1.5-x, 1.5-y, -z; (xiii) -x, 1-y, 1-z; (xiv) -x, 0.5+y, 0.5-z.

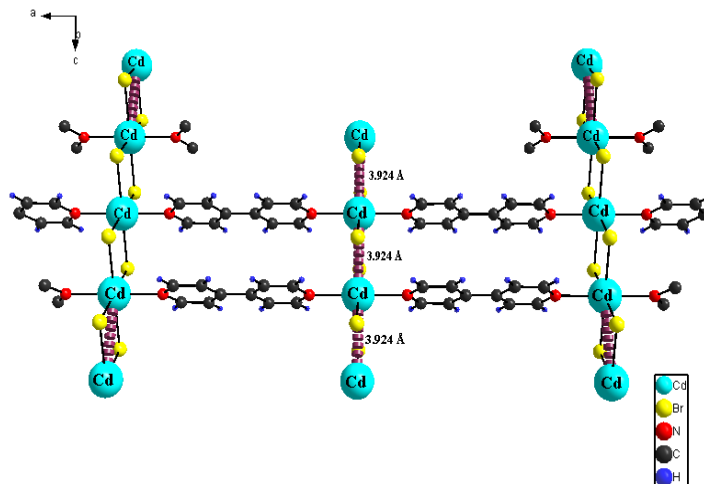


FIGURE-4: Metallophilic [Cd...Cd] Interactions in Poly [di-m2-bromido-m2-4, 4'-bipyridine-cadmium(II)][Cd11]. Displacement ellipsoids are drawn at the 50% probability level.

The 2D chain pattern of Cd...Cd interactions has been observed in Cd11 [Poly [di-m2-bromido-m2-4,4'-bipyridine-cadmium(II)]. The Cd1 atom is in contact with another Cd1 atom at x, y, 1+z with minimum Cd...Cd distance of 3.924(1)Å. The phenomenon of Br...Br interaction with minimum value [i.e. Br...Br = 3.924(1)Å] is also observed in this compound and we found that such type of interactions are also helpful in further stabilization of the structure as shown in **Figure 4**.

TABLE-4: Torsion angle in [CdBr] based hybrid materials.

Code	Torsion Angle [1,2,3,4]°
Cd1	Br1—Cd—Cd ⁱ —Br2 ⁱ = 38.967(1)
Cd2	Br—Cd—Cd ⁱⁱ —Br ⁱⁱⁱ = -180.0(1)
Cd3	Br1—Cd—Cd ^{iv} —Br2 ^{iv} = -9.992(1)
Cd4	Br4—Cd—Cd ^v —Br3 ^v = -33.342(1)
Cd5	Br2—Cd—Cd ^v —Br1 ^v = 180.0(2)
Cd6	Br3—Cd1—Cd1 ^{vi} —Br2 ^{vi} = 68.715(4)
Cd7	Br3—Cd2—Cd3—Br3 ^{vii} = -60.000
Cd8	Br3—Cd—Cd ^v —Br1 ^v = 94.061(4)
Cd9	Br—Cd—Cd ^{viii} —Br ^{viii} = 99.522(3)
Cd10	Br2—Cd1—Cd1 ^{ix} —Br2 ^{ix} = -3.647(3)
Cd11	Br1—Cd1—Cd1 ^x —Br1 ^x = 180.0(1)
Cd12	Br1—Cd1—Cd1 ^{xi} —Br1 ^{xii} = 180.0(2)
Cd13	Br1—Cd1—Cd1 ^{xiii} —Br1 ^{xiii} = -42.897(1)
Cd14	Br1—Cd1—Cd1 ^{xiv} —Br1 ^{xiv} = -124.128(2)

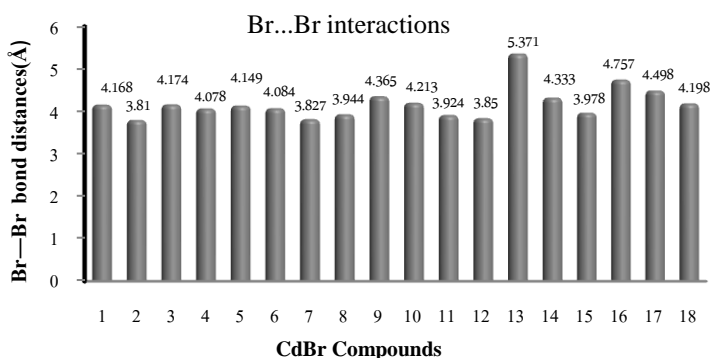


FIGURE-5: Graphical View of Br—Br bond distances (Å).

Cd15	$\text{Br2—Cd1—Cd1}^{\text{xv}}\text{—Br1}^{\text{xv}} = 76.287(3)$
Cd16	$\text{Br1—Cd1—Cd1}^{\text{xvi}}\text{—Br1}^{\text{xvii}} = 180.0(2)$
Cd17	$\text{Br1—Cd1—Cd1}^{\text{xviii}}\text{—Br1}^{\text{xviii}} = 22.434(4)$
Cd18	$\text{Br2—Cd1—Cd1}^{\text{xvii}}\text{—Br1}^{\text{xvii}} = -64.928(3)$

Symmetry Points: (i) 0.5-x, -0.5+y, 0.5-z; (ii) x, 1+y, 1+z; (iii) x, 1+y, z; (iv) 1-x, y, 1-z; (v) x, -1+y, z; (vi) x, y, -1+z; (vii) 2-x, 2-y, -z; (viii) 0.5+x, y, -0.5+z; (ix) -0.5+x, -y, -0.25-z; (x) x, y, 1+z; (xi) 1-x, 1-y, -z; (xii) x, 1-y, -0.5+z; (xiii) 1-x, y, 1.5-z; (xiv) 1.5-x, 1.5-y, -z; (xv) -x, 1-y, 1-z; (xvi) 1+x, y, z; (xvii) 1-x, 1-y, 1-z; (xviii) -x, 0.5+y, 0.5-z

TABLE-5: Torsion angles in [CdBr]⁻ based hybrid materials.

Code	Torsion Angle [1,2,3,4] ^o
Cd1	$\text{Cd—Br2—Br1—H3B}^{\text{i}} = 28.211(1)$
Cd2	$\text{Cd—Br—Br}^{\text{i}}\text{—Cd}^{\text{ii}} = -180.0(1)$
Cd3	$\text{H71—Br1—Br2}^{\text{iii}}\text{—Cd}^{\text{iii}} = 101.440(1)$
Cd4	$\text{Cd—Br1—Br2}^{\text{iv}}\text{—H1}^{\text{v}} = -97.194(1)$
Cd5	$\text{Cd—Br1—Br2—N2}^{\text{vi}} = 78.826(2)$
Cd6	$\text{Cd1—Br2—Br3—H1}^{\text{vii}} = 154.982(1)$
Cd7	$\text{Cd3—Br3—Br3}^{\text{viii}}\text{—Cd2}^{\text{ix}} = -113.794(3)$
Cd8	$\text{Cd—Br2—Br3—Cd}^{\text{i}} = -167.453(4)$
Cd9	$\text{Cd—Br—Br}^{\text{x}}\text{—Cd}^{\text{xi}} = 142.296(2)$

Cd10	$\text{Cd1—Br2—Br2}^{\text{xii}}\text{—Cd1}^{\text{xiii}} = 53.469(2)$
Cd11	$\text{Cd1—Br1—Br1}^{\text{xiv}}\text{—Cd1}^{\text{xiv}} = 180.0(1)$
Cd12	$\text{H2—Br1—Br1}^{\text{iv}}\text{—H5}^{\text{xv}} = -60.104(3)$
Cd13	$\text{Cd1—Br1—Br1}^{\text{xvi}}\text{—Cd1}^{\text{xvi}} = 141.638(2)$
Cd14	$\text{Cd1—Br1—Br1}^{\text{xvii}}\text{—Cd1}^{\text{xviii}} = -180.0(1)$
Cd15	$\text{Cd1—Br1—Br1}^{\text{xix}}\text{—Cd1}^{\text{xix}} = 180.0(4)$
Cd16	$\text{Cd1—Br1—Br1}^{\text{iv}}\text{—Cd1}^{\text{xx}} = 180.0(1)$
Cd17	$\text{Cd1—Br2—Br1}^{\text{xxi}}\text{—Cd1}^{\text{xxi}} = 163.297(3)$
Cd18	$\text{Cd1—Br1—Br2}^{\text{iv}}\text{—Cd1}^{\text{iv}} = 65.948(3)$

Symmetry Points: (i) x, 1+y, z; (ii) x, 1+y, 1+z; (iii) 1-x, y, 1-z; (iv) 1-x, 1-y, 1-z; (v) -1+x, 1+y, z; (vi) x, y, 1.5-z; (vii) -1+x, y, z; (viii) 1-x+y, 2-x, z; (ix) 2-y, 1+x-y, z; (x) -x, 0.5-y, 0.5+z; (xi) -0.5+x, y, 0.5+z; (xii) x, 0.5-y, 0.25-z; (xiii) 0.5+x, y, 0.25+z; (xiv) -x, -y, z; (xv) x, -y, 0.5+z; (xvi) 1.5-x, 0.5+y, 1.5-z; (xvii) 2.5-x, 1.5-y, 1-z; (xviii) 0.5+x, 1.5-y, 0.5+z; (xix) -x, 1-y, 1-z; (xx) 1+x, y, z; (xxi) -x, 0.5+y, 0.5-z

The minimum value of Br...Br bond distances is shown by the derivatives Coded as Cd2, Cd7, Cd8, Cd11, Cd12, Cd15 having values 3.810(2), 3.827(1), 3.944(1), 3.924(1), 3.850(1) and 3.978(2)Å respectively [Figure 5]. The Br—Cd—Cd—Br Torsion angles falls in the range -3.647(3)^o to 180^o with an average value of 91.051^o[Table 4]. Similarly, Cd—Br—Br—Cd Torsion angles falls in the range 28.211(1)^o to 180^o with an average value of 126.036^o[Table 5].

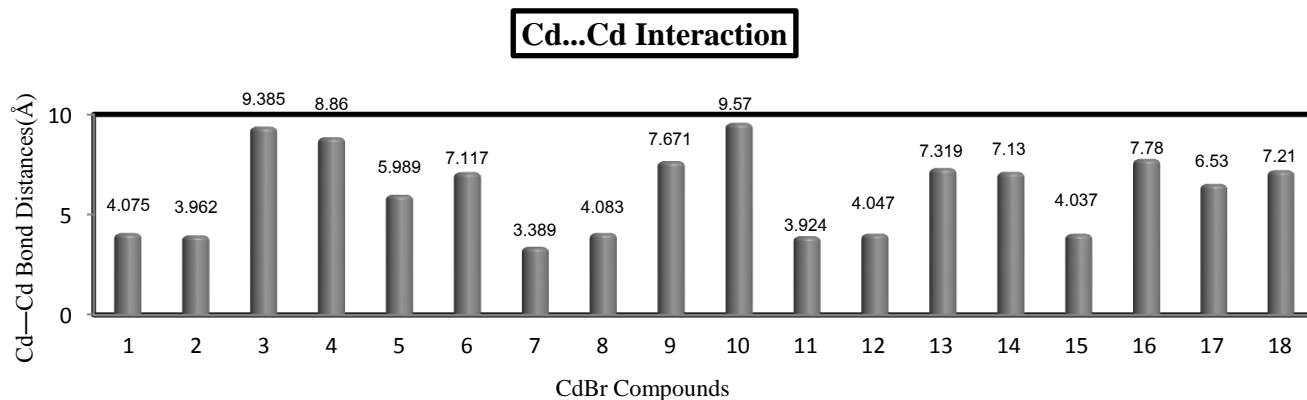


FIGURE-6: Graphical View of Metallophilic [Cd...Cd] Interactions.

The Cd...Cd bond distances for all other derivatives of [CdBr]⁻ have been calculated for their minimum values and it has been observed that these distances are more than their van der Waals radii and hence cannot be considered as metallophilic interactions.

IV. CONCLUSION

Hybrid materials represent one of the most fascinating developments in materials science in recent years. The tremendous possibilities of combination of different properties in

one material initiated an explosion of ideas about potential materials and applications.

The existence of Cd...Cd and Br...Br interactions has been studied. The dispersion term is found as the principal contribution in the stability at the long and short distances. The packing diagrams represent that Cd...Cd type of contacts has an advantage of versatility and flexibility of geometrical characteristics. Similar to other secondary interactions such as X—H...A and Halogen...Halogen, the Cd...Cd interactions could be a collective tool to design the new crystal structures.

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