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Structure and Piezoelectricity Due to B Site Cation Variation in $AB^{n+}Cl_{n+2}$ Hybrid Histammonium Chlorometallate Materials

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Abstract

To provide new insights in understanding the influence of B site cation on structure in chlorometallate materials of the form $AB^{n+}Cl_{n+2}$, we report novel organic-inorganic hybrid

metallates (OIHM) incorporating histammonium (HistNH₃) dications and various transition metal and main group B site cations. Single crystals of OIHMs with the basic formula (HistNH₃Mⁿ⁺Cl_{n+2}, M = Fe, Co, Ni, Cu, Zn, Cd, Hg, Sb, Sn, Pb, Bi) were grown and their structures characterized by single crystal X-ray crystallography. HistNH₃CoCl₄, HistNH₃ZnCl₄, and HistNH₃SbCl₅ crystallized in a non-centrosymmetric space group and were subsequently studied with piezoresponse force microscopy (PFM). While bulk measurements of crystals and poly(vinylidene difluoride) (PVDF)/metallate composite films exhibited low bulk response values, surface measured local response values from PFM of 5.17 pm/V for HistNH₃CoCl₄, 22.6 pm/V for HistNH₃ZnCl₄, and 2.9 pm/V for HistNH₃SbCl₅, compared with 2.50 pm/V for PVDF reference samples. The magnitude of d₃₃ coefficient, net dipole, and cation-Cl bond dipole obtained from the density functional theory calculations confirm the higher response in HistNH₃ZnCl₄ compared to HistNH₃CoCl₄. Density of states and crystal orbital Hamilton population analysis indicate that the higher net dipole in HistNH₃ZnCl₄ compared to HistNH₃CoCl₄ is due to the lower hybridization of the M-Cl bond.

Introduction

Hybrid Organic Inorganic Metallates (OIHMs) are an important class of crystalline materials that are low temperature and solution processable, and are increasingly being studied in photovoltaics,¹ light emitting diodes,² lasers,³ and photodetectors.⁴ Thin film and single crystal OIHMs are relatively easy to synthesize,^{5,6} and a wide variety of A site cations have been utilized in 3-D lead halide halometallates (also termed perovskites in their 3-D and quasi-2-D forms) of the form ABX₃, where A is an organic cation, B is a divalent lead cation, and X is a halide anion like I⁻,

Br^- , or Cl^- .⁷ If the cation is too large to fit within the interstitial spaces between BX_6 octahedra, halide sharing between octahedra will decrease to allow for effective charge compensation between A and B site cations and the structure then turns into a 2-D structure.⁸ A further decrease in halide sharing to just one corner, edge, or facial halide sharing interaction between metal centers can lead to a 1-D structure, while the absence of any halide sharing leads to a 0-D structure.⁹⁻¹¹

While there have been many studies on 3-D, quasi 2-D, and 2-D perovskite systems, less work has been undertaken on the “molecular” 1-D or 0-D systems, that is, those materials with intrinsically separated metal halide anions. It can certainly be argued in these materials that they could be more accurately called by the more general name halometallate, instead of perovskite, which others have also suggested.¹² Therefore, for the rest of this work we will refer to materials of the formula $\text{AB}^{n+}\text{X}_{n+2}$ as hybrid organic inorganic halometallates.

The approach here was to utilize hybrid organic-inorganic halometallates with a dication, histammonium dichloride (HistNH_3), which has two different cation moieties, one primary ammonium cation and one imidazolium cation. Since the two cations have different steric profiles and vastly different hydrogen-bonding patterns, major differences in cation placement within the crystalline framework was expected, and we hypothesized that upon changing the B-site cation identity it would be possible to synthesize metallate materials that crystallize in lower symmetry space groups.

In this work, we report the single-crystal X-ray structures of many novel organic-inorganic hybrid metalate (OIHM) materials and the piezoelectric characteristics of a few, namely materials based on Zn, Co, and Sb. Single crystalline samples of these three materials exhibited piezoelectric properties, however, $\text{HistNH}_3\text{ZnCl}_4$ displayed the highest overall piezoelectric response even

though it is isostructural with $\text{HistNH}_3\text{CoCl}_4$. Theoretical studies and literature data of the two materials indicated that the difference in response was found to be due to the difference in magnitude of the material dipole and M-Cl dipole.

Results & Discussion

Material Synthesis and Crystallographic Analysis

Organic Inorganic Hybrid Materials (OIHMs) were synthesized here, $\text{HistNH}_3\text{M}^{n+}\text{Cl}_{n+2}$, where HistNH_3 = histammonium and $\text{M} = \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}, \text{Cd}, \text{Hg}, \text{Sn}, \text{Pb}, \text{Sb},$ and Bi by mixing equimolar quantities of histammonium dichloride and metal chloride in either concentrated HCl, water acidified with HCl, water/methanol mixtures acidified with HCl, or DMSO. Either slow evaporation of the solution or slow cooling of a concentrated solution led to the growth of X-ray quality single crystals. We started by screening the first row of the transition metals and found much variability in material crystalline structure.

A pale orange $\text{HistNH}_3\text{FeCl}_4$ material crystallized from an equimolar mixture of FeCl_2 and histammonium dihydrochloride (**Figure 1a**) in a centrosymmetric space group ($P2_1/c$) and in stacked networks of a typical 0-D structure, with distorted metal-trigonal pyramidal dianions separated by histamine dications.

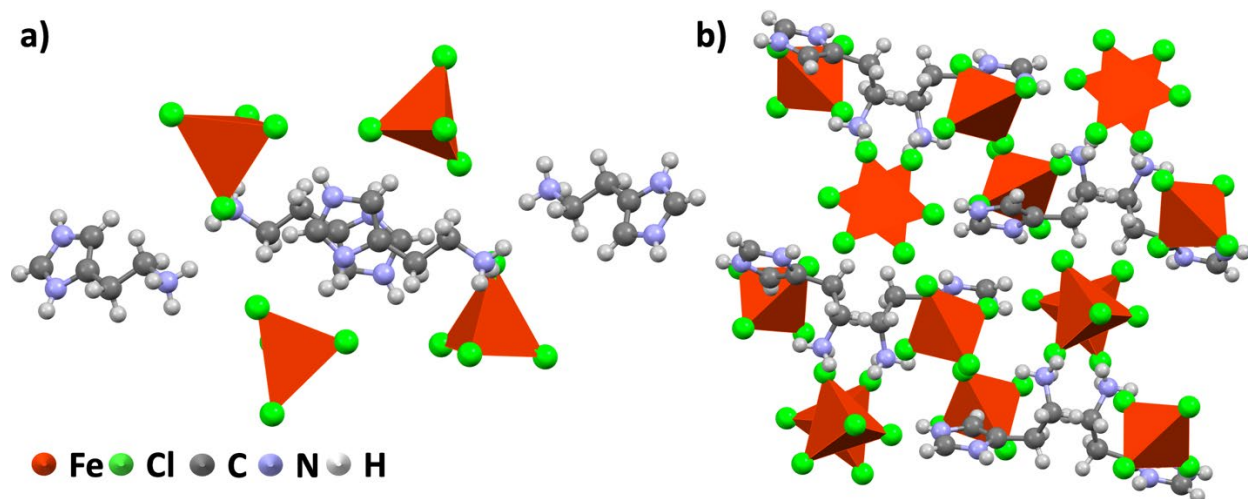


Figure 1. Crystallographically determined X-ray structures of (a) $\text{HistNH}_3\text{FeCl}_4$ and (b) $\text{HistNH}_3(\text{FeCl}_4)_2$.

Each Fe center is bonded to four Cl ligands, with three shorter Fe-Cl bonds (between 2.2826 and 2.3480 Å), and one longer Fe-Cl bond (2.4091 Å). There were three smaller Cl...Fe...Cl bond angles (98.44, 99.32, and 101.73°), two angles at 112.73° and 113.35°, and one larger angle of 125.23°. In each unit cell, there are four MCl_4 and four histammonium molecules, a total of 5 hydrogen bonding interactions per histammonium, to yield 20 hydrogen-bonding interactions within and between each unit cell. The bond angles observed here for $[\text{FeCl}_4]^{2-}$ are substantially different than those observed in past studies on FeCl_4 OIHM materials, in which each exhibited a tetrahedral geometry.¹³⁻¹⁶

When FeCl_3 was combined with histamine in an equimolar ratio, we aimed to form FeCl_5 dianions, however, a yellow $\text{HistNH}_3(\text{FeCl}_4)_2$ material crystallized (**Figure 1b**) in a centrosymmetric space group (*Pbca*). The $\text{HistNH}_3(\text{FeCl}_4)_2$ was comprised of two distorted $[\text{FeCl}_4]^-$ anion tetrahedra that are charge balanced by the histammonium dication. All eight Fe-Cl bond lengths are similar, and range between 2.1833 Å and 2.2119 Å. The Cl...Fe...Cl bond angles range from 105.74° at the smallest to 112.67°. Only one hydrogen-bonding interaction is present

in each charge balanced structure, between the NH_3 cation and one of the Cl ligands. The FeCl_4 dianions in this structure were typical distorted tetrahedra, in comparison to other $\text{Fe}^{\text{III}}\text{Cl}_4$ tetrahedra.¹³

Both colorless $\text{HistNH}_3\text{ZnCl}_4$ and deep blue $\text{HistNH}_3\text{CoCl}_4$ materials are isostructural (**Figure 2a, 2b**) and were both found to crystallize from an equimolar mixture of MCl_2 ($\text{M}=\text{Co}$, Zn) and histammonium dihydrochloride in a non-centrosymmetric space group ($Pna2_1$), in a stacked network of a 0-D structure. We had previously grown crystals of $\text{HistNH}_3\text{ZnCl}_4$ studied its mechanochemical properties by nanoindentation measurements,¹⁷ and during the course of the current work discovered that others had reported the crystal structures of $\text{HistNH}_3\text{ZnCl}_4$ and $\text{HistNH}_3\text{CoCl}_4$ before.^{18, 19}

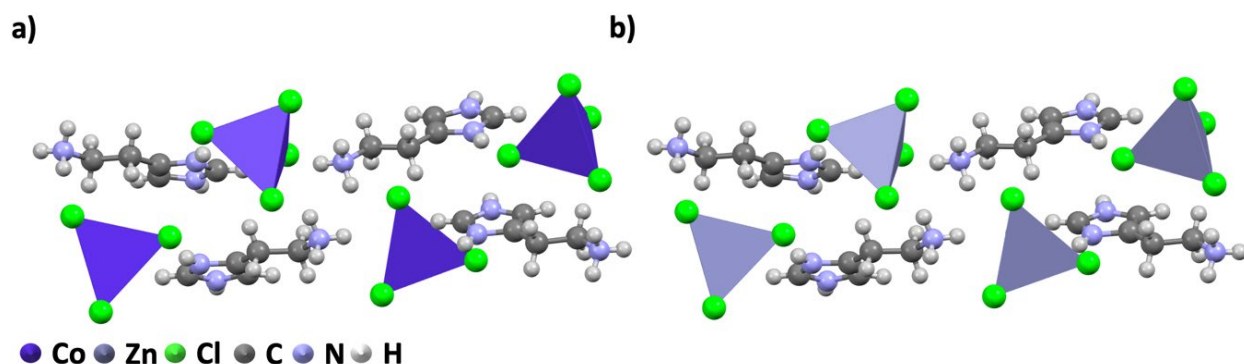


Figure 2. Crystallographically determined X-ray structures of (a) $\text{HistNH}_3\text{CoCl}_4$ and (b) $\text{HistNH}_3\text{ZnCl}_4$.

They are comprised of individual metal atoms bonded to four (4) chloride ions that yield a tetrahedral dianionic chlorometallate that is charge-balanced by the dicationic histammonium.¹⁹ The M-Cl bond distances range from 2.2540 Å to 2.2891 Å when $\text{M} = \text{Zn}$ and from 2.2589 Å to 2.2883 Å when $\text{M} = \text{Co}$. There are two Cl-M-Cl bond angles that are below the ideal tetrahedron angles (106.64° and 107.24° when $\text{M} = \text{Zn}$ and 106.20° and 107.94° when $\text{M} = \text{Co}$) and two that are above (111.15° and 114.16° when $\text{M} = \text{Zn}$ and 111.95° and 114.67° when $\text{M} = \text{Co}$). The

imidazolium cations pack to maximize π - π interactions and are spaced ~ 3.57 Å, with the ammonium cations packing as far as possible from the other cations. Each MCl_4 ($M=Zn, Co$) anionic tetrahedron participates in three hydrogen bonds: one of the Cl ligands participates in two hydrogen bonding interactions with two separate histammonium imidazole N-H groups, with an N...Cl...N H-bond angle of $\sim 156^\circ$ and a hydrogen bond distance of ~ 3.13 Å, while the Cl ligand nearest the first one participates in a hydrogen bond interaction with a nearby histammonium amine N-H group with a hydrogen bond distance of ~ 3.21 Å. In each unit cell, there are four MCl_4 tetrahedra, four histammonium molecules, and in $HistNH_3ZnCl_4$ and $HistNH_3CoCl_4$ a total of 3 hydrogen bonding interactions per histammonium, for a total of 12 hydrogen-bonding interactions within and between each unit cell. The structural parameters of both materials were similar to other $Zn^{II}Cl_4$ and $Co^{II}Cl_4$ tetrahedra reported in the literature.²⁰⁻²⁴

The yellow $HistNH_3Ni(H_2O)Cl_4$ material crystallized from an equimolar mixture of $NiCl_2$ and histammonium dihydrochloride (**Figure 3a**) in a centrosymmetric space group ($P2_1/c$), however the crystals were 4-fold twinned by pseudo-merohedry.²⁵

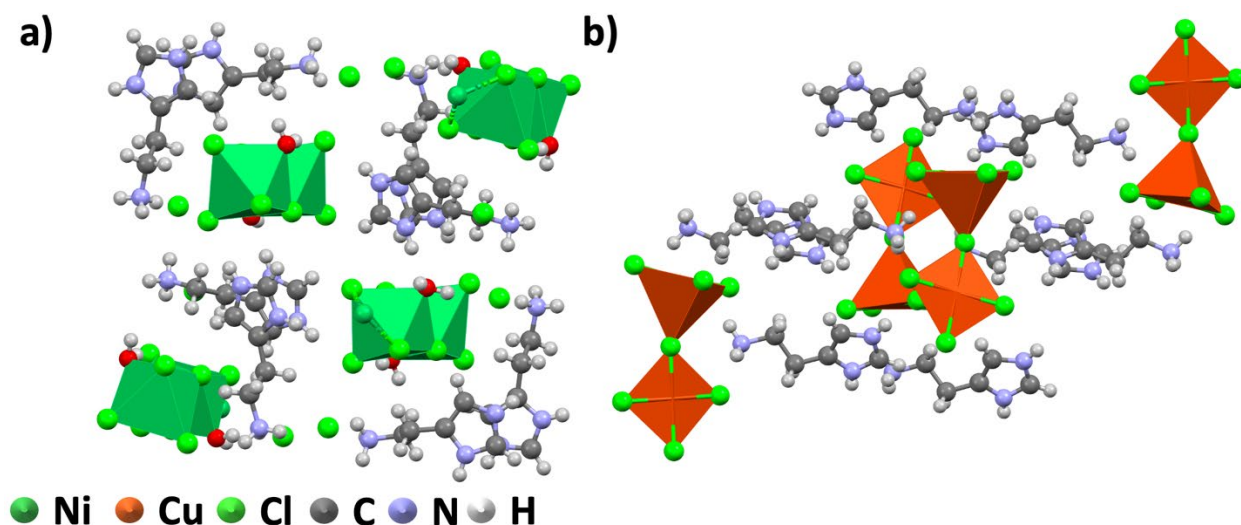


Figure 3. Crystallographically determined X-ray structures of (a) $[\text{HistNH}_3\text{Ni}(\text{H}_2\text{O})\text{Cl}_3]\text{Cl}$ and (b) $\text{HistNH}_3\text{CuCl}_4$.

They exhibited stacked networks of a typical 1-D structure, with metal octahedra extending in long charge-compensated wires. Atypical in this structure, however, is the inclusion of a water molecule coordinated to each Ni center, as is the presence of an uncoordinated Cl ion. The Cl ion is situated near to the coordinated water. In the wires, the Ni...Ni bond distances alternate between 3.446 Å and 3.456 Å, the Ni-Cl bond distances for the shared Cl ligands are 2.394 Å on average, while the unshared Ni-Cl bond has a length of 2.412 Å. The Ni-O bond distance in the wires is 2.132 Å, and the N-Cl distance between the ammonium cation and the Cl ion is 3.681 Å. The ammonium cations are situated towards other ammonium cations and Cl ions and the imidazolium cation is oriented between the $\text{NiCl}_5(\text{H}_2\text{O})$ wires with π - π stacking between imidazolium subunits, with a total of 27 hydrogen-bonding interactions within and between each unit cell. Others have observed other types of linear 1-D chloronickelates,²⁶ chloronickelates with Cl and OH_2 ligands,²⁷ but the most commonly observed chloronickelate geometry is tetrahedral.²⁸⁻³⁰

The green $\text{HistNH}_3\text{CuCl}_4$ material crystallized from an equimolar mixture of CuCl_2 and histammonium dihydrochloride (**Figure 3b**) in a centrosymmetric space group ($P2_1/c$), but were non-merohedric twins.²⁵ They exhibited a unique structure, incorporating one square-planar and one square-pyramidal metal center linked through a bridging chloride ligand with a Cu...Cl...Cu bond angle of 163.16°. In the square pyramidal Cu center one longer Cu-Cl bond (2.3093 Å), two medium Cu-Cl bonds (~2.31 Å average), one short Cu-Cl bond (2.2716 Å) are present at the pyramid base, while the apex Cu-Cl bond (2.952 Å) connecting the two metal polyhedra is much longer. In the square planar Cu center two longer Cu-Cl bonds (~2.304 Å average), and two shorter Cu-Cl bonds (~2.268 Å average) are present. One histammonium cation is present for each of the

dianionic chlorometallate tetrahedra, with each cation packing to maximize hydrogen bonding, with a total of 24 hydrogen-bonding interactions within and between each unit cell. The mixed square-pyramidal/square-planar geometry observed in the structure here is not typical of the structures previously observed for CuCl_4 based OIHMs, as others have observed a variety of structures dependent mostly on the organic cation identity.³¹⁻³³ In one account, a relatively similar structure was found when the dication $(\text{CH}_2)_3(\text{NH}_3)_2$ was used with CuCl_4 , which resulted in an additional Cu-Cl bond and a zig-zag square-pyramidal bonding pattern.³⁴

The colorless $\text{HistNH}_3\text{CdCl}_4$ material crystallized from an equimolar mixture of CdCl_2 and histammonium dihydrochloride (**Figure 4a**) in a centrosymmetric space group ($P2_1/c$) and exhibited a stacked network of corrugated 2-D structures, with metal octahedra sharing chloride ligands.

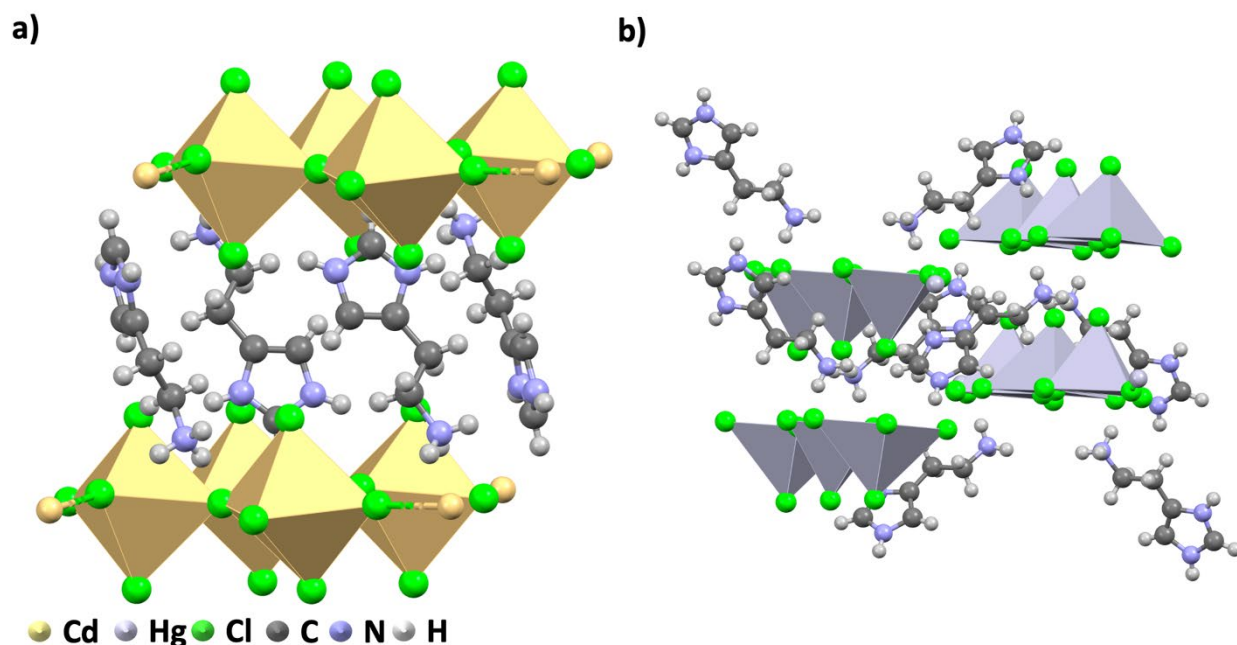


Figure 4. Crystallographically determined X-ray structures of (a) $\text{HistNH}_3\text{CdCl}_4$ and (b) $\text{HistNH}_3\text{HgCl}_4$.

Each octahedron is slightly tilted in reference to its neighbors, and in the opposite orientation. Each histammonium dication is oriented head-to-tail with its organic spacer neighbor. In the 2-D sheets, each of the unshared Cl ligands in the plane of the 2-D sheet have a Cd-Cl bond distance of 2.5424 Å, the shared Cl ligands have bond distances of 2.6576 Å and 2.6410 Å, the Cl ligands orthogonal to the 2-D sheet have bond distances of 2.7576 Å and 2.7199 Å. The Cd...Cl...Cd bond angle of one of the shared Cl is 163.11°, the Cl...Cd...Cl angle is 174.53°, while the Cd...Cl...Cd bond angle of the other shared Cl is 179.27° and the Cl...Cd...Cl bond angle is 171.83°. Hydrogen-bonding interactions are present with each of the protonated nitrogens, one each for the imidazolium cations and four for the primary ammonium cations. Since there are four histammonium spacers per unit cell and six hydrogen bond interactions per histammonium, there are 24 hydrogen-bonding interactions within and between each unit cell. The 2-D structure found here is the typical structure found in chlorocadmicates.³⁵⁻³⁷

The colorless HistNH₃HgCl₄ material crystallized from an equimolar mixture of HgCl₂ and histammonium dihydrochloride (**Figure 4b**) in a centrosymmetric space group (C2/c) and exhibited stacked networks of a corrugated 1-D structure, with each of the metals bound to five Cl ligands in a distorted square pyramidal geometry. Two of the Cl basal ligands are shared, two basal Cl ligands unshared, and the apical Cl ligand unshared as well. The apical Hg-Cl bond distance is 2.632 Å, the shared basal Hg-Cl bond distance is 2.4184 Å, the shared Hg...Cl...Hg bond angle is 148.72° and the Cl...Hg...Cl bond angle is 158.57°, and the unshared Hg-Cl bond distance is 2.857 Å with a Cl...Hg...Cl bond angle of 164.34°. Hydrogen-bonding interactions are present with each of the protonated nitrogens, with each imidazolium cation participating in one interaction and four interactions present for the primary ammonium cations. Since there are eight histammonium spacers per unit cell and six hydrogen-bond interactions per histammonium, there

are 48 hydrogen-bonding interactions within and between each unit cell. Others have reported tetrahedral chloromercurate structures,³⁸⁻⁴⁰ but others have observed a similar corrugated 1-D structure from HgCl_4 .⁴¹

The colorless $\text{HistNH}_3\text{SnCl}_4$ material crystallized from an equimolar mixture of SnCl_2 and histammonium dihydrochloride (**Figure 5a**) in a centrosymmetric space group ($P21/c$) and exhibited stacked networks of a 0-D structure.

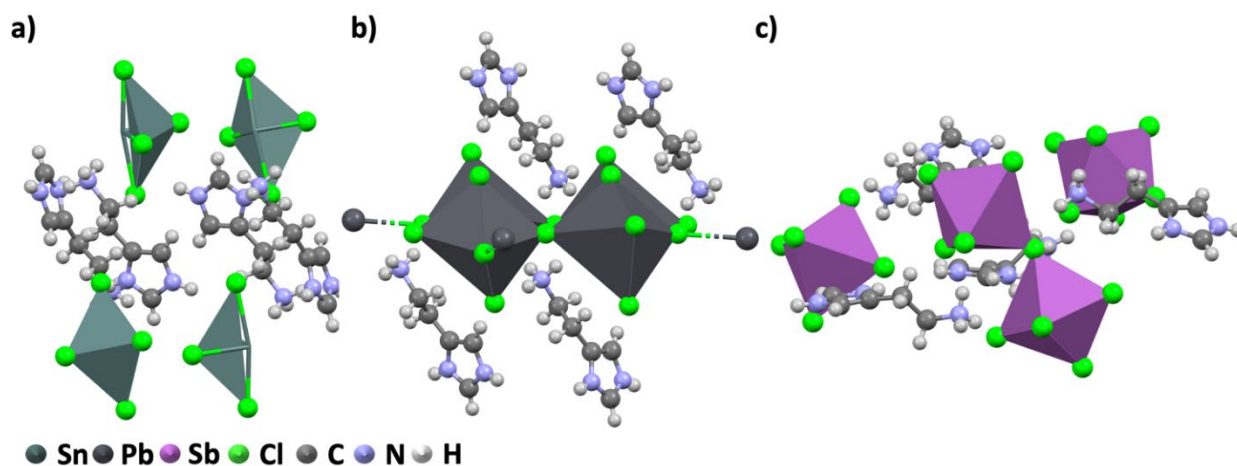


Figure 5. Crystallographically determined X-ray structures of (a) $\text{HistNH}_3\text{SnCl}_4$, (b) $\text{HistNH}_3\text{PbCl}_4$, and (c) $\text{HistNH}_3\text{SbCl}_4$.

Each Sn center is bonded to four Cl ligands in a distorted seesaw geometry, with two shorter Sn-Cl bonds (between 2.5354 and 2.5625 Å), and two longer Sn-Cl bonds (2.7271 and 2.8406 Å). The $\text{Cl}_{\text{ax}}\dots\text{Sn}\dots\text{Cl}_{\text{ax}}$ bond angle was 167.31°, while each of the other Cl...Sn...Cl bond angles was between 84.17 and 87.93°. Three of the Cl ligands participates in hydrogen bonding with the histammonium dication. In each unit cell there are four MCl_4 and four histammonium molecules with a total of five hydrogen bonding interactions per histammonium (three with the ammonium and two with the imidazolium cation), to yield 20 hydrogen-bonding interactions within and between each unit cell. The bond angles observed here for SnCl_4^{2-} are substantially different than those observed in previous studies on 0-D Sn OIHM materials, in which those with

Br and I each exhibited an octahedral geometry.¹¹ In SnCl_x OIHMs, many others have reported exclusive formation of [SnCl₆]²⁻ octahedra after using SnCl₂, which results from Sn²⁺ to Sn⁺⁴ oxidation, or after using SnCl₄.⁴²⁻⁴⁵ In a Cambridge Structural Database search, only one other SnCl₄²⁻ with a seesaw geometry was found.⁴⁶

The colorless HistNH₃PbCl₄ material crystallized from an equimolar mixture of PbCl₂ and histammonium dihydrochloride (**Figure 5b**) in a centrosymmetric space group (P2₁/c) and exhibited a stacked network of corrugated 2-D structures, with metal octahedra sharing chloride ligands. Each octahedron is tilted in reference to its neighbors, as in the HistNH₃CdCl₄ structure, however, each Pb octahedron is tilted much more, with a Pb-Cl-Pb angle of 150.23° vs. the Pb-Cl-Pb angle of 163.11°. Each histammonium dication is oriented head-to-tail with its organic spacer neighbor, with the ammonium cation in close contact with three Cl ligands. In the 2-D sheets, each of the unshared Cl ligands have Pb-Cl bond distances of 2.7901 and 2.8982 Å, the shared Cl ligands have bond distances of 2.7200 Å and 2.9656 Å, 2.759 Å and 3.0610 Å. The Pb...Cl...Pb bond angle of the one of the shared Cl is 150.23°, the Cl...Pb...Cl angle is 170.78°. Hydrogen-bonding interactions are present with each of the protonated nitrogens, one each for the imidazolium nitrogens and three for the primary ammonium cations. Since there are four histammonium spacers per unit cell and five hydrogen bond interactions per histammonium, there are 20 hydrogen-bonding interactions within and between each unit cell. The 2-D structure observed for HistNH₃PbCl₄ was the common *n*=1 structure, where *n* is the inorganic layer number, structure reported by others.⁴⁷⁻⁴⁹

The colorless HistNH₃SbCl₅ material crystallized from an equimolar mixture of SbCl₃ and histammonium dihydrochloride (**Figure 5c**) in a non-centrosymmetric space group (P2₁2₁2₁) and exhibited a stacked network of corrugated 1-D structures, with metal octahedra sharing two

chloride ligands. Each octahedron is therefore tilted in reference to its neighbors, each Sb octahedron is tilted away from its neighbor, with a Sb-Cl-Sb angle of 147.98°. Each histammonium dication is oriented head-to-tail with its organic spacer neighbor, with the ammonium cation in close contact with three Cl ligands and the imidazolium in close contact with two Cl ligands. In each octahedron, three Cl ligands have Sb-Cl bond distances between 2.472 and 2.509 Å and one Cl ligand has a bond distance of 2.822 Å. The Sb...Cl bond distance of one of the shared Cl is 2.868 Å, the other is 2.861 Å. Hydrogen-bonding interactions are present with each of the protonated nitrogens, one each for the imidazolium nitrogens and three for the primary ammonium cations. Since there are four histammonium spacers per unit cell and five hydrogen bond interactions per histammonium, there are 20 hydrogen-bonding interactions within and between each unit cell. The corrugated 1-D structure observed for HistNH₃SbCl₅ is similar to a recently reported pentachlorantimonate,⁵⁰ and to a histammonium iodoantimonate.⁵¹

The colorless (HistNH₃)₃(BiCl₆)₂ material crystallized from an equimolar mixture of BiCl₃ and histammonium dihydrochloride (**Figure 6**) in a centrosymmetric space group (*P-1*) and exhibited stacked networks of a 0-D structure. Also included in the structure are two water and two methanol solvent molecules.

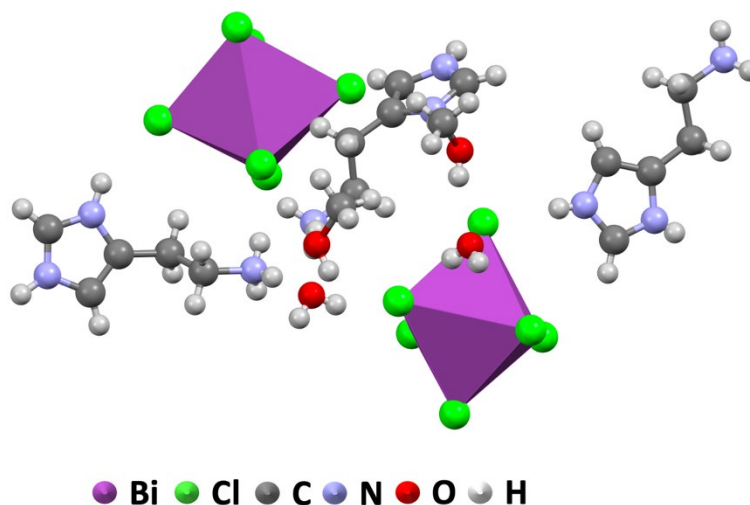


Figure 6. Crystallographically determined X-ray structure of $(\text{HistNH}_3)_3(\text{BiCl}_6)_2$.

In one of the chlorobismuthates, the Bi center is bonded to six Cl ligands in a distorted octahedron, with two shorter Bi-Cl bonds (2.6512 and 2.6641 Å), two intermediate-length Bi-Cl bonds (2.6925 and 2.7019 Å), and two longer Bi-Cl bonds (2.7556 and 2.7638 Å for example). The $\text{Cl}_{\text{ax}}\dots\text{Bi}\dots\text{Cl}_{\text{ax}}$ bond angle was 174.72° , while each of the other $\text{Cl}\dots\text{Bi}\dots\text{Cl}$ bond angles was between 85.68 and 95.74° . In the other chlorobismuthate, the Bi center is also bonded to six Cl ligands in a distorted octahedron, with two shorter Bi-Cl bonds (2.6544 and 2.6824 Å), two intermediate-length Bi-Cl bonds (2.6916 and 2.7032 Å), and two longer Bi-Cl bonds (2.7134 and 2.7781 Å for example). The $\text{Cl}_{\text{ax}}\dots\text{Bi}\dots\text{Cl}_{\text{ax}}$ bond angle was 176.133° , while each of the other $\text{Cl}\dots\text{Bi}\dots\text{Cl}$ bond angles was between 84.28 and 95.20° . Each Cl ligand of the two BiCl_6 trianions participates in hydrogen bonding, but the types of hydrogen bonds are different between them. In one BiCl_6 , two chlorine atoms hydrogen bond with nearby water molecules, one chlorine atom hydrogen bonds with a nearby methanol molecule, and the other three hydrogen bond with histamine molecules. The water molecules also hydrogen bond to histamine molecules or methanol. In the other BiCl_6 group, five of the chlorine atoms hydrogen bond with histamine, but one chlorine is not participating in any hydrogen bonding. In each unit cell there are two MCl_6

and three histammonium molecules. One of the histammines has a total of four hydrogen bonding interactions, one has six, and the other has five. One of the water molecules has three hydrogen bonds and the other has four. One of the methanol molecules has two hydrogen bonds, and the other has three for a total of 27 hydrogen-bonding interactions within and between each unit cell. The bond angles observed here for BiCl_6^{2-} differ from those observed in some previous studies on 0-D Bi OIHM materials, in which the longest Bi-Cl bond lengths here are either longer by <0.05 Å or shorter by >0.13 Å than the longest Bi-Cl bond in a BiCl_6^{3-} octahedron.⁵²⁻⁵⁴ Overall, the crystalline structure of the chlorometallate structures described here changed markedly with a change in metal cation identity (**Table 1**).

Table 1. Properties of hybrid inorganic-organic chlorometallates studied here.

Material	Metal Cation Charge	Space Group	Metal Ionic Radius (pm) ⁵⁵	Material Dimensionality	Chlorides shared per metal atom
HistNH ₃ FeCl ₄	+2	<i>P2₁/c</i>	92	0-D	0
HistNH ₃ (FeCl ₄) ₂	+3	<i>Pbca</i>	78.5	0-D	0
HistNH ₃ CoCl ₄	+2	<i>Pna2₁</i>	88.5	0-D	0
HistNH ₃ ZnCl ₄	+2	<i>Pna2₁</i>	88	0-D	0
[HistNH ₃ Ni(H ₂ O)Cl ₃]Cl	+2	<i>P2₁/c</i>	83	1-D	2
HistNH ₃ CuCl ₄	+2	<i>P2₁/c</i>	87	0-D dimers	1
HistNH ₃ CdCl ₄	+2	<i>P2₁/c</i>	109	2-D	4
HistNH ₃ HgCl ₄	+2	<i>C2/c</i>	116	Corrugated 1-D	1
HistNH ₃ SnCl ₄	+2	<i>P2₁/c</i>	102 ⁵⁶	0-D	0

HistNH ₃ PbCl ₄	+2	<i>P2₁/c</i>	133	2-D	4
HistNH ₃ SbCl ₅	+3	<i>P2₁2₁2₁</i>	90	Corrugated 1-D	1
(HistNH ₃) ₃ (BiCl ₆) ₂	+3	<i>P-1</i>	117	0-D	0

Most of the materials with a divalent metal cation crystallized into the *P2₁/c* space group, with the non-centrosymmetric Co- (*Pna2₁*), Zn- (*Pna2₁*), and centrosymmetric Hg-based (*C2/c*) materials being the only exceptions. None of the materials exhibited a 3-D dimensionality, where all the chloride ligands are shared with neighboring metal centers. Only two materials (based on Cd and Pb) exhibited a 2-D dimensionality, with four chlorides being shared, and two others (Ni and Hg) exhibited a 1-D dimensionality, with two shared chloride ligands. The histammonium dication is much too large to allow 3-D functionality as determined by the Goldschmidt tolerance factor,⁵⁷ and using it resulted in mostly 0-D materials, in metals with varying ionic radii. It is likely that the crystal growth conditions played some role in crystal structure formation (especially for the Ni- and Bi- compounds), which makes precise accounting for the effect of the histammonium cation on dimensionality and space-group more difficult.

While the structures of the materials from **Table 1** depended on the identity of the metal cation, only three of the solved structures were non-centrosymmetric (HistNH₃CoCl₄, HistNH₃ZnCl₄, and HistNH₃SbCl₄). Since we were interested in the potential piezoelectric properties of these chlorometallates, we decided to study further the piezoelectric properties of the non-centrosymmetric materials. The Zn-, Co-, and Sb- based materials were studied, as well as the centrosymmetric HistNH₃CuCl₄, which was chosen at random to serve as a negative control. PFM was performed on the X-ray quality Co, Cu, Sb, and Zn containing single-crystal OIHM samples grown and maintained at room temperature. For each of the materials, it was difficult to

consistently see a response displacement from the sample at the applied voltages. We attribute this to difficulties we had in sample mounting, as the crystals were highly brittle and damaged easily,¹⁷ which led to poor electrical contact in some cases. Only the Zn containing material grew large enough crystals in our hands to measure on a specific face (a-c face). **Table 2** shows results of successful PFM measurements from these single-crystal samples. During measurement, only the Zn-containing metallate was stable to testing and storage in ambient atmosphere, which further made PFM testing on the single-crystalline substrates difficult. Nevertheless, when measurements were successfully taken, multiple repetitive sampling events were taken from several sites on the mounted crystal.

Table 2. Local piezoelectric response from piezoresponse force microscopy measurements on unpoled single-crystalline samples of $\text{HistNH}_3\text{M}^{\text{n}+}\text{Cl}_{\text{n}+2}$ (M=Co, Cu, Zn, Sb) compared to a ferroelectric polymer PVDF reference.⁵⁸

Material	Local Piezoelectric Response (pm/V)
$\text{HistNH}_3\text{CoCl}_4$	5.17
$\text{HistNH}_3\text{CuCl}_4$	0.28
$\text{HistNH}_3\text{ZnCl}_4$	22.6
$\text{HistNH}_3\text{SbCl}_5$	2.9
PVDF	2.5

To rationalize these results, we performed density functional theory (DFT) calculations using the Perdew-Burke-Ernzerhof (PBE)⁵⁹ functional (see Computational details section for more details) for the set of compounds listed in **Table 2**: $\text{HistNH}_3\text{CoCl}_4$, $\text{HistNH}_3\text{SbCl}_5$, $\text{HistNH}_3\text{CuCl}_4$, and $\text{HistNH}_3\text{ZnCl}_4$.

To compare with the experiment by removing any dependency on the structure, the bandgap, charge transfer, net and cation-Cl dipole moments, and d_{33} constants provided in **Table 3** were all calculated with PBE at the experimental geometry. Charge transfer and dipole moments were calculated using DDEC6.⁶⁰⁻⁶²

To examine the variation of the key properties with the different geometries, a comparison of the bandgaps and piezoelectric strain tensors were all calculated with the PBE functional but at four different geometries (see **Tables S9 and S10** of the SI). The four geometries used in this analysis were: (i) experimental; (ii) PBE-partially optimized geometry whereby the volume is fixed but the lattice sites are relaxed; (iii) PBE fully optimized; and (iv) PBE+D3 fully optimized. The comparison between the PBE and PBE+D3 fully optimized geometries were motivated by the fact that the calculated lattice constants and unit-cell volume of the PBE-fully optimized geometries are ca. 10% larger than experiment (see **Table S9**), which is consistent with the previous literature.⁶³ On the other hand, the lattice constants and unit-cell volume with PBE+D3-optimized geometries are calculated to be within 2% of experiment. Small variations in the band gap energies and piezoelectric strain tensors (**Table S10**) were found depending on the geometry; however, the overall trend is the same.

The PBE-calculated bandgaps at the experimental geometry are in good agreement with the measured values, which were determined using UV-Vis-NIR measurements of dropcasted films (**Table 3**). The observed low energy absorbances in the films of the Co-and Cu- based materials were ascribed to spin-forbidden d-d transitions.⁶⁴⁻⁶⁷ The piezoelectric strain constants (d_{ij}) were determined from the PBE-calculated elastic (C_{ij}) and piezoelectric stress (e_{ij}) tensors using the relation $d_{ij} = e_{ij} \times S_{ij}$; here, S_{ij} is the inverse of the matrix C_{ij} .⁶⁸ As shown in **Table 3**, the calculated d_{33} coefficients for $\text{HistNH}_3\text{ZnCl}_4$ and $\text{HistNH}_3\text{CoCl}_4$ are 10.8 pm/V and 7.4 pm/V,

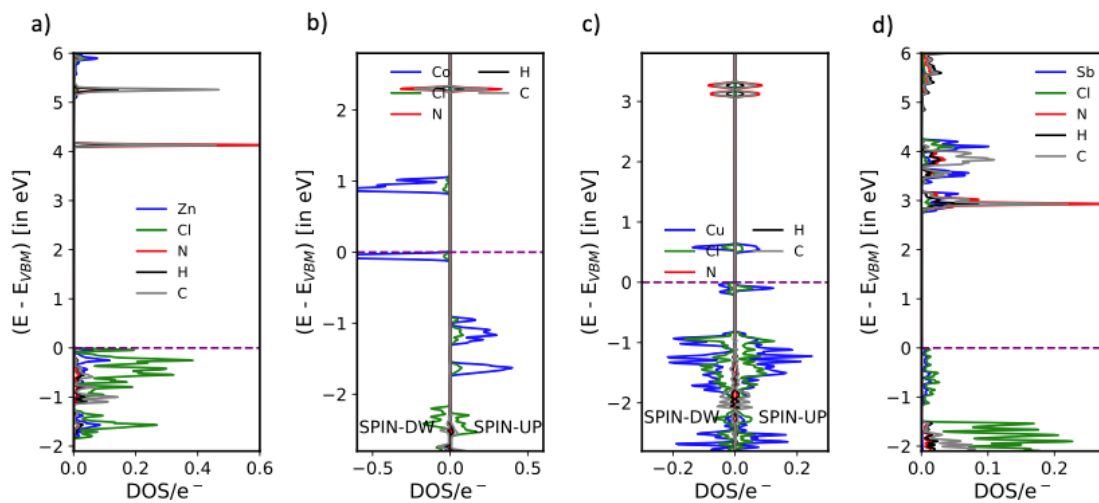
			(e^- /metal atom)	per unit cell (Debye)	moment (Debye)	constant (pm/V)	<i>PFM</i> <i>response</i> (pm/V)
HistNH ₃ CoCl ₄	0.88	0.88	0.630	0.037	0.41	7.39	5.17
HistNH ₃ SbCl ₅	3.22	2.88	0.957	0.0	0.000	0.00	2.9
HistNH ₃ CuCl ₄	0.55	0.53	0.717	0.0	0.000	0.00	0.28
HistNH ₃ ZnCl ₄	4.13	4.15	0.635	0.048	0.48	10.76	22.6

To rationalize the larger dipole moment for HistNH₃ZnCl₄ compared with HistNH₃CoCl₄ and HistNH₃SbCl₅, both the elementwise contribution (partial) of the density of states (pDOS) and the projected crystal orbital Hamilton population (pCOHP) were calculated (see Figure 7). The pDOS and pCOHP are used to calculate the contributions of each element to the conduction band minimum (CBM) and valence band maximum (VBM). The COHP analysis was performed using LOBSTER.⁶⁹

Both the pDOS and pCOHP indicates that the higher calculated dipole for HistNH₃ZnCl₄, is due to the lower hybridization of the Zn-Cl bond compared with Co-Cl. For HistNH₃ZnCl₄, the VBM is dominated by Cl with a slight contribution from Zn and the CBM is dominated by the N atom of HistNH₃. Similarly, the COHP analysis indicates that the Zn-Cl bonding dominates the valence band edge but is largely absent from the conduction band edge. This is consistent with experimental data in the literature suggesting that in ZnCl₄²⁻, the electron density of the highest occupied molecular orbital lies mainly in a molecular orbital with primarily Cl ligand *p*-orbital character.²¹

In the isostructural compound HistNH₃CoCl₄, the CBM and VBM are both dominated by Co and Cl. This is consistent with the literature that suggests in CoCl₄²⁻, the highest occupied

molecular orbital lies mainly in Co-centered $3d-t_2$ orbitals, with little delocalization into the Co-Cl σ bond.²⁰ In $\text{HistNH}_3\text{SbCl}_5$ the VBM and CBM is both dominated by Sb and Cl. This agrees with the literature that the valance band is dominated by the strong hybridization between the occupied Sb-5s and Cl-3p while conduction band is dominated by Sb-5p and Cl-3p.⁷⁰ Both the VBM and CBM in the case of $\text{HistNH}_3\text{CuCl}_4$ is dominated by Cu and Cl as suggested by pDOS and COHP analysis.



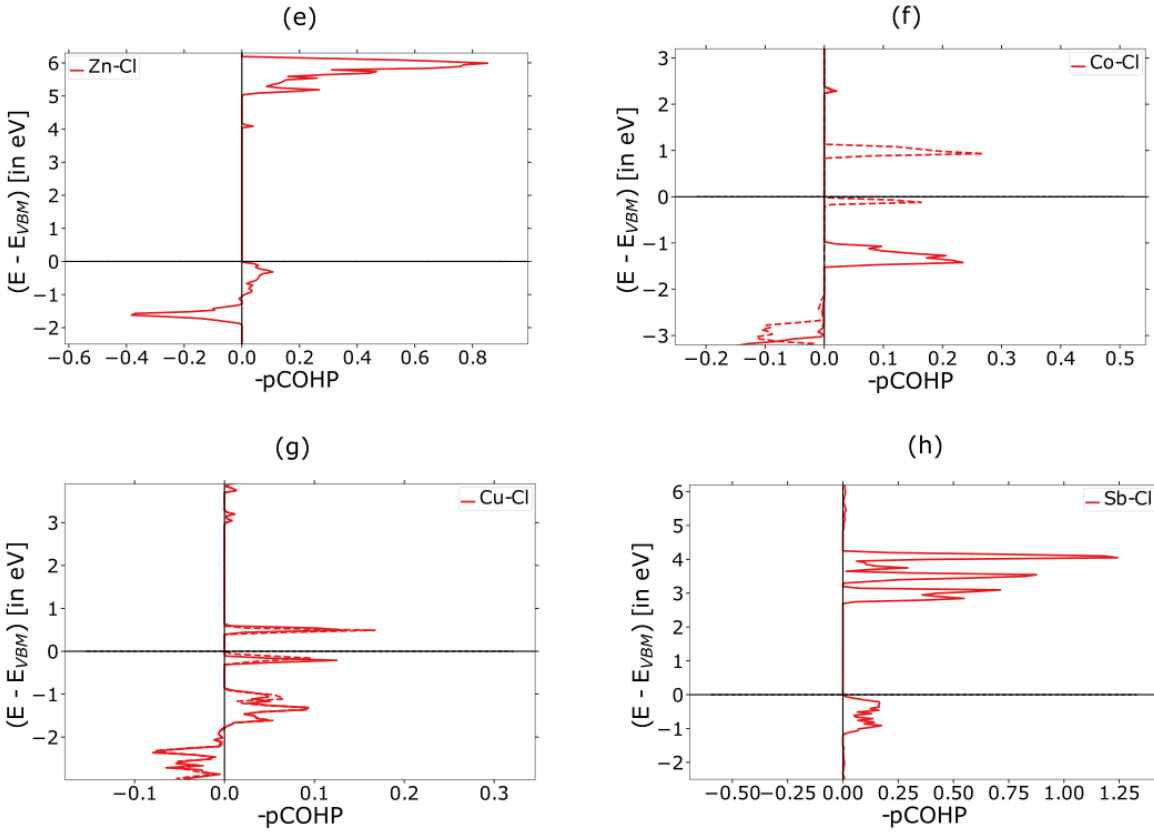


Figure 7. Elementwise contribution on the density of states (DOS) per electrons per atom for (a) $\text{HistNH}_3\text{ZnCl}_4$, (b) $\text{HistNH}_3\text{CoCl}_4$, (c) $\text{HistNH}_3\text{CuCl}_4$, and (d) $\text{HistNH}_3\text{SbCl}_5$ and projected crystal orbital Hamilton population (pCOHP) of cation-Cl bond in (e) $\text{HistNH}_3\text{ZnCl}_4$, (f) $\text{HistNH}_3\text{CoCl}_4$, (g) $\text{HistNH}_3\text{CuCl}_4$, and (h) $\text{HistNH}_3\text{SbCl}_5$.

In the results shown in **Table 2**, the $\text{HistNH}_3\text{MCl}_4$ materials exhibited different local piezoelectric responses compared to the PVDF ferroelectric polymer reference, which was annealed at 100 °C in an oven and measured according to literature methods.⁵⁸ In these trials, the $\text{HistNH}_3\text{CuCl}_4$ material was the lowest performing overall (0.28 pm/V) and very close to zero, as expected, due to the inversion symmetry present in the crystal. This number is not precisely 0, however, because centrosymmetric materials can give very small local piezoelectric response values.⁷¹ The

HistNH₃ZnCl₄ material exhibited the largest average local piezoelectric response, at 22.6 pm/V and HistNH₃CoCl₄ yielded a larger local piezoelectric response than PVDF, but much lower than for HistNH₃ZnCl₄. HistNH₃SbCl₅ exhibited a PFM response that was a little higher than the PVDF reference. The difference in performance between the isostructural Zn and Co based materials is discussed in more detail below. Even though these values are notable, the samples here were tested without any poling treatments, due to difficulty in making electrical connection to the single crystals, thus they are likely underestimated. State-of-the-art approaches towards piezoelectric metallates⁷² have yielded materials with d_{33} piezoelectric coefficients of 73 and 76 pm/V for Pb based metallates,^{73,74} 110 pm/V for an Fe based metallate,⁷⁵ and 139 and 1540 pm/V for Cd based metallates.^{76,77} While others have suggested that a local inverse piezoelectric response observed from PFM could be extrapolated into a bulk d_{33} value,⁷⁸ which would place HistNH₃ZnCl₄ firmly within the state-of-the-art, we were not able to pole these samples as of yet. Efforts are underway to grow sufficiently large crystals to allow poling and bulk d_{33} piezoelectric measurement.

To further investigate whether the piezoelectric response measurements are related to orientation of the mounted single crystals, HistNH₃MCl₄ (M = Cu, Co, Zn)·PVDF composite materials were made by drop-casting, annealing in an oven, and peeling composite films post-anneal to yield a free standing and flexible film. The metallate to PVDF ratio, annealing temperatures, and times were optimized by choosing the compositions and temperatures that led to the easiest-to-peel and handle films after fabrication. The easily handled and non-poled films were then tested by PFM.⁶ For HistNH₃ZnCl₄·PVDF the composite was 8.6 wt.% HistNH₃ZnCl₄ which was annealed at 100 °C for 15 minutes, for HistNH₃CuCl₄·PVDF the composite was 5.1 wt.% HistNH₃CuCl₄ which was annealed at 150 °C for 15 minutes, and for HistNH₃CoCl₄·PVDF the composite was 5.1 wt.% HistNH₃CoCl₄ which was annealed at 180 °C for 15 minutes. Of the composite materials, the

HistNH₃ZnCl₄·PVDF composite films at 8.6 wt.% were more resistant to water-induced film degradation than the other composites, which required storage in dry air after fabrication. In addition, the HistNH₃CuCl₄·PVDF and HistNH₃CoCl₄·PVDF composites with higher than 5.1 wt.% metallate was not easily peeled and were therefore not chosen for further testing. Attempts to make the Sb-containing composites did not yield easily peeled films in our attempts. PXRD measurements of the films indicated similar diffractions for the Zn-based composite and single crystal, but the Co-based composite had no discernable diffraction besides PVDF and the Cu-based composite did not exhibit diffraction peaks that were similar to those simulated from the crystal. Therefore, it is possible that only the Zn-based composite contained the same metallate structure as was solved by powder X-ray diffraction. The 60 x 60 μm topography images shown in the insets of **Figure 8** were taken using contact mode at a scan rate of 0.1 Hz. A linear regression analysis was carried out for each measurement. The slope of the voltage vs displacement was taken to obtain the local piezoelectric response (see *Supporting Information*). **Figure 8** reports the average of the slopes from the 10 different measurements and their standard deviation. To remove the background noise from the measurements, a single measurement was performed on a non-piezoelectric sample (a glass slide) using the same parameters. The measured response of the non-piezoelectric sample was subtracted out of the signals from the polymer composites.

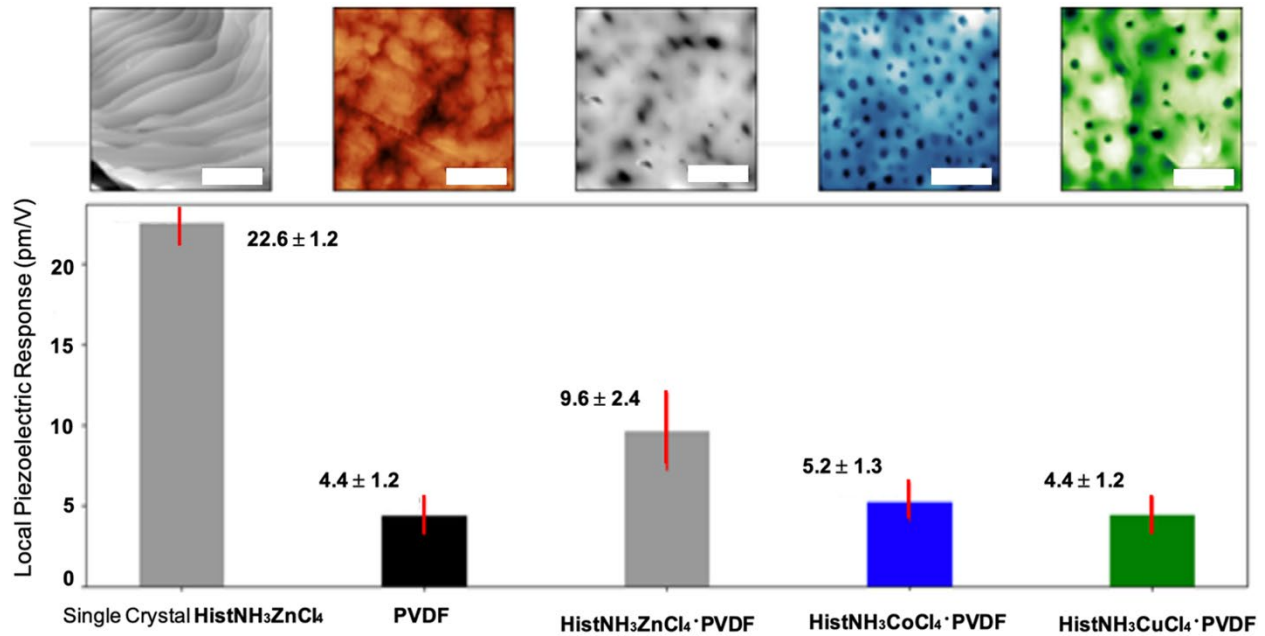


Figure 8. Shown above are the average local piezoelectric responses for all three polymer composite samples without poling, compared with a reference PVDF polymer sample and a single-crystal HistNH₃ZnCl₄ sample. Above each sample is a 60 x 60 μm topography image of each material, taken using contact mode at a scan rate of 0.1 Hz, with a scale bar of 20 μm. Listed from left to right are the HistNH₃ZnCl₄ (single crystal), PVDF reference film, HistNH₃ZnCl₄·PVDF composite, HistNH₃CoCl₄·PVDF composite and HistNH₃CuCl₄·PVDF composite.

From the PFM measurements on the polymer/metallate composite materials, a similar trend to that observed with single-crystal samples was observed. The HistNH₃ZnCl₄·PVDF composite yielded the highest local piezoelectric response (9.6 ± 2.4 pm/V), and the HistNH₃CoCl₄·PVDF yielded a response marginally better than the reference PVDF film (5.2 ± 1.3 pm/V). The HistNH₃CuCl₄·PVDF composite yielded no improvement over the unmodified PVDF films (4.4 ± 1.2 pm/V), as would be expected for a non-piezoelectric material. The piezoelectric longitudinal d_{33} charge coefficients using the Berlincourt method of all the composite samples can be seen in

Table S8. The magnitude of the d_{33} coefficients measured via the Berlincourt method are relatively small compared to the PFM data in **Table 2**, with values of 0.31 pm/V for HistNH₃ZnCl₄•PVDF, 0.24 pm/V for HistNH₃CoCl₄•PVDF, and 0.09 pm/V for HistNH₃CuCl₄•PVDF. We attribute this due to differences between the Berlincourt piezo-meter, which is a bulk measurement of the metallate composite using upper and lower electrodes, and PFM which is a localized surface measurement that brings a sharp conductive probe into contact with the metallate composite surface. Since PFM is a localized surface measurement, it is less influenced by the polymer phase and therefore tends to exhibit high d_{33} values, while the Berlincourt piezo-meter operates through thickness mode, and the polarization and measured d_{33} coefficient is dominated by the continuous polymer phase.

To further confirm that each material was noncentrosymmetric at temperatures similar to those used in PFM measurement, we undertook optical second-harmonic generation (SHG) studies. This is a common way to screen for ferroelectrics because SHG only occurs in materials that lack inversion symmetry.⁷⁹ We used a Zeiss LSM880 upright multiphoton microscope with tunable laser power, excitation wavelength and detection wavelength (**Figure 9**). We were unsuccessful in making crystalline powders with specific particle sizes, so we turned to using single crystals for our measurements. X-ray quality single crystals were used to verify material identity and then they were sliced with a razor blade to reduce surface irregularities and mounted with an arbitrary crystallographic orientation. We compared the values we found to samples of poled PVDF sheets and a large single crystalline potassium dihydrogen phosphate (KDP) sample, both of which are typical piezoelectric reference materials.

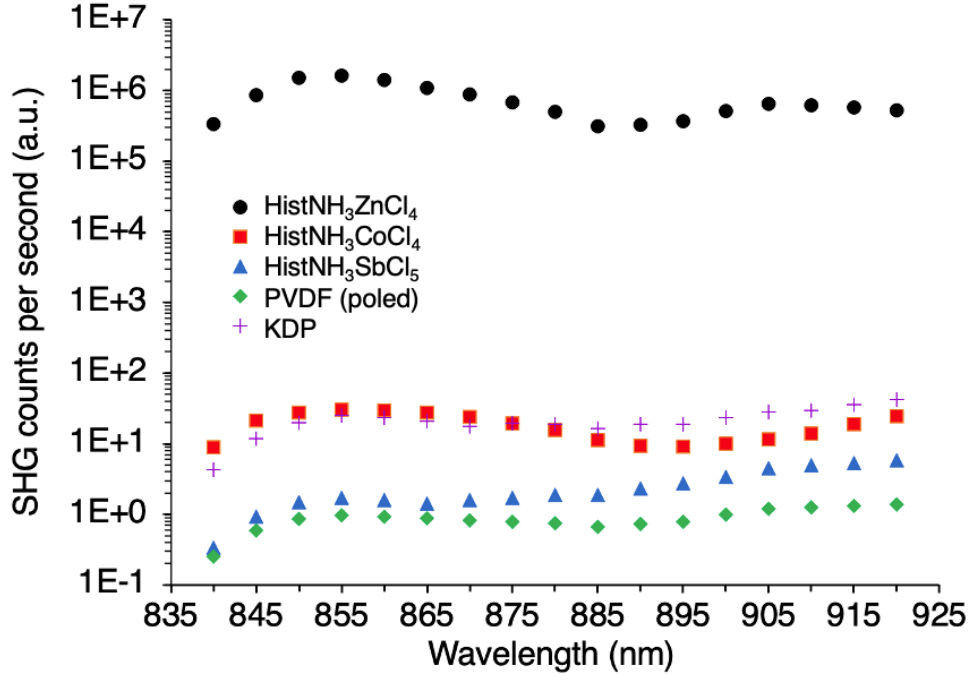


Figure 9. Second Harmonic Generation activity for single crystals of HistNH₃ZnCl₄ (black circles), HistNH₃CoCl₄ (red squares), and HistNH₃SbCl₅ (blue triangles), a sheet of poled PVDF (green diamonds), and single crystals of KDP (purple crosses). The incidence of light has been normalized for each of the samples.

We scanned excitation wavelengths from 920 – 840 nm and observed the intensity of $\lambda/2$ emission. During the measurement, we found that each of the Zn-, Co-, and Sb-containing materials produced $\lambda/2$ light. For samples with an inversion center, no light was observed. For the two reference materials, the poled PVDF and KDP samples both exhibited a SHG response as well. These data confirm that each of the chlorometallate materials are non-centrosymmetric as grown and as measured by PFM, and not only at the low temperature in which their structures were solved by X-ray crystallography. Because sample thickness, light scattering, absorption, and surface irregularities can play a large role in the magnitude of SHG response measured,⁸⁰ these

SHG measurement values are not meant to be quantitative. Until powders of each material with specific particle sizes can be reliably formed, then these figures cannot be presented quantitatively.

Conclusions

In conclusion, we have synthesized a range of novel organic-inorganic hybrid chlorometallates, including three systems that crystallized in a non-centrosymmetric space group. We determined that using different metal B site cations, a range of metallate dimensionality, symmetry, and degree of halide sharing could be accessed when using the histammonium dication. We evaluated the local piezoelectric response of the three materials using piezoresponse force microscopy, $\text{HistNH}_3\text{ZnCl}_4$, $\text{HistNH}_3\text{CoCl}_4$, $\text{HistNH}_3\text{SbCl}_5$ and found that even though they are isostructural, the Zn containing material exhibited a much higher response than the Co containing material. We verified that each non-centrosymmetric structure retained its low-symmetry structure at room temperature using second harmonic generation spectroscopy. We then correlated the piezoelectric response difference of the Co and Zn materials to material properties. It was found that the ZnCl_4 containing material exhibited a higher piezoelectric response than CoCl_4 in crystal and composite form, which was attributed to a higher material dipole moment, larger strain tensors, and a much wider bandgap for the ZnCl_4 material than for the CoCl_4 material. This study provides new insights on the impact of B site cation choice on material piezoelectric and structural properties of the material.

Experimental

General Considerations: Reagents used as received from the following chemical suppliers: hydrochloric acid and histamine dihydrochloride were purchased from Matrix Scientific and the transition metal chlorides from various sources. Differential scanning calorimetry measurements were acquired on a TA-Instruments TRIOS DSC 2500 from 0 to 200 °C.

Materials and Solutions Preparation

The various histammonium HOIP single crystals were grown by dissolving the transition metal halides $M^{x+}Cl_x$ ($M = Fe^{2+}, Fe^{3+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Sn^{2+}, Pb^{2+}, Sb^{3+}, Bi^{3+}$) (1.0 mmol) and histammonium dihydrochloride in either 1 mL of hydrochloric acid, 1 mL of water acidified to pH 3 with HCl, 1 mL of 1:1 methanol:water acidified to pH = 3, or 1 mL of DMSO in a capped 2 mL vial,. In each case, the contents were warmed until dissolution before being left to crystallize. The single-crystal samples were left to grow over the course of several days.

Metallate Composite Film Preparation

Composite films used for PFM measurements were prepared by dissolving PVDF (10 wt%) and histammonium MCl_4 ($M = Co, Cu, Zn$), drop-casting 50 μ L of the solution onto a soda lime glass slide, and then annealed in an oven.

Single-Crystal Characterization

Single-crystal data of the metallates collected on a Bruker D8 Venture κ -axis diffractometer with Mo $K\alpha$ radiation (0.71073 Å) at 90.0 K. The crystal structures were solved by dual-space methods and refined by full-matrix least-squares using the SHELX programs.⁸¹

PFM Characterization

Each sample was mounted onto a polished aluminum puck using carbon sticky tape as a conductive adhesive. Piezoresponse force microscopy (PFM) was performed on all samples as well as a poly(vinylidene difluoride) (PVDF) reference sample at 10 different locations using a Bruker Dimension Icon mounted with a SCM-PIT-V2 platinum-iridium coated conductive tip. To determine the measured displacement of the surface, the tip was calibrated using fused silica to determine the deflection sensitivity. A thermal tuning procedure was also performed to determine the quality factor of the tip ($Q = 184$). A single measurement at a location consisted of measuring the displacement of the sample when applying 0, 2, 4, 6, 8, and 10 V by scanning a $500 \times 167 \text{ nm}^2$ area at an applied load of 68 nN. At each voltage, the response of the sample was taken to be the average response of the resulting image (averaging over $\sim 22,000$ data points).

Piezoelectric charge coefficients, d_{33} , of all samples with top and bottom electrodes were measured before and after corona poling by the Berlincourt method in a higher precision mode of piezometer (PiezoTest PM300, Singapore). For each sample, three measurements in both positive and negative d_{33} were taken before and after corona poling to evaluate the piezoelectric response of all samples.

Second Harmonic Generation Measurement

X-ray quality single crystals of Co, Sb, Zn were first sliced with a razorblade and the sliced crystal mounted on a soda lime glass slide with arbitrary crystallographic orientation. The slide was then mounted into a Zeiss LSM880 upright multiphoton microscope and illuminated with light between 840 nm and 920 at a 5x lens objective. The emitted light matching $\lambda/2$ nm is detected for all in-focus light and plotted versus the wavelength.

Experimental Bandgap Determination

Thin films of Cu, Co, Sb, and Zn OIHMs formed by drop casting 1M precursor solutions onto sodalime glass microscope slides, annealing at 100 °C for 5 min and recording the transmission spectra of the thick, polycrystalline film using a Cary5000 UV/Vis/NIR spectrophotometer.

Computational details

All DFT calculations were performed using the Vienna ab initio simulation package (VASP) code by utilizing the Perdew-Burke-Ernzerhof (PBE)⁵⁹ exchange-correlation functional and the pseudopotentials recommended by VASP. Gaussian smearing with smearing parameter ($K_B T$) of 0.02 eV, energy convergence criterion for the electronic steps equal to 10^{-7} eV and the gamma-centered k-meshes with the smallest allowed spacing between k-points equal to 0.03 \AA^{-1} for the Brillouin zone sampling was used in all the calculations. In addition, the calculations of Cu- and Co-based materials were initialized in three different spin configurations (ferromagnetic, ferrimagnetic, and anti-ferromagnetic). However, the subsequent analyses were performed only on the structure corresponding to the minimum energy. For Cu- and Co-based materials we found the minimum energy corresponding to antiferromagnetic and ferromagnetic spin configuration, respectively. We also computed the elastic tensor following the strain-stress relationship⁸² and the piezoelectric stress tensor^{83, 84} using the linear response theory as described in the literature. Finally, we utilized the Density Derived Electrostatic and Chemical (DDEC6)⁶⁰⁻⁶² approach to obtain the net atomic charges and dipole moment on each atom in the calculated structure. LOBSTER package⁶⁹ version 4.1.0 was utilized for the chemical-bonding interaction using the “pbevaspfit2015” basis set. The necessary static self-consistent calculations were performed by switching off the symmetry as suggested in the LOBSTER manual.

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/>. Additional experimental and theoretical details and materials and methods, including tables and figures.

Accession Codes

CCDC 2202659-2202670 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing 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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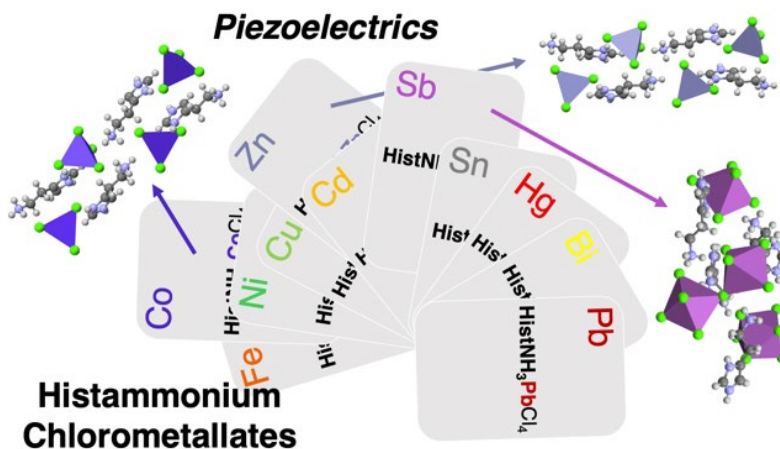
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TOC graphic



TOC SYNOPSIS

To provide new insights in understanding the influence of B site cation on structure in chlorometallate materials of the form $AB^{n+}Cl_{n+2}$, incorporating histammonium (HistNH_3) dications and various transition metal and main group B site cations. $\text{HistNH}_3\text{CoCl}_4$, $\text{HistNH}_3\text{ZnCl}_4$ had no inversion symmetry and were isostructural, however, the Zn-based material had a much higher piezoelectric response. Computational studies indicated material response differences were due to differences in dipole magnitude and M-Cl contribution to the valence band maximum.