

# Structure-Stability Relationship with Weak Secondary Interactions in a Series of Cadmium Chloride Metal-Organic Compounds

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**Abstract:** To scrutinize the role of weak interactions in structure-stability of cadmium based metal-organic compounds a series of sixty four derivatives were analyzed through single crystal X-ray crystallographic data obtained from IUCr. The structural parameters obtained from the cif file were simulated for molecular dynamics to calculate the weak interactions in series of CdCl<sub>2</sub> based metal-organic composites. The structural frameworks depict that the metal halides are holding the organic moieties within the inorganic patterns through X-H...A, C-H... , ... , halogen-halogen and Metallophilic secondary interactions. The comprehensive structural statistics results that the average Cd-X bond distance = 2.931(1)Å [CdCl<sub>2</sub> = 2.921(1)Å] and X-Cd-X bond angles lie in the range of 24.45 to 179.40° in these compounds. The X-H...A hydrogen bond calculations result the average H...A bond length = 2.48Å [CdCl<sub>2</sub> = 2.41Å] and the average X-H...A bond angle = 127.5° [CdCl<sub>2</sub> = 142°]. This indicates that these hydrogen interactions are in the category of strong to moderate type of hydrogen bonds. The minimum value of H... = 2.816(1)Å shows that such interactions are stabilizing the organic moieties within the metal-organic derivatives. It is observed that the minimum value of halogen...halogen weak interaction is 3.436(1)Å and the minimum value of metallophilic interaction distance is observed as 3.322(1)Å which are linking the inorganic components of metal-organic derivatives. The IR and Raman spectra tensors indicate that IR, Raman and Hyper-Raman modes are dominant in CdCl<sub>2</sub> based derivatives. The structural and spectroscopic parameters reveal that such weak interactions can be used to design the materials with spectroscopic applications.

**Keywords:** Weak X-H...A, C-H... , ... interactions, structure stability, Raman tensors.

## 1. Introduction

The hybrid materials can be defined in many different ways. Essentially there are two classes of hybrid materials class I and class II and here we will only consider materials with a covalent link between organic and inorganic moieties, i.e. 'class II' hybrid materials. Class I materials are merely a physical mixture of organic and inorganic components [1, 2]. In general, the benefit of hybrid materials relies in the combination of a closely interacting organic phase with an inorganic phase, inducing new properties that cannot be achieved with only one of these phases separately. Organic materials typically allow for much larger diversity of functional properties than inorganic materials due to the wide variety of organic moieties. This permits fine-tuning of interactions with the surrounding environment. Most inorganic materials only interact with the environment via the surface OH-groups (even though often present with different bond strengths) [3, 4] and the M-O-M groups (in which M is a metal), limiting their versatility. On the other hand, organic materials are characterized by a low stability (chemically, thermally and mechanically) in various operating conditions. For instance, polymers are often only stable in a narrow range of solvents, as they tend to dissolve, swell or tear locally. Similarly, sealing of e.g. polymer membranes is often inadequate due to lack of stability in a wide diversity of solvents or in harsh conditions (e.g. high temperatures, acids) [5]. Inorganic materials are often

very stable under these conditions. In contrast to polymers, they show no swelling and allow for high temperature treatments, e.g. to induce crystallization to further enhance the chemical and mechanical stability, or to attach layers or highly inert glass or ceramic sealings. However, ceramic materials may have stability issues under hydrothermal, acid or basic conditions. For example, amorphous silicates, especially pure silica, are known to have a low hydrothermal stability, giving rise to limited applicability in contact with water. Many metal oxides are unstable in either acids or bases. It is generally accepted that amorphous metal oxides materials are chemically less stable than crystalline ones, although transition metal oxides are often more stable than silica. The crystallization processes itself however can also have drawbacks as uncontrolled crystallization may give rise to structural collapse. While methods exist to control this process for large pores, crystallization can affect the integrity of thin-film microporous and mesoporous structures. This limits the availability of inorganic membranes with subnanometer pores and makes the production of nanofiltration membranes expensive. Although silica materials are less chemically stable, their structure is much easier to shape as uncontrolled crystallization does not occur (with the exception of zeolite membranes that are a separate class of materials). Another important factor is that a rigid pore structure can be more easily introduced in inorganic materials than in organic materials, making them better suited for sieving based on molecular size. These benefits and drawbacks allow both inorganic and organic materials to be utilized in various applications, but limit their applicability as the result of their respective restrictions in adjusting their performance to specific applications. For this reason, hybrid materials are being developed that combine the benefits of both types of materials or even introduce new unique properties.

## 2. Simulation and Computational molecular dynamics

Motivated by the industrial applications of metal-organic materials, as they are the future of nanotechnology of materials science due to combination of two different branches of solid state sciences such as organic and inorganic, in which the properties of two different materials can be clubbed together into single composite, a series of ninety five of cadmium based metal-organic molecules were selected from international union of crystallography, U.K. to analyze the role of secondary interactions in the structure-stability and structure-property relationship. The crystallographic open data base (COD), of international union of crystallography, U.K. was used to gather the available cadmium based metal-organic molecules structural data in the crystallographic information file format. The crystal structure data with IUPAC name for selected series of hybrid derivatives has been deposited in supplementary data Table 1 with codes CdCl-1[13], CdCl-2[14], CdCl-3[15], CdCl-4[16], CdCl-5[17], CdCl-6[18], CdCl-7[19], CdCl-8[20], CdCl-9[21], CdCl-10[22], CdCl-11[23], CdCl-12[24], CdCl-13[25], CdCl-14[26], CdCl-15[27], CdCl-16[28], CdCl-17[29], CdCl-18[30], CdCl-19[31], CdCl-20[32], CdCl-21[33], CdCl-22[34], CdCl-23[35], CdCl-24[36], CdCl-25[37], CdCl-26[38], CdCl-27[39], CdCl-28[40], CdCl-29[41], CdCl-30[42], CdCl-31[43], CdCl-32[44], CdCl-33[45], CdCl-34[46], CdCl-35[47], CdCl-36[48], CdCl-37[49], CdCl-38[50], CdCl-39[51], CdCl-40[52], CdCl-41[53], CdCl-42[54], CdCl-43[55], CdCl-44[56], CdCl-45[57], CdCl-46[58], CdCl-47[59], CdCl-48[60], CdCl-49[61], CdCl-50[62], CdCl-51[63], CdCl-52[64], CdCl-53[65], CdCl-54[66], CdCl-55[67], CdCl-56[68], CdCl-57[69], CdCl-58[70], CdCl-59[71], CdCl-60[72], CdCl-61[73], CdCl-62[74], CdCl-63[75], CdCl-64[76]. The molecular dynamics simulations for studying the physical evolutions of weak interactions were performed with DIAMOND-Crystal and molecular structure visualization and functions program [10].

## 3. Results and Discussion

The structural parameters were calculated by Crystal and molecular structure visualization and function programs which were further used to analyze the role of weak interactions in molecular frameworks of selected series of cadmium based metal-organic derivatives. With the crystallographic information file data, a wide range of structural functions were generated and the weak interactions were calculated and constructed by diamond software [10]. The crystallographic data obtained from the computational simulations for cadmium-centered bond distances and angles are presented in Table 1.

**Table 1:** Crystallographic data for Cd-centered bond distances (Å) and range of bond angles (°) in [CdX]<sup>+</sup> (Where X = Cl)

Code	Cd-X bond distance (Å)	X-Cd-X (°) range
CdCl1	Cd-Cl2 = 2.600(3) Cd-Cl2 = 2.603(3) Cd-Cl1 = 2.614(3) Cd-Cl1 = 2.621(3)	86.10-98.96
CdCl2	Cd1-Cl1 = 2.599(1) Cd1-Cl2A = 2.562(1) Cd1-Cl1A = 2.604(1) Cd1-Cl2 = 2.614(1)	179.40
CdCl3	Cd-Cl1 = 2.502(1) Cd-Cl2 = 2.695(1) Cd-Cl2 = 2.742(1)	91.07-180
CdCl4	Cd-Cl1 = 2.535(1) Cd-Cl2 = 2.664(1) Cd-Cl2 = 2.688(1)	87.15-180
CdCl5	Cd-Cl2 = 2.519(1) Cd-Cl1 = 2.673(1) Cd-Cl1 = 2.679(1)	86.87-180
CdCl6	Cd1-Cl1 = 2.570(3) Cd1-Cl1 = 2.577(2) Cd3-Cl4 = 2.582(2) Cd3-Cl6 = 2.583(2) Cd1-Cl2 = 2.596(2) Cd2-Cl2 = 2.608(2) Cd3-Cl6 = 2.609(2) Cd2-Cl3 = 2.614(2) Cd2-Cl5 = 2.617(2) Cd3-Cl5 = 2.638(3) Cd1-Cl3 = 2.650(3) Cd2-Cl4 = 2.679(3)	85.10-176.60
CdCl7	Cd1-Cl1 = 2.458(2) Cd1-Cl3 = 2.474(3) Cd1-Cl2 = 2.565(3) Cd1-Cl4 = 3.345(3)	94.98-135.79

CdCl8	Cd-Cl3 = 2.429(1) Cd-Cl4 = 2.443(2) Cd-Cl1 = 2.470(1) Cd-Cl2 = 2.504(1)	99.48-114.77
CdCl9	Cd-Cl1 = 2.567(1) Cd-Cl2 = 2.600(1) Cd-Cl2 = 2.613(1) Cd-Cl1 = 2.729(1)	86.11-174.71
CdCl10	Cd1-Cl1 = 2.578(4)	180
CdCl11	Cd-Cl2 = 2.581(1) Cd-Cl2 = 2.630(1) Cd-Cl1 = 2.694(1)	85.49-180
CdCl12	Cd1-Cl1 = 2.425(1)	180
CdCl13	Cd1-Cl2 = 2.609(1) Cd1-Cl1 = 2.612(1) Cd1-Cl2 = 2.627(4) Cd1-Cl1 = 2.631(1)	85.52-167.67
CdCl14	Cl6-Cd1 = 2.515(1) Cl7-Cd2 = 2.519(1) Cl2-Cd1 = 2.568(1) Cl8-Cd3 = 2.577(1) Cl1-Cd3 = 2.596(1) Cl8-Cd2 = 2.602(1) Cl2-Cd2 = 2.613(1) Cl5-Cd1 = 2.624(1) Cl5-Cd2 = 2.629(1) Cl3-Cd3 = 2.645(1) Cl4-Cd2 = 2.652(1) Cl3-Cd3 = 2.665(1) Cl4-Cd3 = 2.670(1) Cl1-Cd1 = 2.684(1) Cl4-Cd1 = 2.737(1) Cl3-Cd2 = 2.782(1)	82.75-177.83
CdCl15	Cd1-Cl3 = 2.453(1) Cd1-Cl2 = 2.578(1) Cd1-Cl2 = 2.660(1)	82.09-113.61

CdCl16	$Cd1-Cl2 = 2.561(1)$ $Cd2-Cl2 = 2.567(1)$ $Cd2-Cl1 = 2.640(1)$ $Cd1-Cl1 = 2.664(1)$	88.44-180
CdCl17	$Cd-Cl = 2.552(1)$ $Cd-Cl = 2.752(1)$	84.40-178.73
CdCl18	$Cd1-Cl1 = 2.551(1)$	58.65
CdCl19	$Cd1-Cl1 = 2.631(1)$	180
CdCl20	$Cd-Cl = 2.468(1)$	114.83
CdCl21	$Cd1-Cl4 = 2.461(1)$ $Cd1-Cl2 = 2.539(1)$ $Cd1-Cl2 = 2.617(1)$	86.30-115.31
CdCl22	$Cd-Cl = 2.521(1)$	24.45-180
CdCl23	$Cd1-Cl1 = 2.579(2)$ $Cd1-Cl2 = 2.591(2)$ $Cd1-Cl1 = 2.595(2)$ $Cd1-Cl2 = 2.599(2)$	86.87-178.37
CdCl24	$Cd2-Cl7 = 2.581(1)$ $Cd2-Cl4 = 2.593(1)$ $Cd1-Cl1 = 2.594(1)$ $Cd2-Cl6 = 2.607(1)$ $Cd2-Cl5 = 2.633(1)$ $Cd1-Cl2 = 2.631(1)$ $Cd1-Cl3 = 2.691(1)$	84.50-180
CdCl25	$Cd1-Cl1 = 2.647(1)$	180
CdCl26	$Cd1-Cl1 = 2.410(2)$ $Cd1-Cl2 = 2.537(1)$	100.53
CdCl27	$Cd1-Cl1 = 2.405(1)$ $Cd1-Cl2 = 2.465(1)$	114.31
CdCl28	$Cd1-Cl1 = 2.552(1)$ $Cd1-Cl1 = 2.750(1)$	84.86
CdCl29	$Cd1-Cl1 = 2.572(1)$	180
CdCl30	$Cd2-Cl3 = 2.490(1)$ $Cd1-Cl1 = 2.498(1)$ $Cd1-Cl2 = 2.535(1)$ $Cd2-Cl4 = 2.582(1)$	86.19-106.43

	Cd2-CI4 = 2.656(1) Cd1-CI2 = 2.674(1)	
CdCI31	Cd1-CI2 = 2.483(2) Cd1-CI1 = 2.604(2) Cd1-CI1 = 2.653(2)	90.84-170.82
CdCI32	Cd1-CI1 = 2.537(1)	94.84
CdCI33	Cd2-CI1 = 2.571(1) Cd2-CI2 = 2.535(1) Cd2-CI3 = 2.674(1) Cd2-CI4 = 2.584(1) Cd2-CI3 = 2.759(1) Cd2-CI5 = 2.652(1) Cd3-CI3 = 2.637(1) Cd3-CI4 = 2.561(1) Cd3-CI5 = 2.678(1) Cd3-CI6 = 2.552(1) Cd3-CI7 = 2.616(1) Cd4-CI6 = 2.575(1) Cd4-CI7 = 2.655(1) Cd4-CI8 = 2.541(1) Cd4-CI5 = 2.657(1) Cd4-CI7 = 2.793(1) Cd4-CI1 = 2.573(1)	83.65-176.93
CdCI34	Cd1-CI1 = 2.587(2) Cd1-CI3 = 2.615(1) Cd1-CI3 = 2.617(1) Cd1-CI2 = 2.625(1)	90.10-165.42
CdCI35	Cd1-CI3 = 2.469(2) Cd1-CI2 = 2.483(2) Cd1-CI1 = 2.669(2) Cd1-CI1 = 2.902(2)	84.90-173.60
CdCI36	Cd1-CI1 = 2.564(1) Cd1-CI1 = 2.578(1)	90.93
CdCI37	Cd1-CI2 = 2.385(1) Cd1-CI1 = 2.388(1)	121.18
CdCI38	Cd1-CI1 = 2.440(1)	180

	Cd1-Cd1 = 3.321(1)	
CdCl39	Cd1-CI2 = 2.522(1) Cd1-CI1 = 2.534(1) Cd1-CI5 = 2.680(1) Cd1-CI3 = 2.690(1) Cd1-CI4 = 2.692(1) Cd1-CI6 = 2.767(1) Cd2-CI10 = 2.518(1) Cd2-CI11 = 2.527(1) Cd2-CI6 = 2.670(1) Cd2-CI3 = 2.677(1) Cd2-CI9 = 2.730(1) Cd2-CI4 = 2.747(1) Cd3-CI8 = 2.508(1) Cd3-CI7 = 2.544(1) Cd3-CI5 = 2.628(1) Cd3-CI9 = 2.669(1) Cd3-CI4 = 2.720(1) Cd3-CI6 = 2.721(1)	78.45-175.58
CdCl40	Cd1-CI1 = 2.597(1) Cd1-CI1 = 2.607(1) Cd1-CI2 = 2.614(1) Cd1-CI2 = 2.688(1)	85.47-166.09
CdCl41	Cd1-CI2 = 2.627(1) Cd1-CI1 = 2.638(1)	85.68-180
CdCl42	Cd1-CI1 = 2.521(1) Cd2-CI2 = 2.592(1) Cd2-CI1 = 2.613(1) Cd1-CI3 = 2.637(1) Cd1-CI2 = 2.641(1) Cd1-CI3 = 2.648(1)	83.37-180
CdCl43	Cd1-CI1 = 2.519(1) Cd1-CI1 = 2.683(1)	83.92
CdCl44	Cd-CI1 = 2.489(1) Cd-CI2 = 2.507(1)	104.21
CdCl45	Cd1-CI1 = 2.536(2)	90.20

	Cd1-C11 = 2.708(1)	
CdCl46	Cd1-C11 = 2.607(1)	180
CdCl47	Cd1-C11 = 2.583(1)	180
CdCl48	Cd1-C11 = 2.620(1) Cd1-C11 = 2.708(1)	85.59
CdCl49	Cd2-C14 = 2.506(2) Cd1-C12 = 2.547(2) Cd2-C15 = 2.636(1) Cd2-C13 = 2.691(1) Cd1-C13 = 2.694(1) Cd2-C12 = 2.777(2)	78.43-180
CdCl50	Cd1-C11 = 2.544(1) Cd1-C11 = 2.637(1)	89.91
CdCl51	Cd1-C11 = 2.571(1) Cd1-C11 = 2.618(1)	87.08-179.01
CdCl52	Cd1-C13 = 2.563(1) Cd1-C12 = 2.578(1) Cd2-C11 = 2.580(1) Cd1-C11 = 2.616(1) Cd1-C13 = 2.627(1)	86.95-171.72
CdCl53	Cd1-C11 = 2.484(1) Cd2-C14 = 2.589(4) Cd1-C12 = 2.637(2) Cd2-C13 = 2.657(3) Cd1-C14 = 2.682(1) Cd1-C13 = 2.713(3) Cd1-Cd2 = 3.458(2)	79.95-180
CdCl54	Cd-C11 = 2.626(1) Cd-C12 = 2.622(1) Cd-C12 = 2.658(1) Cd-C11 = 2.670(1)	83.24-174.32
CdCl55	Cd2-C13 = 2.518(1) Cd1-C16 = 2.526(1) Cd1-C12 = 2.530(1) Cd2-C15 = -2.543(1) Cd1-C11 = 2.558(1)	79.84-170.83



	Cd1-C14 = 2.585(1) Cd2-C16 = 2.669(1) Cd2-C12 = 2.716(1) Cd2-C11 = 2.725(1) Cd2-C14 = 2.797(1)	
CdCl56	Cd1-C12 = 2.549(1) Cd1-C13 = 2.643(1) Cd1-C11 = 2.665(1) Cd1-C14 = 2.667(1) Cd1-C14 = 2.792(1)	82.58-175.27
CdCl57	Cd1-C16 = 2.580(1) Cd1-C12 = 2.618(1) Cd1-C14 = 2.633(1) Cd1-C13 = 2.639(1) Cd1-C15 = 2.698(1) Cd1-C15 = 2.784(1)	81.68-175.69
CdCl58	Cd1-C12 = 2.441(1) Cd1-C11 = 2.479(1)	102.49-115.92
CdCl59	Cd1-C11 = 2.543(1) Cd1-C12 = 2.674(1) Cd1-C13 = 2.676(2)	88.87-180
CdCl60	Cd2-C13 = 2.471(1) Cd2-C14 = 2.512(1) Cd1-C11 = 2.626(1) Cd2-C12 = 2.634(1) Cd1-C11 = 2.699(1) Cd1-C12 = 2.720(1) Cd2-C14 = 2.753(1) Cd1-C13 = 2.893(1)	80.91-178.16
CdCl61	Cd1-C12 = 2.422(1) Cd1-C11 = 2.482(1) Cd1-C13 = 2.490(1) Cd1-C13 = 2.764(1) Cd1-C11 = 2.784(1)	81.49-170.23
CdCl62	Cd1-C11 = 2.550(1) Cd1-C11 = 2.809(1)	88.55

CdCl63	Cd2-Cl1 = 2.534(1) Cd2-Cl2 = 2.546(1) Cd2-Cl2 = 2.647(1) Cd1-Cl1 = 2.673(1)	85.48-113.42
CdCl64	Cd1-Cl3 = 2.485(1) Cd2-Cl6 = 2.520(1) Cd1-Cl4 = 2.545(1) Cd2-Cl1 = 2.555(1) Cd2-Cl2 = 2.590(4) Cd2-Cl4 = 2.601(1) Cd1-Cl2 = 2.615(4) Cd1-Cl1 = 2.624(1) Cd1-Cl5 = 2.715(4) Cd2-Cl5 = 2.729(4) Cd1-Cl5 = 2.942(1) Cd2-Cl5 = 2.948(1)	81.82-173.21

### 3.1. Hydrogen Bonding

*[CdCl<sub>2</sub>]<sup>-</sup> based metal-organic compounds*

The hydrogen bond geometry for CdCl<sub>2</sub> derivatives indicates that the acceptor bond length lies in the range of 1.72Å to 3.17Å and the donar-acceptor length exist in between 2.574(3) Å to 4.099(3)Å and H-centered D-A angle has values from 103° to 179°.

The d- scatter plot for hydrogen bonding interactions shows that most of the data points exist in H...A distance range of 3.4 to 3.9 Å and X-H...A angle ranges from 70° to 170° in the selected series of metal-organic compounds which indicate these interactions are moderate type of hydrogen bonds as shown in Figure 1.

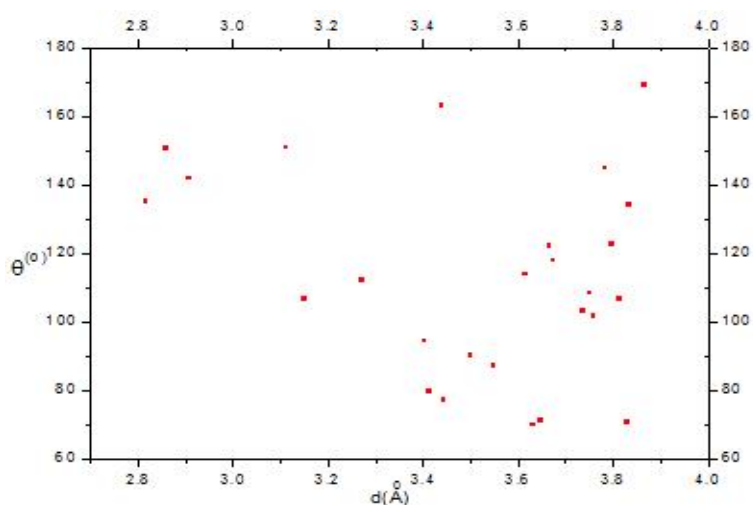


Figure 1. d- scatter plot for hydrogen bonding interactions

### 3.2 -interactions

The -interactions were constructed by selecting the center of two phenyl rings and their corresponding distances and torsion angles were calculating, which shows that the minimum value of ... distance in cadmium chloride is 3.561(9)Å for compound CdCl27 with torsion angle 116.69(3)° having symmetry position 1-x,1-y,1-z and the maximum ... interaction is 3.913(1)Å for compound CdCl4 with torsion angle 162.10(2)° having symmetry position x,1+y,z. as shown in Table 2.

**Table 2:** ... interactions in selected series of metal-organic compounds.

Code	... interaction	... (Å) Distance	Max. torsion angle (°)
CdCl4	... i	3.913(1)	C2- ... -C2=162.1(2)
CdCl27	... ii	3.561(9)	C2- ... -C18=116.69(3)
CdCl36	... ii	3.709(2)	C2- ... -C17 <sup>iv</sup> = -87.66(2)
CdCl51	... iii	3.731(7)	C5 <sup>v</sup> - ... -C6 <sup>vi</sup> = 62.79(3)
CdCl57	...	3.757(6)	C4 <sup>vii</sup> - ... -C13=119.69(2)

Symmetry Codes: (i) x, 1+y, z (ii) 1-x, 1-y, 1-z (iii) 1.5-x, 0.5+y, 0.5-z (iv) 2-x, 2-y, z (v) 1.5+x, -0.5+y, z (vi) 0.5+x, 0.5+y, z (vii) 0.5-x, 0.5-y, -1+z

The minimum value of H... interactions bond distance for cadmium chloride is 2.816(1)Å in CdCl43 compound and maximum is 3.865(1)Å for CdCl51 compound where as the minimum C-H... bond angle is 69.90(2)° for CdCl27 compound and 169.28(3)° is the maximum bond angle for CdCl51 as calculated in supplementary data Table 3.

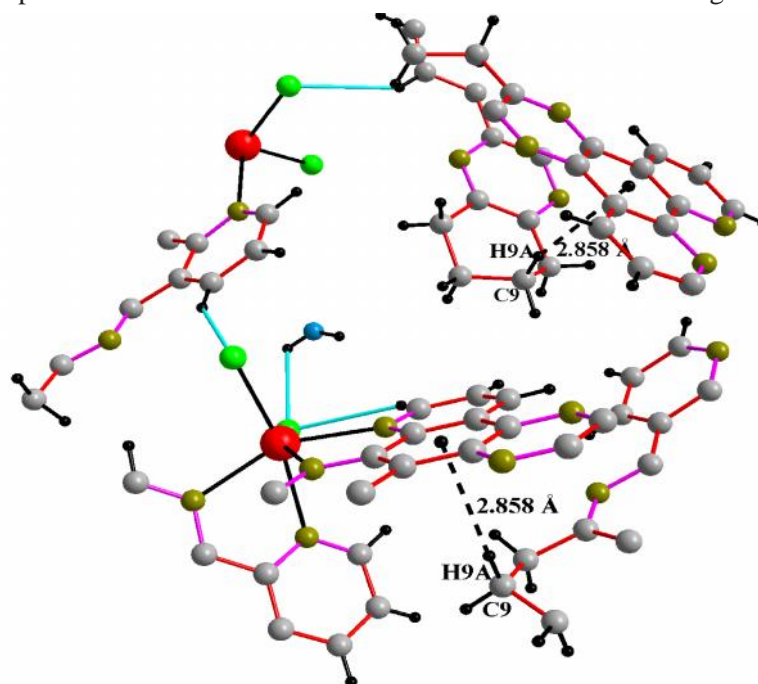
**Table 3:** C-H... interactions in selected series of metal-organic compounds.

Code	C-H... interaction	H... (Å) Distance	C-H... (°)
CdCl3	C3-H3 <sup>i</sup> ...	2.908(3)	141.84(3)
CdCl4	C5-H5 <sup>ii</sup> ...	3.112(4)	150.92(4)
CdCl6	C11-H11C <sup>iii</sup> ...	3.796(9)	122.76(6)
CdCl27	C2-H2... <sup>iii</sup>	3.630(1)	69.90(2)
CdCl28	C3-H3 <sup>iv</sup> ...	3.403(2)	94.41(2)
CdCl30	C20-H4A...	3.833(1)	134.27(3)
CdCl32	C2-H2 <sup>iii</sup> ...	3.443(1)	76.92(2)
CdCl35	C11-H11C <sup>v</sup> ...	3.151(5)	106.69(2)
CdCl36	C18-H18... <sup>vi</sup>	3.413(2)	79.75(2) <sup>iii</sup>
CdCl37	C17-H17A <sup>iii</sup> ...	3.271(2)	111.96(2)
CdCl38	C11-H11B <sup>vii</sup> ...	3.647(3)	71.27(3)
CdCl39	C13-H13A...	3.674(1)	117.83(1)
CdCl40	C9-H9 <sup>viii</sup> ...	3.750(9)	108.34(2)
CdCl42	C12-H12A... <sup>ix</sup>	3.499(1)	90.04(3)
CdCl43	C1-H1B <sup>x</sup> ...	2.816(1)	135.09(3)
CdCl44	C9-H9A <sup>xi</sup> ...	2.858(4)	150.76(3)
CdCl45	C7-H7 <sup>iii</sup> ...	3.812(2)	106.64(1)
CdCl46	C7-H7A <sup>xii</sup> ...	3.736(1)	103.29(1) <sup>xiii</sup>

CdCl47	C1-H4... <sup>xiv</sup>	3.666(1)	122.19(2) <sup>xv</sup>
CdCl50	C5-H5A <sup>iii</sup> ...	3.548(9)	87.14(2)
CdCl51	C5-H5 <sup>xvi</sup> ...	3.865(1)	169.28(3) <sup>xvii</sup>
CdCl57	C13-H13...	3.829(6)	70.63(2)
CdCl58	C10-H10B <sup>iii</sup> ...	3.783(6)	144.90(3)
CdCl59	C16-H16C <sup>iii</sup> ...	3.615(1)	113.96(4)
CdCl61	C8-H8A <sup>xviii</sup> ...	3.439(8)	163.13(2)
CdCl62	C1-H1 <sup>xix</sup> ...	3.758(3)	101.58(2)

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

Different structural motifs were obtained within the organic moiety through  $\pi$ -interactions such as a bifurcated C-H... interaction in CdCl44 with H9A atom at symmetry position x, 1.5-y, -0.5+z in which acts as acceptor of H9A atom at symmetry position x, -1+y, z of organic moiety of the metal-organic derivatives linking the organic components in 1D chain of C-H... interactions as shown in Figure 2.



**Figure 2.** C-H... interaction in CdCl44 with H9A atom at symmetry position x, 1.5-y, -0.5+z, acts as bifurcated acceptor.

### 3.3. Halogen-Halogen interactions

#### *[CdCl<sub>2</sub>]<sup>-</sup> based metal-organic compounds*

The bond lengths of Cd-Cl bond lies in an average range of 2.385 Å to 2.647 Å. The bond distances for these derivatives illustrate that most of the data points lie in between 2.45 to 2.60 Å whereas the data points for CdCl8, CdCl12, CdCl13, CdCl19, CdCl25, CdCl26, CdCl27, CdCl37, CdCl38, CdCl41, CdCl46, CdCl48, CdCl54, CdCl58, and CdCl61 shows some deviation from this range and it could be due to variety of X-H...A

interactions. The Cl-Cd-Cl bond angles have wide variety with minimum range of  $86.10^\circ$  to  $98.96^\circ$  for the molecule CdCl1 to maximum range of  $79.95^\circ$  to  $180^\circ$  for the molecule CdCl53 as shown in Table 1. The Cl...Cl and Cd...Cd bond distances with their symmetry positions are given in supplementary data Table 2 respectively. The Cd...Cd bond distance in compound CdCl1 is calculated as  $3.641(1) \text{ \AA}$  which shows that the structure is stabilized by metallophilic interactions apart from X-H...A and Cl...Cl secondary. The minimum value of Cl...Cl contacts in CdCl16 [Cl1...Cl2 =  $3.651(1) \text{ \AA}$ , Cl1...Cl2 =  $3.713(1) \text{ \AA}$ ], CdCl17 [Cl...Cl =  $3.565(1) \text{ \AA}$ ], CdCl18 [Cl1...Cl1 =  $5.144(2) \text{ \AA}$ ], CdCl21 [Cl2...Cl2 =  $3.527(1) \text{ \AA}$ ] and CdCl23 [Cl1...Cl1 =  $3.571(3) \text{ \AA}$ ] with minimum Cd...Cd [Cd...Cd =  $3.560(1) \text{ \AA}$  (CdCl16), Cd...Cd =  $3.931(2) \text{ \AA}$  (CdCl17), Cd...Cd =  $3.849(1) \text{ \AA}$  (CdCl18), Cd...Cd =  $3.762(4) \text{ \AA}$  (CdCl21) and Cd...Cd =  $3.708(2) \text{ \AA}$  (CdCl23)] bond distances show that these smaller values could be due to Cl...Cl interactions and are also helpful in the stabilization of the crystal structures as shown in supplementary Figures 1, 2, 3, and 4.

The Cd...Cd bond distances in the compounds of CdCl45, CdCl48, CdCl49, CdCl50, CdCl51, CdCl52, CdCl53, CdCl54, CdCl55, CdCl56, CdCl60, CdCl61, CdCl62, CdCl63 and CdCl64 are calculated as  $3.703(1) \text{ \AA}$ ,  $3.901(4) \text{ \AA}$ ,  $3.519(2) \text{ \AA}$ ,  $3.667(1) \text{ \AA}$ ,  $3.731(1) \text{ \AA}$ ,  $3.747(1) \text{ \AA}$ ,  $3.458(2) \text{ \AA}$ ,  $3.619(4) \text{ \AA}$ ,  $3.870(1) \text{ \AA}$ ,  $3.963(1) \text{ \AA}$ ,  $3.924(1) \text{ \AA}$ ,  $3.985(1) \text{ \AA}$ ,  $3.841(4) \text{ \AA}$ ,  $3.815(1) \text{ \AA}$  and  $3.952(2) \text{ \AA}$  respectively, which shows that the structures are well stabilized by metallophilic interactions apart from X-H...A and Cl...Cl secondary interactions as shown in supplementary Figures 5,6, 7 and 8. The minimum value of torsion angle [Cl-Cd...Cd-Cl] is  $10.34(2)^\circ$  for the compound CdCl64 having  $-1+x$ ,  $1+y$ ,  $1+z$  symmetry positions and maximum value of torsion angle is  $178.01(1)$  for compound CdCl51 having  $-x$ ,  $-1+y$ ,  $0.5-z$  symmetry positions.

### 3.4. Metallophilic Interactions

*[CdCl<sub>2</sub>]<sup>-</sup> based metal-organic compounds*

The secondary interactions in CdCl38 shows the minimum value between Cd...Cd atoms in these compounds comes out to be  $3.322(1) \text{ \AA}$  with symmetry position of  $-x$ ,  $2-y$ ,  $1-z$  respectively.

## 4. IR and Raman Tensors

IR and Raman spectra tensors have been calculated by using fractional co-ordinates obtained from single crystal XRD data as presented in supplementary data Table 3. In which the lattice parameters and the fractional coordinates were used to study spectral active modes of IR and Raman spectra tensors in the SAM structural utility tool of Bilbao crystallographic server [11-12]. The quantitative comparison of the crystal structures of the selected series of metal-organic compounds through theoretically structural models shows that these compounds have the promising results for spectroscopic applications.

## 5. Conclusion

The analysis of weak interactions such as X-H...A, C-H... , ... , halogen...halogen and Cd...Cd in cadmium based metal-organic derivatives results that these interactions are responsible for holding the inorganic and organic moieties in single composite. The ... interactions are binding the organic moieties into dimmer patterns whereas the halogen-halogen and metallophilic interactions are holding the inorganic constituents into 1D chain and 2D layer patterns. The metallic constituents of these derivatives provide the mechanical strength to the composite whereas the organic moiety is responsible for its optical as well as spectroscopic properties. The spectroscopic studies for IR, Raman and Hyper-Raman tensors show that these materials can be used in junction diodes of hybrid solar cells in which the stability of the hybrid structure is maintained by these weak interactions. 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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