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SYNTHESIS AND STRUCTURAL INVESTIGATIONS OF LAYERED PEROVSKITE SYSTEM: $[NH_3\text{-}(CH_2)_3\text{-}COOH]_2MCL_4$ (M= Cd, Hg)

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ABSTRACT

A new organic-inorganic hybrids $[NH_3\text{-}(CH_2)_3\text{-}COOH]_2$ MCl_4(M= Hg, Cd) were synthesized; the single crystals were obtained by diffusion voice at room temperature. The structures were solved from single-crystal X-ray diffraction at room temperature. The first compound $[NH_3\text{-}(CH_2)_3\text{-}COOH]_2HgCl_4$ (1) crystallizes in the monoclinic system with C2/c space group, a=29.2762(2) Å, b=11.0408(1) Å, c=11.3944(1) Å, β=112.532(2)° and Z=8. The second compound $[NH_3\text{-}(CH_2)_3\text{-}COOH]_2CdCl_4$ (2) crystallizes in the monoclinic system with P21 space group, a= 7.409(1) Å, b= 7.490(1) Å, c= 15.298(2) Å, β = 100.084(2)° and Z=2. The both structures might be described two dimensional layered systems with two parallel anionic and cationic layers. Three dimensional network of hydrogen – bonding assures the cohesion between these layers and stabilizes the crystal. In this work we present the comparison of both structures and we show the influence of the metal nature in the crystalline structure.

Keywords: Organic-inorganic hybrid structural phase transition, Single crystal, Differential scanning calorimetry (DSC).

Contribution/ Originality

This structural study of organic inorganic hybrid like perovskite system contributes in the existing literature. The aim of this work is to synthesis and to study by single crystal XRD of two news composites based on amino acid with two metals different. To understand the structural behavior by just changing the metal is very crucial.

1. INTRODUCTION

The 2D layered perovskites systems include two typical groups of compounds: $(R\text{-}NH_3)_2MX_4$

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and $(NH_3\text{-}R\text{-}NH_3)MX_4$, where R is an aliphatic or aromatic ammonium cation, M is a divalent metal that can adopt an octahedral or tetrahedral coordination, and X is a halogen: Cl, Br or I. In recent years, this family of compounds has attracted much attention due to their possibility to combine organic and inorganic properties within a single material. In these systems Fig.1, the perovskites consist of single layers of oriented in organic sheets separated by bilayers of organic ammonium cation where the organic groups R self-assemble via π - stacking interaction (when the organic group contains aromatic groups), through Van der Waals force or hydrogen bonding when the organic group contains acid function as in the titled compounds. The inorganic sheets connect to organic sheets by hydrogen bonding, provided by the N-H…X interactions between the ammonium head of the $R\text{-}NH_3^+$ cation and two bridging halogens and one axial halogen (bridging halogen configuration) or to two axial halogens and one bridging halogen (axial halogen configuration). These components can form a wide variety of structures with varying dimensionality. However, the most common structure is the perovskite-like structure [1]. A wide variety of different organic and inorganic starting compounds are successfully incorporated in this type of organic-inorganic hybrids perovskites and have been used in many research and practical fields such as thermal energy storage (the advantage of remaining solid after the phase change) [2-6]. Now that certified energy conversion efficiencies for solar cells based on mixed organic–inorganic are above 20% [7-9]. Gamma-Amino Butyric acid tetrachlorometalate $[NH_3\text{-}(CH_2)_3\text{-}COOH]_2MCl_4$ (M= Hg, Cd) belong to the $((R\text{-}NH_3)_2 MX_4$ group, which have been widely investigated because of the enormous variety and their potential technological applications. As known the crystallography plays a crucial role for undressing the behavior of materials and make relationship structure properties. In this manuscript, we present a systematic study on the crystal structure at room temperature of two (2D) layered perovskites systems with the same organic part and two different metals; we focus our attention on the structural investigation and comparing their structures.

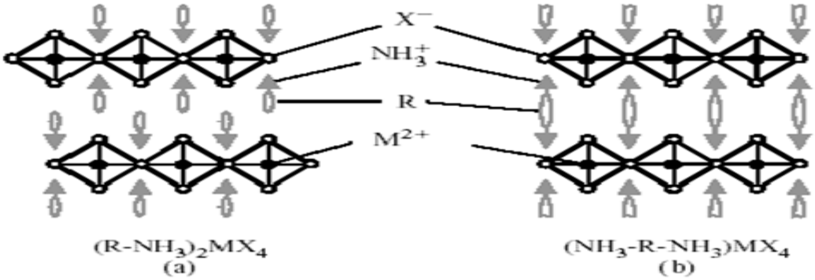

Fig-1. Schematic representation of 2D-layered perovskites with organic monoammonium cations (a) and organic diammonium cation (b)

2. EXPERIMENTA

2.1. Crystal Growth

The single crystals of organic-inorganic hybrids $(NH_3\text{-}(CH_2)_3\text{-}COOH)_2HgCl_4$ (denoted 1) and $(NH_3\text{-}(CH_2)_3\text{-}COOH)_2CdCl_4$ (denoted 2) were grown in aqueous solution at room temperature: the yellow single crystals of compound (1) were obtained by mixing an aqueous solution of Gamma-Amino

Butyric acid protonated by 1 ml of HCl (37%) and another aqueous solution of $HgCl_2$. The mixture between these solutions was carried out at room temperature in glass tube. The white single crystals of compound (2) were obtained by the same protocol. The obtained crystals remained stable under normal conditions of temperature and humidity.

2.2. Crystallographic Studies

A single crystal of about 0.14x0.12x0.10 mm^3 and 0.25 x 0.20 x 0.01 mm^3 were selected under an optical microscope for X-ray diffraction experiments. The X-ray data collection was carried out on Nonius Kappa CCD with Mo-Kα radiation from graphite monochromator. The collection data was made at room temperature using φ, ω scan mode, the crystal to detector distance was (26 mm and 34 mm) and further details are given in Table1. The cells refinements and data reduction were carried using DENZO-SMN. All structures were solved by SIR 97 [10] and the refinement of atomic parameters based on full – matrix least squares technique on F^2 were performed using the SHELX 97 [11]. All hydrogen atoms were located theoretically. The above programs were used within the WINGX package [12]. The molecular graphics were prepared using and MERCURY [13] programs. The crystallographic Data of the structure described in this paper were deposited to the Cambridge crystallographic Data Center as supplementary publication No. CCDC 1403764 and CCDC 1405885

Table-1. Crystal data and structure refinement for the structure solved by wing x package

Data crystal	$2CHgCl_4$	$2CCdCl_4$
Empirical formula	C8 H20 Cl4 Hg N2 O4	C8 H20 Cd Cl4 N2 O4
Formula weight	550.65	462.46
Temperature	293(2) K	290(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	P21
Unit cell dimensions	a = 29.2762(2) Å b = 11.0408(1) Å, c = 11.3944(1) Å β=112.532(2)°.	a = 7.409(1) Å. b = 7.490(1) Å c = 15.298(2) Å β= 100.084(2)°.
Volume	3401.9(3) $Å^3$	835.8(3) $Å^3$
Z	8	2
Density (calculated)	2.150 Mg/m^3	1.838 Mg/m^3
Absorption coefficient	9.685 mm^{-1}	1.954 mm^{-1}
F(000)	2096	460
Crystal size	0.14x 0.12x 0.10 mm^3	0.25 x 0.20 x 0.01 mm^3
Theta range for data collection	3.89 to 26.37°.	3.84 to 26.36°.
Index ranges	$-36 \leq h \leq 36, -13 \leq k \leq 13, -14 \leq l \leq 14$	$-9\leq h \leq 9, -9\leq k \leq 9, -19\leq l \leq 18$
Reflections collected	3742	3363
Independent reflections	2399 [R(int) = 0.0439]	3363 [R(int) = 0.0000]
Completeness to theta = 26.37°	68.8 %	98.5 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	2399 / 0 / 174	3363 / 1 / 172
Goodness-of-fit on F^2	1.027	1.104
Final R indices [I>2sigma(I)]	R1 = 0.0499, wR2 = 0.1322	R1 = 0.0202, wR2 = 0.0511
R indices (all data)	R1 = 0.0542, wR2 = 0.1410	R1 = 0.0205, wR2 = 0.0514
Largest diff. peak and hole	1.632 and -2.642 e.$Å^{-3}$	0.398 and -0.838 e.$Å^{-3}$

3. RESULTS AND DISCUSSION

3.1. Crystal Structure Description

$(NH_3\text{-}(CH_2)_3\text{-}COOH)_2HgCl_4$ (1)

All crystallographic data, measurements details and refinement at room temperature are summarized in Table.1. The compound (1) crystallize in monoclinic system with C2/c space group, a=29.2762(2) Å, b=11.0408(1) Å, c=11.3944(1) Å, β=112.532(2)° and Z=8. The asymmetric unit containing two protonated, Gamma-Amino Butyric $[NH_3\text{-}(CH_2)_3\text{-}COOH]^{1+}$ cations and one tetrachloridomercuratate $[HgCl_4]^{2-}$ anion (Fig.2.b). The structure can be described by an alternation of organic and inorganic layers stacked along a axis. The anionic layer is built up of $HgCl_4^{2-}$ sandwiched between two different organic layers (Fig.2.c.). Indeed, within the inorganic sheet, the nearest distance between neighboring metallic sites connected by Hg-Cl-Hg bridge is about d_{intra} = 5.704 Å along c axis and d_{intra} = 5.521 Å along b axis, while the distance between two adjacent inorganic layer is about d_{inter} =13.462 Å. The large value of the ratio d_{inter}/d_{intra}= 2.360 or 2.438 gives the 2D properties for this compound. The compound cohesion is assured by two different interactions: The bonding between the organic and inorganic layers is established by N-H…Cl hydrogen bonds type (Fig.2.d). The N...Cl distances vary between 3.256(9) Å and 3.38(1) Å (Table 2). We deduce that the two chains of unit cell are connected by two strong bridging halogens and one axial halogen (bridging halogen configuration) of inorganic layer [14]. The cohesion of the organic layer is obtained by O-H...O between acid function of organic chains. Indeed, each cation of the asymmetric unit forms a dimer with itself. The O…O distances is about 2.61(1) Å for the first chain and 2.62(1) Å for the second chain of the unit cell (Table 2).

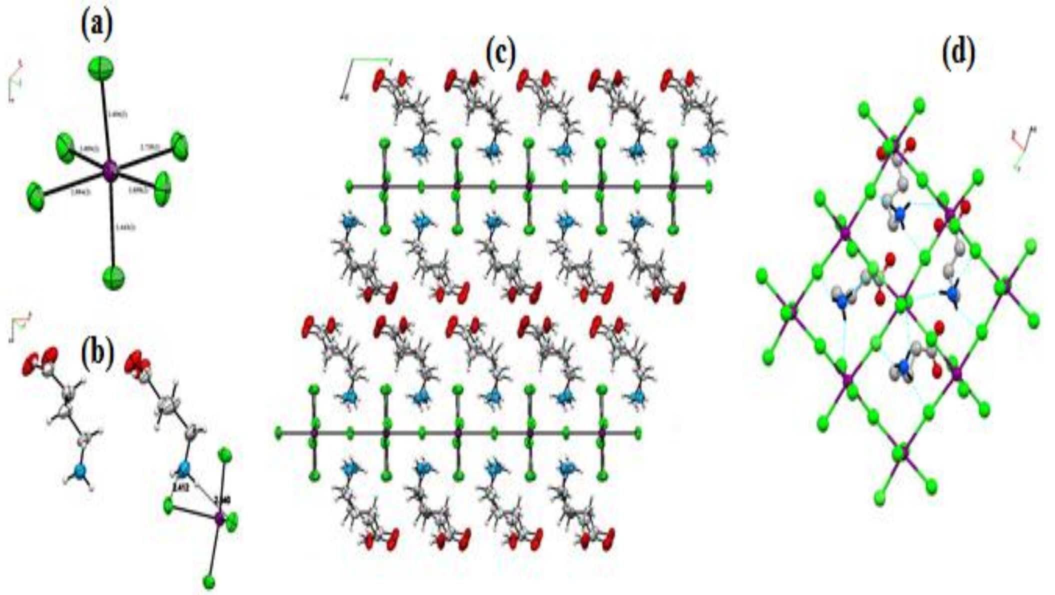

Fig-2. View of $HgCl_6$ octahedra scheme (a), View of the molecular structure (Asymmetric unit) (b) and Overall view of the crystal packing along axis b showing alternating organic and inorganic layers staked along a axis (c). View along c showing the connection between inorganic and organic layers by N-H…Cl hydrogen bonds (dashed lines) (d).
Mercury program is used to represent all these structural view

Table-2. Main Bond length (Å) and angles (°) in the hydrogen-bonding scheme in $(NH_3\text{-}(CH_2)_3\text{-}COOH)_2HgCl_4$

N—H	H···Cl	N···Cl	N-H...Cl	O...O
0.97	2.54	3.38(1)	163.3	
0.97	2.412	3.28(1)	150.1	2.61(1)
0.97	2.56	3.342(9)	153.3	2.61(1)
0.97	2.556	3.337(9)	146.1	2.62(1)
0.97	2.423	3.33(1)	156.1	2.62(1)
0.97	2.481	3.256(9)	161.2	

All these bonds and angles are from Tex file generated by Wing x package

The geometry of the anionic part is octahedral, the Hg-Cl distances vary between 2.406(2) and 2.884(2) Å and the Cl-Hg-Cl angle values are in the 86.08(6)° – 177.90(6)° range (Table 3). Taking into account these parameters and considering the calculated average values of the Baur distortion indices {ID Hg-Cl =0.0680, ID Hg-Cd-Hg = 0.253} [15]. We deduce that the HgCl$_6$ octahedron is distorted (Fig.2.a).

Table-3. Main inter-atomic distances (Å) and bond angles (°) in anionic part of $[NH_3\text{-}(CH_2)_3\text{-}COOH]_2HgCl_4$

Distance (Å)		Angle (°)	
Hg(1)-Cl(2)	2,406(2)	Cl(1)-Hg(1)-Cl(3)	86.08(6)
Hg(1)-Cl(1)	2,884(2)	Cl(1)-Hg(1)-Cl(4)	93.57(5)
Hg(1)-Cl(4)	2,858(2)	Cl(1)-Hg(1)-Cl(2)	86.56(6)
Hg(1)-Cl(3)	2,433(1)	Cl(3)-Hg(1)-Cl(4)	89.05(6)
Hg(1)-Cl(4)^{i}	2,735(2)	Cl(4)-Hg(1)-Cl(2)	89.24(6)
Hg(1)-Cl(1)^{ii}	2,850(2)	Cl(3)-Hg(1)-Cl(2)	172.33(7)
		Cl(4)^{i}-Hg(1)-Cl(1)	92.07(5)
		Cl(4)^{i}-Hg(1)-Cl(3)	92.58(6)
		Cl(4)^{i}-Hg(1)-Cl(2)	89.86(6)
		Cl(1)^{ii}-Hg(1)-Cl(3)	93.64(6)
		Cl(1)^{ii}-Hg(1)-Cl(4)	88.50(5)
		Cl(1)^{ii}-Hg(1)-Cl(2)	93.79(6)
		Cl(1)^{ii}-Hg(1)-Cl(4)^{i}	85.86(5)
		Cl(1)^{ii}-Hg(1)-Cl(1)	177.90(6)
		Cl(4)^{i}-Hg(1)-Cl(4)	174.22(5)

Symmetry code: i: x, 2-y, - ½+z; ii: ½-x, ½+y, ½-z

An examination of the organic moiety geometrical features shows that, the unit cell contains two organic chains [NH$_3$-(CH$_2$)$_3$-COOH]$^+$ twisted in the level of NH$_3^+$ Head (Fig.3). Evidence is provided for the existence of a conformational disorder of the cation between « trans » and «twisted» states, superimposed on orientational disorder; the «twisted» states of the chains are less stable than the «trans» ones and are thermally activated. For «trans» conformation, the torsion angle is about 180° but if the value of this angle is surrounded to 60° very inferior we have twisted conformation. For 2CHgCl$_4$, the first chain is twisted near of NCCC, the torsion angle NCCC is about -71.2°. The same, the second chain is also twisted near of NCCC, the value of torsion angle CCCC is about -73.7°.

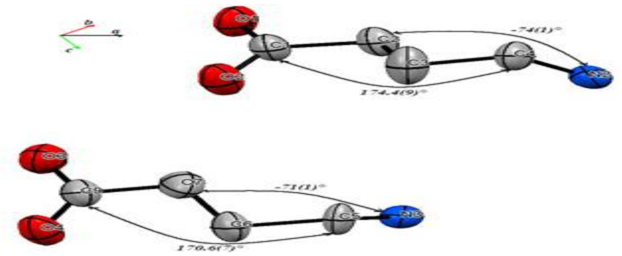

Fig-3. View showing the conformation (‹ trans › and ‹ twisted ›) of the two organic chains of unit cell and their torsion angles. Hydrogen atoms are omitted for clarity.
Mercury program is used to represent this view

$(NH_3\text{-}(CH_2)_3\text{-}COOH)_2CdCl_4$ (2)

All crystallographic data, measurements details and refinement at room temperature are summarized in Table.1. The compound (1) crystallize in monoclinic system with P21 space group, a = 7.409(1) Å, b = 7.490(1) Å, c = 15.298(2) Å, β= 100.084(2)° and Z=2. The asymmetric unit containing two protonated, Gamma-Amino Butyric $[NH_3\text{-}(CH_2)_3\text{-}COOH]^+$ cations and one tetrachloridocadmate $[CdCl_4]^{2-}$ anion which form a square centered by cadmium (Fig.4.b). The structure can be described by an alternation of organic and inorganic layers stacked along c axis. The anionic layer is built up of $CdCl_4^{2-}$ sandwiched between two different organic layers (Fig.4.c). Indeed, within the inorganic sheet, the nearest distance between neighboring metallic sites connected by Cd-Cl-Cd bridge is about d_{intra} = 5.258 Å, while the distance between two adjacent inorganic layer is about d_{inter} =15.059 Å. The large value of the ratio d_{inter}/d_{intra}=2.864 gives the 2D properties for this compound. The compound cohesion is assured by two different interactions: The bonding between the organic and inorganic layers is established by N-H…Cl hydrogen bonds type (Fig.4.d). The N...Cl distances vary between 3.176(5) Å and 3.474(3) Å (Table 4). We deduce that the two chains of unit cell are connected by two strong hydrogen bonds with chlorines (axial, equatorial) and form bifurcated weak hydrogen bond with chlorines (axial, equatorial) of inorganic layer [14]. The cohesion of the organic layer is obtained by O-H…O between acid function of neighboring chains. The O…O distances vary between 2.628(3) Å and 2.665(3) Å.

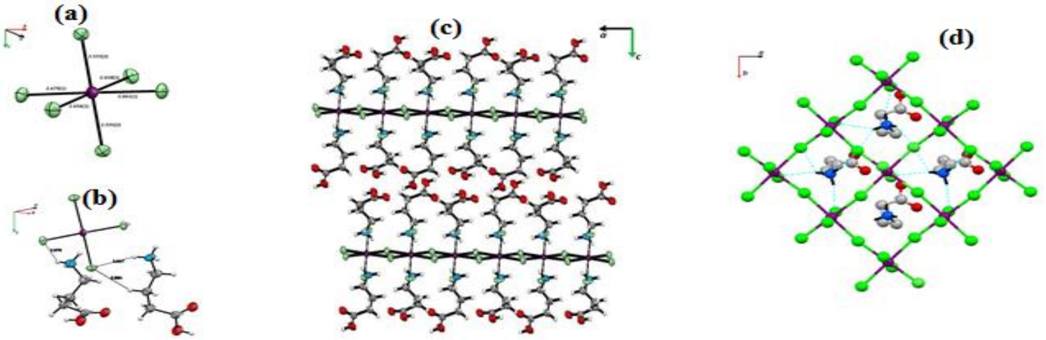

Fig-4. View of $CdCl_6$ octahedra scheme (a), View of the molecular structure (Asymmetric unit) (b) and Overall view of the crystal packing along axis b showing alternating organic and inorganic layers staked along c axis (c). View along c showing the connection between inorganic and organic layers by N-H…Cl hydrogen bonds (dashed lines) (d).
Mercury program is used to represent all these structural view

Table-4. Bond length (Å) and angles (°) in the hydrogen-bonding scheme in $(NH_3\text{-}(CH_2)_3\text{-}COOH)_2CdCl_4$

N—H	H···Cl	N···Cl	N-H...Cl	O...O
	2.3574	3.278(3)	156.4	
0.89	2.753	3.474(3)	155.1	
0.89	2.6787	3.176(5)	120.9	2.628(3)
0.89	2.5214	3.283(4)	170.8	2.665(3)
0.89	2.2944	3.408(4)	143.8	2.628(3)
0.89	2.8480	3.442(3)	139.8	2.665(3)
0.89	2.647	3.217(6)	135.2	
	2.4431	3.392(3)	162.5	

All these bonds and angles are from Tex file generated by Wing x package

The geometry of the anionic part can be compared to those found in the Cambridge Structural Database (CSD) for other Cd(II) salts containing isolated $[CdCl_4]^{2-}$ tetrahedral anions [16]. The variation of Cd-Cl distances average is between 2.45 Å and 2.47 Å. In our case the Cd-Cl distances vary between 2.5552(11) and 2.6790(16) Å and the Cl-Cd-Cl angle values are in the 88.12(3)° – 179.17(2)° range (Table 5). Taking into account these parameters and considering the calculated average values of the Baur distortion indices {ID Cd-Cl = 0.01828, ID Cl-Cd-Cl = 0.2643} [16]. We deduce that the $CdCl_6$ octahedron is distorted (Fig.4.a).

Table-5. Main inter-atomic distances (Å) and bond angles (°) in anionic part of $[NH_3\text{-}(CH_2)_3\text{-}COOH]_2CdCl_4$

Distance (Å)		Angle (°)	
Cd(1)-Cl(4)	2.5552(11)	Cl(4)-Cd(1)-Cl(3)	179.13(3)
Cd(1)-Cl(3)	2.5555(11)	Cl(4)-Cd(1)-Cl(2)	89.79(3)
Cd(1)-Cl(2)	2.6557(15)	Cl(3)-Cd(1)-Cl(2)	89.47(3)
Cd(1)-Cl(1)	2.6581(15)	Cl(4)-Cd(1)-Cl(1)	89.24(3)
Cd(1)-Cl(2)^{ii}	2.6611(16)	Cl(3)-Cd(1)-Cl(1)	91.51(3)
Cd(1)-Cl(1)^{i}	2.6790(16)	Cl(2)-Cd(1)-Cl(1)	178.90(3)
		Cl(4)-Cd(1)-Cl(2)^{ii}	90.82(3)
		Cl(3)-Cd(1)-Cl(2)^{ii}	88.75(3)
		Cl(2)-Cd(1)-Cl(2)^{ii}	91.80(5)
		Cl(1)-Cd(1)-Cl(2)^{ii}	88.73(7)
		Cl(4)-Cd(1)-Cl(1)^{i}	88.35(3)
		Cl(3)-Cd(1)-Cl(1)^{i}	92.08(3)
		Cl(2)-Cd(1)-Cl(1)^{i}	88.12(7)
		Cl(1)-Cd(1)-Cl(1)^{i}	91.34(5)
		Cl(2)^{i}-Cd(1)-Cl(1)^{i}	179.17(2)

Symmetry code: i: 1-x, -½+y, -z; ii: -x, ½+y, -z

An examination of the organic moiety geometrical features shows that, the unit cell contains two organic chains $[NH_3\text{-}(CH_2)_3\text{-}COOH]^+$, one chain is completely twisted and the second chain is twisted in the level of NH_3^+ Head (Fig.5). For the twisted chain, the value of torsion angle NCCC and CCCC are respectively about 67.1° and 71.6°. The second chain is twisted near of CCCC, the value of torsion angle CCCC is about 71.7°.

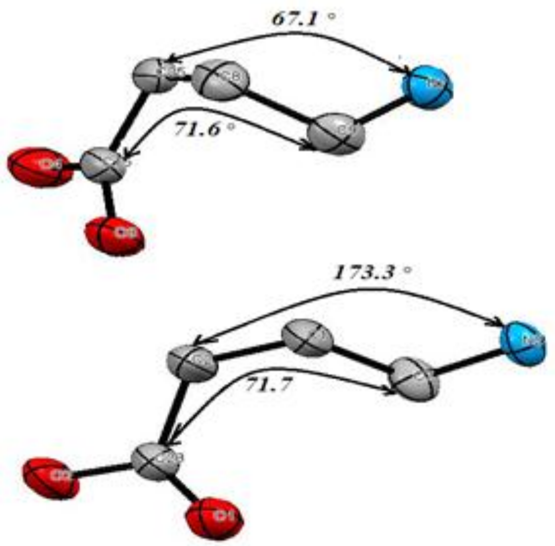

Fig-5. View along b axis showing the conformation (‹ trans › and ‹ twisted ›) of two cations of unit cell and their torsion angles. Hydrogen atoms are omitted for clarity.
Mercury program is used to represent this view

4. CONCLUCION

In summary, we have synthesized two new organic and inorganic hybrids $[NH_3\text{-}(CH_2)_3\text{-}COOH]_2CdCl_4$ and $[NH_3\text{-}(CH_2)_3\text{-}COOH]_2HgCl_4$ .Crystals of these hybrid materials have been prepared by slow evaporation of aqueous solutions at room temperature. The atomic arrangement of the both compounds can be described by alternating layers of organic and inorganic material stacked parallel to the ab and bc planes respectively. The material cohesion for all compounds is assured by two different bonds. The bonding between the inorganic and organic layer is established by N – H...Cl interaction, and the cohesion of the organic layer is assumed by O-H…O hydrogen bond type between acid function of neighboring chains for compound(2) but for the compound(1) each organic chain form dimer with itself. The existence of twisted conformations allows us to predict that these compounds will present phase transitions.

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