Synthesis, Crystal Structures, Hirshfeld Surfaces Analysis and Physico-Chemical Characterization of Two New ZnII and CdII Halidometallates

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Abstract

Two new organic-inorganic hybrid materials, based on 1,3-CycloHexaneBis-(Methyl Amine), abbreviated CHBMA, namely $(\text{H}_2\text{CHBMA})\text{ZnCl}_4\cdot2\text{H}_2\text{O}$ (CP1) and $(\text{H}_2\text{CHBMA})\text{CdI}_4\cdot2\text{H}_2\text{O}$ (CP2), have been synthesized under mild conditions in acidic media and characterized by single-crystal X-ray diffraction, spectroscopic techniques ($^{13}\text{C}$ NMR, FT-IR, RAMAN) and thermal analysis. The crystal structures of the two compounds were solved by single-crystal X-ray diffraction methods. Both compounds show a 3-dimensional supramolecular structure directed by various interactions between tetrahalidometallate anions ($\text{ZnCl}_4^{2-}$, $\text{CdI}_4^{2-}$), water molecule and organic cations $(\text{H}_2\text{CHBMA})^{2+}$. For both compounds, the cyclohexane ring of the template cation is in a chair conformation with the methyl-ammonium substituent in the equatorial positions and the two terminal ammonium groups in a cis conformation but with two different orientations (upward for CP1 and downward for CP2) which influences the supramolecular architecture of the two structures. Hirshfeld surface analysis and the associated two-dimensional fingerprint plots were used to explore and quantify the intermolecular interactions in the crystals.

Introduction

In recent years, hybrid compounds represent a novel class of materials that could combine both organic and inorganic components into a single material in the solid state [1-2]. Inside the structures of these materials, the organic and inorganic components are connected through covalent, ionic or hydrogen bonds. This symbiosis between two domains of chemistry considered for a long time as antagonists can also conduct to totally new properties, and open up a new and an ample area of research in chemistry. In particular, metalhalides may be assembled with organic amines to generate two different categories of hybrid materials based on the bonding chemical nature between organic molecule and inorganic units. This means that the structure of the final product and its properties are dependent on many factors, such as the selection of organic amine molecule, the suitable metal halide and the synthetic conditions (pH value of the reaction medium, anions, temperature, solvent type...etc.)) [3].

When the organic amine and the metal ion or metal halide are connected together via strong chemical bonds (covalent, ionic-covalent or coordination bonds); the resulting product being part of organically coordinated metal halide family. The design and construction of these complexes have been attracted significant attention due to their fascinating structures and their promising applications in diverse fields such as catalysis [4-6], fluorescence and sensing [7], medicinal chemistry as pharmaceutical compounds [8-9]. In this case, the choice of organic amine ligand is especially significant in obtaining desirable materials, because the architecture of coordination complexes can be considerably impacted by the shape, symmetry, flexibility and the number of amine groups available for coordination. It is well known that structural geometry changes have an important impact on the properties of the final complexes [10].

When the components are associated as perhalidometallate anions and organic cations, the resulting products belong to the organically templated perhalidometallate family. In that event, the cohesion of the whole structure is ensured only by weak bonds, namely hydrogen bonding, ionic bonds and Van der
Waals interactions. The class of these hybrid compounds is very wide and very often conserves the properties of the individual parts, i.e. the organic component offer structural diversity (great flexibility in the choice of molecules, length, polarizability, degree of saturation...) and also remarkable luminescent properties and potential of conductivity while the inorganic component potentially contributes to thermal stability, mechanical resistance, interesting magnetic or ferroelectric transitions and electric properties (conductor, semiconductor, insulator...) [11-12]. Most of these ionicorganic-inorganic hybrid metal halides experience multiple structural phase transitions frequently related to the reorientation dynamics of the organic ammonium groups [13-16] and some even show interesting physical properties, such as, pyroelectricity, ferroelectricity, ferroelasticity and low dimensional magnetism [13, 17, 18]. Moreover, these materials were applied as catalysts in catalytic reactions such as acetylation [19], Henry reaction [20] at room temperature under mild conditions in the presence of methanol, as solvent. As a contribution to the investigation of the above materials, we report the synthesis, crystal structure study, Hirshfeld surface analysis, spectroscopic measurement and thermal analysis of two novel organically templated perhalidometallates, namely (H$_2$CHBMA)ZnCl$_4$.2H$_2$O (CP1) and (H$_2$CHBMA)CdI$_4$.2H$_2$O (CP2) where CHBMA is 1,3-CycloHexaneBis(MethylAmine).

**Experimental Section**

2.1 Materials and methods

All the used chemicals [Zin(II) chloride (ZnCl$_2$), Cadmium(II) iodide (CdI$_2$), Hydrochloric acid (HCl; 37%), Sulfuric acid (H$_2$SO$_4$; 98%) and 1,3-CycloHexaneBis(MethylAmine), abbreviated CHBMA, were obtained from commercial sources and used without further purification. CHBMA was purchased from Aldrich as a mixture of cis and trans isomers.

Infrared spectrum was recorded at a room temperature on a Nicolet 470 FTIR spectrophotometer in the 4000-400 cm$^{-1}$ region. Thin transparent pellet was made by compacting an intimate mixture obtained by shaking 2 mg of the sample in 100 mg of KBr. Thermogravimetric and differential thermal analyses (TGA-ATD) were carried out on a Setaram TG-DTA 92-16.18 thermal analyzer. Sample was placed in an open platinum crucible and heated, under air, from room temperature to 600°C with 10°C/min heating rate; an empty crucible was used as reference.

2.2. Synthesis

2.2.1. Synthesis of (H$_2$CHBMA)ZnCl$_4$.2H$_2$O , (CP1).

Crystals of (H$_2$CHBMA)ZnCl$_4$.2H$_2$O(CP1) was obtained by slow evaporation, at room temperature. 1,3-CycloHexyl(MethylAmine) (CHBMA) was dissolved with ZnCl$_2$ in 15 ml of distilled water and hydrochloric acid HCl with the metal/amine/acid molar ratio of 1:1:2. The reaction can be schematically written as:

CHBMA + (Zn$^{2+}$,2Cl$^-$)+ 2(H$_3$O$^+$, Cl$^-$) (H$_2$CHBMA)ZnCl$_4$.2H$_2$O
The reaction mixture was stirred for about a period of 20 min until the complete dissolution. After slow evaporation of the solution at room temperature during a period of 7 days, air stable colorless crystals of CP1 suitable for X-ray diffraction were selected (yield 55%).

2.2.1. Synthesis of \((\text{H}_2\text{CHBMA})\text{CdI}_4.2\text{H}_2\text{O}\), (CP2).

The new compound \((\text{H}_2\text{CHBMA})\text{CdI}_4.2\text{H}_2\text{O}(\text{CP2})\) was synthesized by slow evaporation, at room temperature. 1,3-cyclohexyl(methylamine) (CBM) was dissolved with CdI\(_2\) in about 20 ml of distilled water and sulfuric acid H\(_2\)SO\(_4\) with the metal/amine/acid molar ratio of 2:1:1. The reaction can be schematically written as:

\[
2(\text{Cd}^{2+}, 2\text{I}^-)+\text{CHBMA} + (2\text{H}_3\text{O}^+, \text{SO}_4^{2-}) (\text{H}_2\text{CHBMA})\text{CdI}_4.2\text{H}_2\text{O} +(\text{Cd}^{2+}, \text{SO}_4^{2-})
\]

After stirring over a period of about 30 min, the final mixture was preserved at room temperature. After a few days, colorless crystals appeared (yield 49%), from which crystals suitable for X-ray analysis were chosen. In addition, they are also stable in normal conditions of temperature and humidity.

2.3 Crystal structures determination and refinement.

The crystal structures of compounds (CP1) and (CP2) were determined by single-crystal X-ray diffraction. The crystal parameters and experimental details of the data collection are summarized in Table 1. All H atoms were located in difference Fourier maps. C- and N-bounds H atoms were included in calculated positions and refined with isotropic displacement parameters riding on those of the parent atoms. The H atoms of the water molecules of CP1 were refined freely, while those of CP2 were placed in their expected calculated positions and refined as riding, with OW-H = 0.85 Å and with U\(_{\text{iso}}\) = 1.5 U\(_{\text{eq}}\)(OW).

2.4 Hirshfeld surface calculation

The Hirshfeld surfaces and their corresponding two-dimensional fingerprint plots were calculated using the CrystalExplorer[21] software package, which accepts a structure input file in the CIF format. Graphical plots of the Hirshfeld surfaces are mapped with the normalized contact distance (d\(_{\text{norm}}\)), and these points out the regions of particular importance to intermolecular interactions. To visualize the intermolecular interactions on the Hirshfeld surface mapped over d\(_{\text{norm}}\), a color scale of red, white, or blue is used when the intermolecular contacts are shorter, equal, or longer than the van der Waals separation, respectively. The two-dimensional fingerprint plot furnishes breakdown of Hirshfeld surfaces into relative contribution of different intermolecular interactions existing in the crystal structures.

Results And Discussion

3.1. Structures description

3.1.1. \((\text{CBMH}_2)\text{ZnCl}_4.2\text{H}_2\text{O}\), (CP1).
The single-crystal X-ray diffraction investigation has exhibited that the new organic-inorganic hybrid compound CP1 crystallizes in the monoclinic system with space group P2\(_1\)/c. The asymmetric unit is made up of one (H\(_2\)CHBMA\(^{2+}\)) organic cation, an isolate [ZnCl\(_4\)]\(^{2-}\) anion and two crystallographically independent uncoordinated molecules water as shown in Fig. 1a. The cohesion between these entities is ensured by a complex hydrogen bonding system and by Columbic interactions. The distribution of the different species is shown in Fig. 2c.

The central divalent Zn is surrounded by four chlorine atoms in a slightly distorted tetrahedral geometry. The bond length of the Zn-Cl lie in the range 2.2590 (5) - 2.2989 (5) Å (Zn-Cl\(_{av}\) = 2.274Å) and the bond angles Cl-Zn-Cl vary from 104.23 (2) to 114.49 (2)° (Cl-Zn-Cl\(_{av}\) = 109.44°), are in agreement with those observed in analogous compounds [22-25]. These geometric parameters in ZnCl\(_4\)\(^{2-}\) are related to the number of hydrogen bonds accepted by the Cl atoms. To quantify the distortion of the [ZnCl\(_4\)]\(^{2-}\) anion from the ideal tetrahedral conformation, \(s_4\) is a structural parameter introduced by Yang et al. (2007) [26] which can be used to gauge mainly the geometries of four-coordinate metal complexes. This parameter is defined as \(s_4 = \frac{\text{Valence angle 1} + \text{Valence angle 2}}{2} - 109.5^\circ\), where and are the two largest valence angles around the central atom and = 109.5° is the ideal tetrahedral angle. \(s_4\) can vary from 0 to 1, passing from an absolute square planar to an ideal tetrahedral conformation. The \(s_4\) value of the present structure is 0.952 which proves a little distortion of the Zn atom from a regular tetrahedron. BVS calculations using the Brown and Altermatt method [27] revealed that the zinc atom have valence sums equal with a value of 2.045, close to the ideal value of 2 for Zn\(^{II}\).

In the crystal structure, the four chlorine atoms of the [ZnCl\(_4\)]\(^{2-}\) anion are acting as acceptors of hydrogen bonds. Each ZnCl\(_4\)\(^{2-}\) anion bridge the water molecules (O1W, O2W) by means of O-HCl hydrogen bonds, forming an infinite two dimensional supramolecular (ZnCl\(_4\)-OW)\(_n\) sheets extending parallel to (001) plane (Table 2, Fig. 2b). Within the anionic supramolecular layers, rings with graph-set motifs [28] of and are observed, lying at x = ½.

The (CHBMAH\(_2\))\(^{2+}\) cations are arranged on both side of these anionic layers through non covalent interactions, to form 3-dimensional supramolecular structure. Hence, each (CBMH\(_2\))\(^{2+}\) cation engages its hydrogen atoms bonded to N1 and N2 atoms in hydrogen bonds and participates in the structure stability via inter molecular H-bonds established between the organic and inorganic layers. The hydrogen-bonds details are given in Table 2 and are shown in Fig. 1c. The hydrogen bond interactions link the three components into a supramolecular 3D network.

In CP1, the C6-ring of the template cation adopts a typical chair conformation, four carbon atoms are coplanar, and the other two are puckered out of this plane, with normal distances C-C, C-N and angles C-C-C, C-C-N (Table 3). Interestingly, although CBM was employed as a mixture of cis and trans isomers, the organic cation (CBMH\(_2\))\(^{2+}\) present is conformation in the title compound (Fig.1a). Similar phenomenon was observed in the preparation of TJPU3, in which solely cis-CBM is used as template [29].
3.1.2. \((\text{H}_2\text{CBHMA})\text{CdI}_4\cdot \text{2H}_2\text{O} \), (CP2).

CP2 crystallizes in the monoclinic centrosymmetric space group P2\(_1\)/m, the formula unit contains one \((\text{CBMH}_2)_2^{2+}\) cation, one \(\text{CdI}_4^{2-}\) anion and two molecules water of crystallization (Fig.2a). As shown in Fig. 2b, the central \(\text{Cd}^{II}\) atom, together with \(\text{I}_2\) and \(\text{I}_3\) atoms of the \(\text{CdI}_4^{2-}\) anion and carbon atoms \(\text{C}_4\) and \(\text{C}_5\) of the cyclohexane ring lie in a specific crystallographic location, namely on mirror plane \(m\). The remaining atoms of the cation, anion and water molecules, lying outside the plane, are necessarily mirror images of each other. Crystal structure study proves that in CP2, the \(\text{Cd}^{II}\) ion is in a slightly distorted tetrahedral geometry, with a four coordinate index, \(\tau_4\) [26], of 0.97. Selected bond lengths and angles are listed in Table 5 and are in agreement with the values reported for analogous compounds [30-32]. The bond angles implying the \(\text{Cd}^{II}\) atom range between 100.13(3) and 111.585(18) Å. The short value, significantly smaller than all the other bond angles, is observed for the \(\text{I}_2\)-\(\text{Cd}\)-\(\text{I}_3\) angle. This distortion can be explained by the fact that the iodine atoms are involved in a complex system of hydrogen bonds \(\text{O(N)}\cdot\cdot\cdot\text{H}\cdots\text{I}\) responsible for the phenomenon.

In the material, the discrete \(\text{CdI}_4^{2-}\) anions alternately bridge the water molecules (OW) via \(\text{O-H}\cdots\text{I}\) hydrogen bonds, building an infinite two-dimensional supramolecular \(\{\text{CdI}_4\cdot \text{OW}\}_\infty\) undulated layers extending parallel to (001) plane (Fig.2c). Within the anionic supramolecular layer, rings with a graph-set ring motif [28] of and are observed, lying at \(x = \frac{1}{2}\) (Fig. 2c). The \((\text{H}_2\text{CBHMA})^{2+}\) cations are confined between these anionic layers to maximize the electrostatic interactions and are connected to \(\text{CdI}_4^{2-}\) anion and \(\text{H}_2\text{O}\) molecule via \(\text{N-H1C}\cdots\text{OW}, \text{N-H1A}\cdots\text{I}_1\), \(\text{N-H1B}\cdots\text{I}_3\) and \(\text{C5-H5A}\cdots\text{I}_3\) hydrogen bonds, thus forming a three-dimensional supramolecular structure.

It is worth to note that the existence of the uncoordinated water molecule consolidates the \(\text{H}\)-bonding network. It can participate as \(\text{H}\)-bond donor with the iodide ligands of the isolated tetrahedral \(\text{CdI}_4^{2-}\) units (\(\text{OW-H2}\cdots\text{I}_1, \text{OW-H2}\cdots\text{I}_2, \text{OW-H1}\cdots\text{I}_3\)) and as \(\text{H}\)-bond acceptor with the positively charged ammonium groups of \((\text{CBMH}_2)^{2+}\) cations ((\(\text{N-H1C}\cdots\text{OW}\)). The hydrogen-bond details are given in Table 4 and are shown in Fig. 2d. The hydrogen bond interactions link the \(\text{CdI}_4^{2-}\) anion, \((\text{CBMH}_2)^{2+}\) cations and \(\text{H}_2\text{O}\) molecule, to create a two-dimensional (2-D) hydrogen bond network.

Other interesting noticing is the template CHBMA molecule. As in the case of compound CP1, the cyclohexane ring of the organic cation in CP2 adopts also a chair conformation which is the most stable. Furthermore, although CBM molecule was used as a mixture of cis and trans isomers, the two methylamine groups exist in the cis conformation in both CP1 and CP2. For the same cis conformation, the two terminal ammonium groups in organic moiety are pointing upward for CP1 and downward for CP2. This difference has an impact on the topological nature of the anionic layers and is reflecting in a different anchoring of the organic cations on the anionic layers, built a three-dimensional hydrogen bonded network in the case of CP1 and two-dimensional hydrogen bonded network in the case of CP2.
Interestingly, the synthesis of CP1 and CP2 show selectivity for cis CBM isomers. The trans conformation has been also observed with the same organic cation (CBMH$_2$)$_2^{2+}$ in other compounds [29, 33]. This may be a possible technique for separation and recognition of cis and trans isomers of CBM.

3.2. Hirshfeld Surface Analysis

Hirshfeld surface analysis have been carried out in order to decrypt and quantify the intermolecular interactions involved in the crystal packing of compounds CP1-CP2. Fig. 3 displays Hirshfeld surfaces mapped over the $d_{\text{norm}}$ (normalized contact distance) property in two orientations and the associated full 2-dimensional fingerprint plots. The surfaces are represented as transparent to permit visualization all atoms of the asymmetric unit for the title compounds. To visualize the intermolecular interactions in the $d_{\text{norm}}$ map, a color scale is used. The red areas imply contacts with distances shorter than the sum of van der Waals (vdW) radii, while the blue and white regions indicate contacts with distances longer than and equal to the sum of Van der waals radii, respectively [34]. For both compounds, the different intermolecular contacts are quantified with the breaking down of the full fingerprint region and their relative contributions, in percentage terms, to the overall crystal packing are exhibited as histograms in Fig. 3.

In compound CP1, the large red spots labeled 1’ in Fig. 3 represent H···Cl/Cl···H contacts, which are relevant in the $d_{\text{norm}}$ maps. These contacts are attributed to N-H···Cl and O-H···Cl hydrogen bonds, which can be seen in the fingerprint as a pair of symmetrical spikes at $(d_e + d_i) 2.30 \, \AA$ in agreement with the expected higher strength for N1-H1E···Cl3 hydrogen bond (Table 2). The H···Cl/Cl···H contacts are dominant for the complex CP1 with higher contributions of 55.6% of the overall packing (Fig. 3). The large deep-red spots labeled 2’ in the $d_{\text{norm}}$ map show also strong H···O/O···H contacts attributed to N-H···O hydrogen bonds, which are viewed as a pair of symmetrical spikes with minimum $(d_e + d_i) 1.94 \, \AA$ in agreement with the anticipated higher strength for N2-H2B···O2W. The H···O/O···H represent 5.5% of the total Hirshfeld surface area. The H···H interactions labeled 3’ in Figure 3, contributing 36.90% to the overall crystal packing. The two symmetrical broad peaks in the middle region of fingerprint with minimum contact $(d_e + d_i) 2.4 \, \AA$ is due to a short interatomic H···H contact.

In compound CP2, the H···I/I···H contacts labeled 1 in Figure 3 have the highest contribution (61.90%) to the overall Hirshfeld surface area. These contacts which appear as tiny red spots in the $d_{\text{norm}}$ surface are attributed to N-H···I and O-H···I hydrogen bonds. The next most contribution to the overall crystal packing arise from the H···H and H···O/O···H interactions, respectively. In fact, the H···H contacts labeled 3 in the middle region of FP, are showed as two symmetrical broad peaks with minimum $d_e + d_i 2.1 \, \AA$ (shorter than the sum of van der Waals radii), representing a 29.2% contribution to the entire HS area in this Cd complex. Finally, like in the structure CP1, the large deep-red spots labeled 2 in the $d_{\text{norm}}$ map (Figure 3) indicate also strong H···O/O···H interactions corresponding to the strongest N-H1C···OW hydrogen bond (Table 4), which also appear as two sharp symmetrical spikes at $d_e + d_i 1.90 \, \AA$ in the FP with 5.5% contribution to the overall crystal packing.
The dominant XH/HX (X : Cl for Zn complex and I for Cd complex), OH/HO and HH interactions, suggest that hydrogen bonding and van der Waals interactions play the main roles in the crystal packing of the two compounds.

### 3.3. Thermal analysis (DTA/TGA)

To investigate the thermal stability of compounds CP1 (Figure 4) and CP2 (Figure 5), thermal analysis (DTA/TGA) were carried out under an N\textsubscript{2} atmosphere with a heating rate of 10°C/min in the temperature range from 25° to 600 °C. Overall, the TGA curves for these compounds indicate that the two H\textsubscript{2}O molecules per formula unit are released between 25 and 130°C. The experimental mass losses of 9.27% and 4.49% are in good agreement with the calculated values of 9.29% and 4.50% for CP1 and CP2, respectively. After dehydration, the anhydrous compounds derivatives of CP1 and CP2 remain stable up to their melting points at 225 °C and 153°C, respectively. These melting points are confirmed by an additional thermal treatment in a separate furnace with run heating of 5°C/min, from room temperature to 250 °C for CP1 and from room temperature to 200°C for CP2. After that, the compounds undergo a considerable decomposition, suggesting the loss, amongst others, organic cations and the halogen atoms.

### 3.4. Spectroscopic study

#### 3.4.1. \(^{13}\text{C}\) NMR spectral analysis

High-resolution NMR spectroscopy is a powerful technique for the characterization of organic-inorganic hybrid materials.

The \(^{13}\text{C}\) NMR solution spectrum of \((\text{CBMH}_2)_\text{ZnCl}_4.2\text{H}_2\text{O}\) (CP1) (Figure 6) shows five signals at 24.094, 28.905, 33.076, 34.873 and 45.077 ppm due to the C4, (C3, C5), C1, (C2, C6) and (C7, C8), respectively. In fact, among the eight crystallographically independent carbons, we find the pairs (C3, C5), (C2, C6) and (C7, C8) that each one presents the same electronic environment. Therefore, they resonate at the same frequency and are characterized by the same chemical shift.

The \(^{13}\text{C}\) NMR solution spectrum of \((\text{CBMH}_2)_\text{CdI}_4.2\text{H}_2\text{O}\) (CP2) (Figure 7) exhibits five signals corresponding to five carbon atoms crystallographically independent. From the spectrum, the signals centered at 24.102, 28.915, 33.076, 34.876 and 44.787 ppm are attributed to C1, C2, C3, C4 and C5 respectively.

It is clear that the high values of chemical shifts are attributed to carbons (C7, C8) for CP1 C1 for CP2, which are the close sto coordination place (N). This is explained by effect of the electronegative nitrogen atoms.

The low intensity signal observed experimentally at chemical shift 33.076 ppm, assigned to (C2, C6) carbon atoms for CP1 and to C2 carbon atoms for CP2, is due to the lack of attached protons.

#### 3.4.2. Infrared spectra
To obtain further information upon the crystal structures of CP1 and CP2, we have undertaken vibrational analyses using infrared spectroscopy and Raman scattering. The IR absorption spectra of the two compounds CP1 (Figure S1) and CP2 (Figure S2) are similar, each shows clearly the bands corresponding only to vibrations of the 1,3-cyclohexanebis(methylammonium) cation, because the vibrational modes of $\text{ZnCl}_4^{2-}$ or $\text{CdI}_4^{2-}$ anions appear below 400 cm$^{-1}$ in IR spectrum. Therefore, the following IR analysis for the CP1 compound equally applies to the CP2 other compound.

Tentative attribution of the observed absorption bands are based on comparisons with the free organic molecule 1,3-cyclohexanebis(methylamine) and previously reported homologous compounds[35].

The high-frequency region between 4000-2000 cm$^{-1}$ in the spectrum is characterized by OH, NH and CH stretching modes, harmonics and combination bands.

Water molecules vibration modes: Three bands are given for free water vibrational modes in the Tables of Molecular Vibrational Frequencies [36]. These frequencies are at 3756 cm$^{-1}$, 3657 cm$^{-1}$ and 1595 cm$^{-1}$ for the asymmetric stretching ($a_s$), symmetric stretching ($s$) and the bending (scissoring) ($i_p$) modes, respectively. The observed FTIR bands at 3487 cm$^{-1}$ and 3422 cm$^{-1}$ for CP1 and at 3514 cm$^{-1}$ and 3438 cm$^{-1}$ for CP2 are attributed respectively to asymmetric and symmetric stretching vibrations (O-H) of the crystallization water. As O-H of the crystallization $\text{H}_2\text{O}$ is involved in hydrogen bonds OH···N and OH···Cl(I), the wave numbers of these modes are shifted towards lower values. The ($\text{H}_2\text{O}$) deformation mode is determined at 1608 cm$^{-1}$ for CP1 and at 1595 cm$^{-1}$ for CP2 in the FT-IR spectra.

Vibration of $\text{NH}_3^+$ groups: The amino groups of 1,3-cyclohexanebis(methylamine) are protonated. The $\text{NH}_3^+$ group may vibrate mainly in three different modes namely: asymmetric stretching ($a_s$), symmetric stretching ($s$) and the in plane bending mode ($i_p$). The observed FTIR bands at 3133 cm$^{-1}$ and 3077 cm$^{-1}$ for CP1 (Fig. S1) and those observed at 3153 cm$^{-1}$ and 3028 cm$^{-1}$ for CP2 (Fig. S2) are assigned to asymmetric and symmetric $\text{NH}_3^+$ stretching, respectively. These frequencies of the stretching modes of $\text{NH}_3^+$ groups in the title compounds are lower compared to $-\text{NH}_2$ frequencies ($a_s = 3371$ cm$^{-1}$, $s = 3292$ cm$^{-1}$) in 1,3-cyclohexanebis(methylamine). The most reasonable reason for this difference is the modification of $\text{NH}_2$ chemical environment as a result of N-H···Cl(I) and N-H···O hydrogen bonds formation. The $\text{NH}_3^+$ in plane bending vibration is found to be at 1502 cm$^{-1}$ for CP1 and 1489 cm$^{-1}$ for CP2.

- Vibration of $\text{CH}_2$ group: The $\text{CH}_2$ group may vibrate in different fashions namely: asymmetric stretching, symmetric stretching and the in plane bending mode: In this instance, the $\text{CH}_2$ asymmetric and symmetric stretch vibrations appear respectively at 2922 cm$^{-1}$ and 2879 cm$^{-1}$ for CP1 and at 2921 cm$^{-1}$ and 2854 cm$^{-1}$ for CP2. The band located at 1450 cm$^{-1}$ (Fig. S1) and that located at 1441 cm$^{-1}$ (Fig. S2) are due to the ($-\text{CH}_2$) scissor mode, while the bands observed at 1439 cm$^{-1}$ and 1390 cm$^{-1}$
and those observed at 1434 cm\(^{-1}\) and 1392 cm\(^{-1}\) (Fig. S2) are ascribed to asymmetric and symmetric deformation modes of the (-CH\(_2\))

- Harmonics and combination bands: The bands situated in the 25502000 cm\(^{-1}\) region are ascribed to the harmonics and combination bands.
- Vibrations of C-N and C-C groups: The medium intensity absorption band observed at 1137 cm\(^{-1}\) for CP1 and that observed at 1125 cm\(^{-1}\) for CP2 correspond to the stretching vibration mode of C–N, while the stretching vibration mode of C–C bond is not detected on the IR spectra because of the low intensity of the corresponding absorption band.

3.4.3. Raman spectra

The presence of a heavy metal atom in a tetrahedral coordination such as ZnCl\(_4^{2-}\) or CdI\(_4^{2-}\), gives rise to low frequency vibration modes which appear below 350 cm\(^{-1}\) in Raman spectrum.

Typically, the ideally tetrahedral MX\(_4\) (ZnCl\(_4^{2-}\), CdI\(_4^{2-}\)) generate nine basal vibrations, as follows; 1(A1) and 3(F2) correspond to M-X (Zn-Cl, Cd-I) stretching vibrations, 2(E) and 4(F2) correspond to X-M-X (Cl-Zn-Cl, I-Cd-I) deformation vibrations. In the crystal, the ideally tetrahedral MX\(_4\) (ZnCl\(_4^{2-}\), CdI\(_4^{2-}\)) is deformed and as a result there is a splitting on the vibrational modes of E and F2 symmetries.

Figure 8 shows the Raman spectrum of (CBMH\(_2\))ZnCl\(_4\).2H\(_2\)O. According to previous studies and by comparison with the Raman spectrum of analogous compounds containing ZnCl\(_4^{2-}\), we may propose a tentative attribution of the observed bands [14, 37]. The bands observed at 244 and 276 cm\(^{-1}\) can be allocated to the symmetric and asymmetric Zn-Cl stretching modes of ZnCl\(_4^{2-}\). The bands at 137 cm\(^{-1}\) and 176.5 cm\(^{-1}\) can be assigned to the symmetric and asymmetric bending mode of Cl-Zn-Cl bonds.

Figure 9 shows The Raman spectrum of (CBMH\(_2\))CdI\(_4\).2H\(_2\)O. The bands at 115.4 and 125.3 cm\(^{-1}\) can be attributed to the symmetric and asymmetric Cd-I stretching modes that are in good agreement with other tetrahedral compound with CdI\(_4^{2-}\)[30, 38]. The band at 54 cm\(^{-1}\) can be assigned to the I-Cd-I deformation mode.

As is clear from the above discussion, these FT–IR and Raman spectroscopic results were coherent with the single-crystal X-ray results.

**Conclusion**

In summary, (H\(_2\)CHBMA)ZnCl\(_4\).2H\(_2\)O, (CP1), and (H\(_2\)CHBMA)CdI\(_4\).2H\(_2\)O, (CP2), have been synthesized by conventional methods under the acidic conditions supplied by hydrochloric acid and sulfuric acid, respectively. X-ray diffraction analysis reveals that the two compounds CP1 and CP2 crystallize in the same monoclinic crystal system with space groups (P2\(_1\)/c) and (P2\(_1\)/m), respectively. The crystals packing of the two compounds are stabilized by non-covalent interactions which are in close agreement
with the Hirshfeld surface analysis. Albeit the template $\text{H}_2\text{CHBMA}$ adopts a cis configuration in both compounds, CP1 presents 2D H-bonded architecture, while CP2 shows a diamond 3D H-bonded framework. By comparing the structures of CP1 and CP2, we can discover the role of the orientations of two terminal ammonium groups (upward for CP1 and downward for CP2) of the organic cation in controlling the different supramolecular architectures. Interestingly, while the templates sit in the cis configuration in both compounds CP1 and CP2, they are in the trans configuration in other compounds. This result has the potential for separation and recognition of CHBMA isomers.

The thermal analysis of these compounds were examined by TGA/DTA and the results indicate that all the $\text{H}_2\text{O}$ molecules are released between 25 and 120 °C and that the anhydrous compound derivative of CP1 is more stable than that of CP2. The FT–IR, Raman and $^{13}\text{C}$ NMR spectroscopic results are in agreement with the single-crystal X-ray results.

The synthesized compounds were evaluated for acetalization reaction of aldehydes and demonstrated high catalytic activity which will be published later in a new paper.

**Supplementary material**

CCDC 1825834 and 1563308 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44 1223 336033.

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Tables

Table 1 Experimental details
|                        | CP1                              | CP2                              |
|------------------------|----------------------------------|----------------------------------|
| Crystal data           |                                  |                                  |
| Chemical formula       | (CBMH\textsubscript{2})ZnCl\textsubscript{4}.2H\textsubscript{2}O | (CBMH\textsubscript{2})CdI\textsubscript{4}.2H\textsubscript{2}O |
| Formula weight (g mol\textsuperscript{-1}) | 387.46                           | 800.29                           |
| Crystal system, space group | Monoclinic, P2\textsubscript{1}/c | Monoclinic, P2\textsubscript{1}/m |
| Temperature (K)        | 293                              | 293                              |
| a, b, c (Å)            | 6.791, 19.122, 13.139            | 7.2260(4), 13.4994(10), 10.4976(6) |
| (°)                   | 99.77                            | 95.774(4)                        |
| V(Å\textsuperscript{3}) | 1681.5                           | 1018.81(11)                      |
| Z                     | 4                                | 2                                |
| Radiation type        | Mo K                             | Mo K                             |
| (mm\textsuperscript{-1}) | 2.089                           | 7.128                            |
| Crystal size (mm)      | 0.32 0.18 0.10                   | 0.14 0.11 0.08                   |
| Data collection        |                                  |                                  |
| Diffractometer        | Bruker SMART CCD                 | Bruker APPEXII                   |
| Absorption correction | multi-scan                       | (SADABS; Bruker, 2008)           |
| T\textsubscript{min}, T\textsubscript{max} |                                  |                                  |
| No. of measured, independent and observed [l \ 2 (l)] reflections | 18449, 3130, 2816               | 6486, 2080, 1826                |
| R\textsubscript{int}  | 0.030                            | 0.046                            |
| (sin/\lambda)\textsubscript{max} (Å\textsuperscript{-1}) |                                  |                                  |
| Refinement             |                                  |                                  |
| R[F\textsuperscript{2} > 2(F\textsuperscript{2})], wR(F\textsuperscript{2}), S | 0.026, 0.068, 1.07          | 0.0367, 0.0841, 1.121 |
| No. of reflections     | 3130                             | 2080                             |
| No. of parameters      | 172                              | 89                               |
| No. of restraints      | 0                                | 0                                |
| H-atom treatment       | H atoms treated by a             | H atoms treated by a mixture     |
Table 2 Hydrogen – bond geometry (Å, °) of (CBMH₂)ZnCl₄·2H₂O.

| D-HA                  | D-H | HA     | DX       | D-HX    |
|-----------------------|-----|--------|----------|---------|
| N1-H1CO1              | 0.89| 2.03   | 2.899 (3)| 165     |
| N1-HIDCl₄           i | 0.89| 2.38   | 3.258 (2)| 170     |
| N1-H1ECl₃         ii | 0.89| 2.34   | 3.210 (7)| 166     |
| N2-H2ACl₂        iii | 0.89| 2.76   | 3.634 (2)| 166     |
| N2-H2BO2            | 0.89| 1.95   | 2.838 (3)| 176     |
| N2-H2C01          iv | 0.89| 2.07   | 2.950 (3)| 170     |
| C1-H1BCl4          5  | 0.97| 2.83   | 3.720 (2)| 154     |
| O1-H1O1-Cl4        6  | 0.77 (3)| 2.62(3)| 3.331(2)| 153 (3) |
| O1-H2O1-Cl3        6  | 0.78 (4)| 2.52 (4)| 3.292 (2)| 168 (4) |
| O2-H1O2-Cl1       vi | 0.85 (4)| 2.52 (4)| 3.369 (2)| 174 (3) |
| O2-H2O2-Cl2       iv | 0.76 (4)| 2.63 (4)| 3.348 (2)| 158 (4) |

Symmetry codes: (i) x, −y+1/2, z−1/2; (ii) x−1, −y+1/2, z−1/2; (iii) −x, y+1/2, −z+3/2; (iv) x, −y+1/2, z+1/2; (v) x−1, y, z; (vi) −x+1, y+1/2, −z+3/2.

Table 3 Selected bond distances (Å) and angles (°) in (CBMH₂)ZnCl₄·2H₂O.
### Table 4

| Angles (°) | Distances (Å) |
|------------|---------------|
| **Tetrahedron[ZnCl₄]²⁻** | |
| Cl₂ – Zn – Cl₄ | 110.83 (2) | Zn – Cl₁ | 2.2768 (6) |
| Cl₂ – Zn – Cl₁ | 108.57 (2) | Zn – Cl₂ | 2.2590 (5) |
| Cl₄ – Zn – Cl₁ | 114.49 (2) | Zn – Cl₃ | 2.2989 (5) |
| Cl₂ – Zn – Cl₃ | 111.26 (2) | Zn – Cl₄ | 2.2640 (6) |
| Cl₄ – Zn – Cl₃ | 107.30 (2) | |
| Cl₁ – Zn – Cl₃ | 104.23 (2) | |
| **Organic molecule** | |
| C₅ – C₄ – C₃ | 112.45 (18) | C₈ – N₁ | 1.491 (3) |
| C₂ – C₁ – C₆ | 111.94 (18) | C₇ – N₂ | 1.491 (3) |
| C₄ – C₃ – C₂ | 112.15 (16) | C₁ – C₂ | 1.525 (3) |
| C₈ – C₂ – C₃ | 113.90 (17) | C₁ – C₆ | 1.527 (3) |
| C₈ – C₂ – C₁ | 108.41 (16) | C₂ – C₈ | 1.518 (3) |
| C₃ – C₂ – C₁ | 110.45 (16) | C₂ – C₃ | 1.519 (3) |
| C₂ – C₃ – C₄ | 111.45 (18) | C₃ – C₄ | 1.522 (3) |
| C₇ – C₆ – C₅ | 113.87 (18) | C₄ – C₅ | 1.520 (3) |
| C₇ – C₆ – C₁ | 108.69 (16) | C₅ – C₆ | 1.518 (3) |
| C₅ – C₆ – C₁ | 110.25 (16) | C₆ – C₇ | 1.512 (3) |
| N₂ – C₇ – C₆ | 112.68 (17) | |
| N₁ – C₈ – C₂ | 112.76 (17) | |

*Table 4* Hydrogen – bond geometry (Å, °) of (CBMH₂)CdI₄·2H₂O.
Table 5 Selected bond distances (Å) and angles (°) in (CBMH$_2$)$_4$CdI$_4$.2H$_2$O.

| Angles (°)       | Distances Å) |
|------------------|--------------|
| **Tetrahedron[ Cd$_4$]$^{2-}$:** |
| I1 – Cd – I1     | 110.90 (3)   | Cd– I1 | 2.7593 (6) |
| I1 – Cd – I2     | 111.113 (18) | Cd– I2 | 2.7735 (9) |
| I1 – Cd – I3     | 111.585 (18) | Cd– I3 | 2.8162 (9) |
| I2 – Cd – I3     | 100.13 (3)   |       |            |
| **Organic molecule:** |
| C3 – C2 – C5     | 111.2 (6)    | C2 – C3 | 1.496 (9) |
| C3 – C2 – C1     | 109.3 (6)    | C2 – C5 | 1.503 (8) |
| C5 – C2 – C1     | 111.7 (6)    | C2 – C1 | 1.520 (9) |
| C2 – C5 – C2     | 110.9 (7)    | N1 – C1 | 1.470 (10) |
| C2 – C3 – C4     | 110.0 (6) 111.4 (8) | C3 – C4 | 1.509 (9) |
| C3 – C4 – C3     |               |       |            |
| N1 – C1 – C2     | 112.7 (6)    |       |            |