Infrared and thermal studies in methylammonium trichloromercurate (II) single crystals

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Methylammonium trichloromercurate (II) (CH$_3$NH$_3$HgCl$_3$) single crystals have been grown by slow evaporation method at room temperature. The crystals obtained are colourless, bright, transparent and square-shaped platelets with an average size of 5x1.5x0.3 cm. The grown crystals have been characterized through elemental analysis, powder XRD, thermogravimetry (TG), differential scanning calorimetry (DSC), FTIR and NMR spectroscopic techniques. The elemental analysis confirms the molecular formula of the title compound. The crystallinity of the synthesized compound is evident from well-defined and sharp Bragg peaks obtained in the powder XRD pattern. The decomposition pattern of the compound is formulated using the TG. Thermal anomalies observed in the DSC curves at 0.6 and -15.9 °C during the heating and cooling cycles are indicative of first-order structural phase transition in the crystal. The FTIR and far IR spectra show the characteristic absorption bands due to CH$_3$NH$_3^+$ and HgCl$_3^-$ ions. The NMR spectrum indicates the presence of only one kind of chemically and magnetically equivalent protons of the methyl group present in the compound.

Keywords: Single crystals, Crystal growth, FTIR spectra, NMR spectra, Far-IR spectra, Thermal studies, Methylammonium trichloromercurate

1 Introduction

Structural phase transitions occurring in ABX$_3$ crystals like A$_2$BX$_5$2H$_2$O type crystals (where A=univalent metal cation, NH$_4^+$ and its alkyl derivatives; B= divalent metal and X=halogen) are quite interesting. Some of the AB$_3$ family hexagonal perovskites exhibit crystal structure distortions at low temperatures. Dielectric properties around the structural and magnetic phase transitions in some of the AB$_3$ crystals were summarized by Morishita et al.$^1$. But, detailed studies on the structural phase transitions of alkyl ammonium mercuric chloride compounds of AB$_3$ type are not found in the literature.

Methylammonium trichloromercurate(II) (CH$_3$NH$_3$HgCl$_3$, hereafter, MATC-Hg) belongs to ABX$_3$ type crystals. This crystal adopts a monoclinic symmetry (space group C2) above the transition temperature, $T_c = 60$ °C and a trigonal space group P3$_2$, at room temperature$^1$. It is known that, mercury(II) halides form a variety of complexes with ammonium halides. Grdenic$^2$ has reviewed structures of different complexes of mercury(II) crystals. The crystal structures of complexes of methylammonium chloride and mercury(II) chloride were determined by Ben Salah et al.$^3$. Mercury(II) compounds have a strong tendency to form almost linear X-Hg-X units$^4$. Ben Hassen et al.$^5$ have studied birefringence, XRD powder pattern and Raman spectra of the compound, CH$_3$NH$_3$HgBrCl$_2$, in the polycrystalline form and found that, the substitution of chlorine atom by a bromine atom decreased the phase transition temperature. Fuess et al.$^6$ have measured the dielectric constant and DSC for MATC-Hg crystals. They have reported a ferro to paraelectric phase transition for this crystal around 60 °C.

In this paper, the synthesis and characterization of MATC-Hg single crystals through elemental analysis, powder XRD, TG-DTA, low temperature DSC, FTIR, far IR and NMR spectra have been reported. Raman spectroscopic studies of structural phase transitions in this crystal are in progress.

2 Experimental Details

Single crystals of MATC-Hg were grown from a saturated solution by slow evaporation method at room temperature. The components of the compound, methylammonium chloride (E-Merck, Germany) and mercury(II) chloride (AR Grade) were dissolved in water and ethanol respectively, in
1:1 stoichiometric ratio. After mixing the two solutions thoroughly, the resulting solution was filtered through Whatmann 42 filter paper and kept for growth in a tall beaker covered with a watch glass. Care was taken to minimize temperature fluctuations and mechanical disturbances. In about 12-14 days time colourless, bright, transparent and square-shaped single crystals were obtained (Fig. 1). The compound was formed according to the reaction:

\[ \text{CH}_3\text{NH}_3\text{Cl} + \text{HgCl}_2 \rightarrow \text{CH}_3\text{NH}_3\text{HgCl}_3 \]

(MATC-Hg)

![Figure 1 - Photograph of MATC-Hg single crystals](image)

The melting point of the grown crystals was recorded as 235°C. Elemental (C, H and N) analysis of MATC-Hg was undertaken by using Heraeus Carlo Erba 1108 instrument. The powder XRD pattern of the compound was carried out in a JEOL (Japan) JDX 8030 XRD instrument using CuKα radiation (\(\lambda = 1.5418\) Å). The TG-DTA curves were obtained using NETZSCH-Geratebau GmbH thermal analyser in nitrogen atmosphere, with a heating rate of 10 K min\(^{-1}\). Low temperature DSC for MATC-Hg crystals was carried out, using NETZSCH DSC analyser under nitrogen atmosphere with a heating rate of 10 K min\(^{-1}\). The cooling run was recorded from 22 to -150 °C and the heating run from -150 to 25 °C. The FTIR and far IR spectra for the crystals were obtained by means of Bruker IFS 66V model spectrometer employing KBr pellet technique between 4000 and 100 cm\(^{-1}\) frequency region. The NMR spectrum of the crystals was recorded using a 250 MHz Bruker DPX instrument in D$_2$O solvent.

### 3 Results and Discussion

The C, H and N elemental analysis of the synthesized compound, MATC-Hg, confirms the formation of the compound in accordance with the reaction predicted earlier. The experimental and theoretical values (given in brackets) of C, H and N are:

- C=3.55% (3.54%), H=1.92% (1.77%) and N=3.58% (4.13%). The differences between the experimental and theoretical values are found to be very small and within the experimental errors. The elemental analysis confirms the molecular formula of MATC-Hg. The sharp and well-defined Bragg peaks in the powder XRD pattern (Fig. 2) clearly indicate the crystallinity of the compound.

![Figure 2 - X-ray powder pattern of MATC-Hg crystals](image)
Step I

\[ \text{CH}_3\text{NH}_2\text{HgCl}_3 \xrightarrow{239 \text{ to } 333\,\text{ºC}} \text{CH}_3\text{NH}_2\text{Cl} + \text{HgCl}_2 \uparrow \]

Formula weight = 339.1 67.5 271.6

(80% weight loss)

Step II

\[ \text{CH}_3\text{NH}_2\text{Cl} \xrightarrow{333 \text{ to } 456\,\text{ºC}} \text{CH}_3\text{Cl} \uparrow + \text{NH}_3 \uparrow \]

67.5 50.5 17

(20% weight loss)

In step I, 80% weight loss occurs between 239 and 333 °C. This weight loss fits exactly well with the loss of a HgCl₂ molecule from the compound. Ben Salah et al. have also predicted discrete HgCl₂ units in the crystal structure of MATC-Hg. The decomposition proposed in step I is further justified by the fact that, HgCl₂ when once formed should vapourise at 333 °C, since its boiling point is 302°C.

In step II, the remaining part of the residue viz., CH₃NH₂Cl decomposes completely between 333 and 456 °C. This step of decomposition of CH₃NH₂Cl into the gaseous products accounts for the remaining 20% weight loss.
Table 1 — FTIR and far IR spectral data and assignments of MATC-Hg crystals

<table>
<thead>
<tr>
<th>Wave number cm⁻¹</th>
<th>Assignments</th>
</tr>
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<tbody>
<tr>
<td>3524.3</td>
<td>Asymmetric N-H and C-H stretching vibrations in CH₃NH₃⁺ group</td>
</tr>
<tr>
<td>3180.8</td>
<td>Symmetric N-H and C-H stretching vibrations in CH₃NH₃⁺ group</td>
</tr>
<tr>
<td>3140.2</td>
<td>(weak bands)</td>
</tr>
<tr>
<td>2726.3</td>
<td>N-H bending (scissoring)</td>
</tr>
<tr>
<td>2399.5</td>
<td>Asymmetric deformation of CH₃ and NH₃ groups</td>
</tr>
<tr>
<td>1611.6</td>
<td>Symmetric deformation of CH₃ and NH₃ groups</td>
</tr>
<tr>
<td>1478.2</td>
<td>Out-of-plane twisting modes of CH₃ and NH₃ groups</td>
</tr>
<tr>
<td>1424.5</td>
<td>Rocking modes of CH₃ and NH₃ groups</td>
</tr>
<tr>
<td>1253.7</td>
<td>979.8</td>
</tr>
<tr>
<td>1046.3</td>
<td>923.9</td>
</tr>
<tr>
<td>488.1</td>
<td>488.1</td>
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<tr>
<td>478.3</td>
<td>478.3</td>
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<td>460.9</td>
<td>460.9</td>
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<tr>
<td>451.5</td>
<td>451.5</td>
</tr>
<tr>
<td>390.1</td>
<td>390.1 (weak band)</td>
</tr>
<tr>
<td>322.3</td>
<td>Asymmetric and symmetric HgCl₃ internal vibrations</td>
</tr>
<tr>
<td>177.8</td>
<td>CH₃NH₃⁺ group vibrations</td>
</tr>
<tr>
<td>131.9</td>
<td>Hg-Cl-Hg stretching</td>
</tr>
<tr>
<td>116.2</td>
<td>CH₃-Hg-Cl stretching</td>
</tr>
</tbody>
</table>

In the DTA curve shown in Fig. 4, the first endothermal dip at 231°C is due to the melting of MATC-Hg crystals (235°C). The second endothermal dip occurring between 244 and 327 °C closely corresponds to the decomposition of MATC-Hg into methylammonium chloride and mercury(II) chloride (i.e. step I of TG). The nature of this portion of the DTA thermogram suggests that the first step of decomposition of the compound is a low thermal energy absorption process. This implies that the first step decomposition products viz, CH₃NH₃Cl and HgCl₂ are loosely held together in the crystal. The large endothermal dip, taking place in the temperature range 327 and 460°C is due to the high energy requirement for the decomposition of methylammonium chloride into the gaseous products, namely, methylchloride and ammonia. (i.e step II of TG).

![Far IR spectrum of MATC-Hg crystals](image)

Fig. 7 — Far IR spectrum of MATC-Hg crystals

![NMR spectrum of MATC-Hg crystals](image)

Fig. 8 — NMR spectrum of MATC-Hg crystals
In the DSC curves (Fig. 5), thermal anomaly occurs at 0.6°C during the heating cycle and at -15.9°C during the cooling cycle showing thermal hysteresis behaviour which indicates first-order structural phase transition in the compound as predicted by Ishibashi & Dvorak.

The various absorption bands observed in FTIR and far IR spectra and the corresponding assignments made are given in Table 1. The FTIR and far IR spectra are shown in Figs 6 and 7, respectively. The strong absorptions at 3524, 3181 and 3140 cm\(^{-1}\) are due to N-H and C-H asymmetric stretching vibrations in CH\(_3\)NH\(_3\)\(^+\) group. The weak absorptions found at 2726 and 2400 cm\(^{-1}\) are assigned to N-H and C-H symmetric stretchings in CH\(_3\)NH\(_3\)\(^+\) group. The NH\(_3\) deformation occurs at 1612 cm\(^{-1}\). Absorption at 1478 and 1425 cm\(^{-1}\) are assigned, respectively, to asymmetric and symmetric deformations of both NH\(_3\) and CH\(_3\) groups. The out-of-plane twisting modes of these groups are found at 1254 cm\(^{-1}\). The weaker absorption at 1046 cm\(^{-1}\) is due to the rocking modes of these two groups. The skeletal vibrations of the tetrahedral methylammonium cation are observed between 980 and 442 cm\(^{-1}\). The absorption at 178 cm\(^{-1}\) is due to librational mode of methylammonium group. The Hg-Cl-Hg stretching vibration is found at 132 cm\(^{-1}\) (Ref. 6). The absorption due to Cl-Hg-Cl stretching vibration occurs at 116 cm\(^{-1}\) (shoulder) (Ref. 6). In the FTIR spectra, no characteristic absorption frequencies are observed for water molecule in any form in the crystal.

The single peak at 2.6 ppm in the NMR spectrum of MATC-Hg crystals shown in Fig. 8 confirms the presence of only one kind of protons of the methyl group of the compound.

4 Conclusion

Single crystals of MATC-Hg grown from saturated solutions using slow evaporation method at room temperature. The grown crystals are bright, transparent, colourless and square-shaped platelets. The crystals were characterized through elemental (C, H and N) analysis, powder XRD pattern, TG, DTA, DSC, FTIR, far IR and NMR spectra. While the elemental analysis confirms the formation of the compound in the stoichiometry proposed, the crystallinity is identified by well-defined peaks in the powder XRD pattern. The decomposition pattern of the title compound was formulated, based on TG which is confirmed by DTA. The thermal hysteresis observed at 0.6 and -15.9°C suggests first-order structural phase transition in the crystal. The characteristic absorption bands due to CH\(_3\)NH\(_3\)\(^+\) and HgCl\(_2\) groups were appropriately assigned, using FTIR and far IR spectra. It is also evident from the FTIR spectrum that, water molecule is absent in any form in the crystal. The NMR spectrum of the compound shows the presence of only one kind of protons of the methyl group present in it. Laser Raman spectroscopic studies of structural phase transitions in this crystal and the morphological studies of the crystals are in progress.

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References