

Thermal decomposition paths in A_2CuCl_4 complexes: anilinium and its derivatives

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Abstract The thermal decomposition paths of anilinium, 4-chloro anilinium tetrachlorocopper(II) complexes are compared to their benzilinium derivative. All these complexes crystallize in the layered structure, typical for a A_2MX_4 family, are studied in literature for their magnetic, semiconducting properties. TG analyses of (anilinium) $_2CuCl_4$ (**A**) and (4-chloro anilinium) $_2CuCl_4$ (**B**) loses one molecule of organic ammonium hydrochloride along with one molecule of amine, to form (H)CuCl $_3$, which subsequently completely decomposes to Cu above 500 °C. On the other hand, (benzilinium) $_2CuCl_4$ (**C**) loses two molecules of hydrochloride along with chlorine molecule first then two molecules of benzyl amine with formation of Cu above 300 °C. DSC studies on **C** have shown reversible endothermic phase transition at 130.95 °C (-1.98 J g^{-1}) while heating and exothermic phase transition at 117.07 °C (0.93 J g^{-1}) while cooling. Thus, the observed changes in the decomposition pathway can be correlated to the order–disorder phase transition occurred in the compound **C**.

Keywords A_2CuCl_4 · Phase transition · Order–disorder · Organic–inorganic hybrid compounds

Introduction

The formation of AMX_4 or A_2MX_4 (A = organic ammonium cation, M = metal, and X = halogen) by reaction of

organic ammonium cation with metal chloride generally gives layered structure [1]. A great interest has been shown in these types of compounds because of their various properties such as semiconducting, ferromagnetic, and antiferromagnetic behavior which is well reported in the literature [2–6]. These materials are unique because they have combine properties from both inorganic and organic counter parts. In this type of compounds, metal chloride forms layer of corner-sharing metal chloride octahedra which are well isolated from each other by interposed sheet of organic ammonium salts. The tetra chlorocopper(II) complexes having different organic ammonium cation shows variety of geometry around the central metal atom and is influenced by non-covalent interactions such as hydrogen bonding [7]. The hydrogen bond-driven orientation of organic ammonium molecules forces these complexes to undergo interesting structural phase transitions [5, 8–10]. The $CuCl_4^{2-}$ compounds also showed thermochromic behavior and polymorphism. Thus, the preliminary goal is to study hydrogen bonding in these organic–inorganic hybrids and correlate structure–property relationship. The high temperature thermal degradation studies on these compounds are as compared less explored in the literature. This article focuses on the interesting thermal degradation pathway possibly due to such type of phase transition in the family of A_2CuCl_4 complexes, where A is anilinium, 4-chloro anilinium, and benzilinium salts.

Experimental

Synthesis procedure for different aromatics ammonium salts of tetra chlorocuprate(II)

In the synthesis procedure, all chemicals used were of analytical grade. The sample was prepared by dissolving of

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appropriate amounts of different aromatic ammonium chloride and copper (II) chloride (2:1 ratio) in ethanol by reflux it for about 3–4 h. After 1 week, good quality of crystals was obtained [11].

FTIR data for the complexes

All FTIR measurements were obtained using Perkin Elmer Spectrum RX1 FTIR instruments. Samples were diluted with spectroscopic KBr and pressed into a pellet. Scans were run over the range 400–4000 cm^{-1} . Analytical data for the complexes are below.

(Anilinium)₂CuCl₄ FTIR (KBr) 2997 (vs), 1555 (s), 1493 (s), 1321 (m), 1201 (m), 1102 (s), 806 (w), 738 (s), 681 (s) cm^{-1} . (4-Chloroanilinium)₂CuCl₄ 3047 (vs), 1611 (w), 1553 (m), 1488 (s), 1312 (w), 1195 (s), 1016 (w), 810 (s), 640 (w), 488 (m) cm^{-1} . (Benzilinium)₂CuCl₄ 3154 (vs), 1566 (s), 1488 (s), 1456 (m), 1389 (m), 1217 (m), 1098 (s), 1050 (m), 968 (w), 864 (w), 754 (s), 017 (s) cm^{-1} .

Thermal analysis

Thermogravimetry-differential thermal analysis (TG-DTA) measurements were carried out by using a SII TG/DTA6300 instrument under nitrogen atmosphere at a scanning rate of 10 $^{\circ}\text{C min}^{-1}$. Samples were taken in aluminum/platinum pan and reference left empty. The flow was used 100 mL min^{-1} for TG/DTA analysis. While the differential scanning calorimeter (DSC) were carried out by Shimadzu DSC-60 instruments, Al₂O₃ used as a reference material in aluminum pan. The sample were packed in aluminum pan and kept in the flow of nitrogen gas with heating/cooling rate 10 $^{\circ}\text{C min}^{-1}$. The flow was used 50 mL min^{-1} for thermal analysis.

Result and discussion

The FTIR spectra were recorded in the 4000–400 cm^{-1} (Fig. Supporting Information). The ammonium salts of the CuCl₂ complexes characterized by strong absorptions triplets bands around 3170 and 3021 cm^{-1} due to the N–H stretching bands of the ions $-\text{NH}_3^+$ (cf. the C–H stretching bands in this region) and bending vibrations around the 1556 cm^{-1} region. The two features about 2576 cm^{-1} are assigned to the Fermi resonance processes corresponding to combination bands of NH_3^+ deformation modes and NH_3^+ rocking modes [12]. The bands at 1494 and 1055 cm^{-1} are assigned NH_3^+ deformation and rocking, respectively. Vibration also observed at 2885 cm^{-1} in (benzilinium)₂CuCl₄ due to aliphatic C–H stretching. The bands around 842 cm^{-1} is due to the out of plane deformation (para substituent) for (4-chloro anilinium)₂CuCl₄.

The compound (anilinium)₂CuCl₄ [13] and (4-chloro anilinium)₂CuCl₄ [11] crystallized in monoclinic $P2_1/c$ with unit cell dimensions $a = 15.050$ (2) \AA , $b = 7.443$ (1) \AA , $c = 7.180$ (1) \AA , $\beta = 100.71$ (1) $^{\circ}$ and $a = 7.3736$ (3) \AA , $b = 32.0689$ (13) \AA , $c = 7.1611$ (3) \AA , $\beta = 101.51$ (2) $^{\circ}$, respectively. While (benzilinium)₂CuCl₄ [14] belongs to Orthorhombic $Pbca$ space group $a = 31.30$ \AA , $b = 7.59$ \AA , and $c = 7.28$ \AA . In these complexes, copper–halide layer is characterized by two kinds of copper–halide distances, the equatorial (D_S) and axial (D_L) distances caused by the Jahn–Teller effect. The values of D_S and D_L suggest small distortion from perfect octahedral geometries for the copper metals that we previously reported.

The TG-DTA of these layered organic–inorganic complexes was performed on the powder samples. Figure 1 shows the thermal analysis of **A**, **B**, and **C**. Complexes **A** and **B** follows a similar degradation pathway as compared to **C**, as tabulated below.

$(\text{C}_6\text{H}_5\text{NH}_3)_2\text{CuCl}_4$ Temp. 171.1 $^{\circ}\text{C}$ ↓ $\text{C}_6\text{H}_5\text{NH}_2\text{HCl} + \text{C}_6\text{H}_5\text{NH}_2$ Loss = 56.57% (theory) Loss = 58.10% (found)	$(4\text{-Cl-C}_6\text{H}_4\text{NH}_3)_2\text{CuCl}_4$ Temp. 212.1 $^{\circ}\text{C}$ ↓ $4\text{-Cl-C}_6\text{H}_4\text{NH}_2\text{HCl} + 4\text{-Cl-C}_6\text{H}_4\text{NH}_2$ Loss = 63.04% (theory) Loss = 65.04% (found)	$(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{CuCl}_4$ Temp. 288.0 $^{\circ}\text{C}$ ↓ $2\text{HCl} + \text{Cl}_2$ Loss = 34.17% (theory) Loss = 32.36% (found)
$(\text{H})\text{CuCl}_3$ Temp. 503.4 $^{\circ}\text{C}$ ↓ $\text{HCl} + \text{Cl}_2$ Loss = 27.29% (theory) Loss = 21.32% (found)	$(\text{H})\text{CuCl}_3$ Temp. 579.2 $^{\circ}\text{C}$ ↓ $\text{HCl} + \text{Cl}_2$ Loss = 23.23% (theory) Loss = 17.08% (found)	$(\text{H})\text{CuCl}_3$ Temp. 295.8 $^{\circ}\text{C}$ ↓ $2\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ Loss = 50.41% (theory) Loss = 53.45% (found)
Cu 16.14% (theory) 20.58% (found)	Cu 13.74% (theory) 17.87% (found)	Cu 15.09% (theory) 14.49% (found)

Fig. 1 The TG-DTA curves of (Anilinium) $_2CuCl_4$ (**a**) (4-chloro anilinium) $_2CuCl_4$ (**b**) and (benzylinium) $_2CuCl_4$ (**c**) showing the decomposition paths

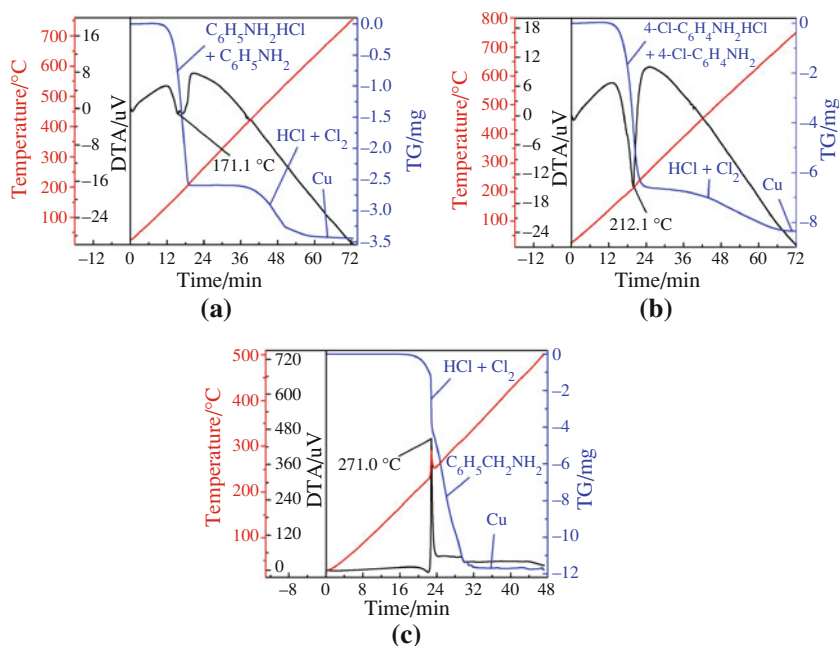
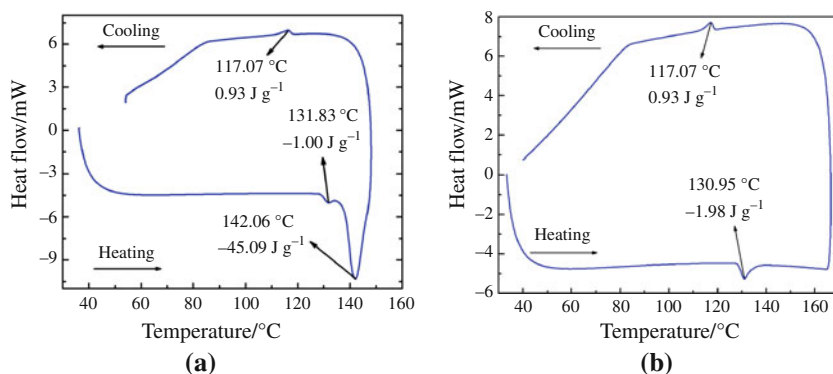


Fig. 2 DSC plots for benzilinium chloride (**a**) and (benzylinium) $_2CuCl_4$ (**b**) showing the reversible transitions



Aniline being reducing agent a part of $CuCl_2$ converted into $CuCl$ on heating [15]. In case of **B**, DTA shows endothermic peak at 212.1 °C due to thermal decomposition. At this temperature it loses one mole of 4-chloro anilinium chloride along with 4-chloro aniline. After the loses of organic ammonium chloride along with amine $(H)CuCl_3$ is left. $[CuCl_3]^-$ species are known in literature and prefer to remain in dimeric form if the cation are small [16]. At high temperature, above 500 °C, it again loses chlorine molecule in reducing atmosphere of hydrochloric acid so as to convert to Cu . Calculation of second loss come very close to the evaporation of HCl and Cl_2 molecule per formula unit, but it is not completely evaporated. This decomposition path of **B** is very similar to **A**. While in case of **C** the thermal decomposition path is totally different. Here, two moles of hydrochloride are lost along with chlorine molecule in initial heating, instead of benzilinium chloride and benzyl amine, then two molecules of benzyl amine, with subsequent formation of Cu above

300 °C. The DTA of **C** shows exothermic peak at 271.0 °C. Normally exothermic transition is observed due to crystallization or desolvation/dehydration. In this case, this exothermic mass loss accounts for Cl_2 , a process of dechlorination? Thus, thermal analysis shows different thermo chemical reactions operating these complexes, leading to cleavage of bond or rearrangement of ligand.

To confirm the different degradation pathway and exothermic behavior of DTA, we carried out DSC on all organic ammonium hydrochloride salts and their complexes. Both benzilinium chloride and its complex with $CuCl_2$, **C**, show presence of reversible phase transition in the temperature range 100–150 °C, as shown in Fig. 2. TG-DTA studies of these compounds are not showing any mass loss in this temperature range. The DSC of benzilinium chloride shows two endothermic transitions at 131.83 °C ($-1.00 J g^{-1}$), 142.06 °C ($-45.09 J g^{-1}$) while heating and exothermic transition at 117.07 °C ($0.93 J g^{-1}$) while cooling. Complex **C** shows only one endothermic transition

at 130.95 °C (1.98 J g⁻¹) while heating and 117.07 °C (0.93 J g⁻¹) while cooling. These transitions are reversible in nature and can be repeated for many cycles without any change. While the DSC study on anilinium chloride, 4-chloro anilinium chloride, (anilinium)₂CuCl₄ (**A**) and (4-chloro anilinium)₂CuCl₄ (**B**) only anilinium chloride shows the phase transition around -28 °C that is also proved by Raman which is already reported [10]. In literature for (anilinium)₂CuCl₄ also reported the phase transition around 100 °C, but TG measurement also shows the small loss at that region, it may be due to they used the low boiling solvent for the synthesis [15]. We also did the DSC measurement but not observed any change around this region from DSC.

Conclusions

In summary we have prepared layered compounds of the formula, A₂CuCl₄, where A is anilinium, 4-chloroanilinium and benzilinium, which are studied for thermal behavior. DSC studies have shown that (Benzilinium)₂CuCl₄ undergoes order-disorder phase transition above 130 °C, which is reversible in nature. This phase transition changes its thermal degradation pathway substantially than its analogues (anilinium)₂CuCl₄, (4-chloroanilinium)₂CuCl₄ complexes. Detailed studies, using high temperature spectroscopic techniques, are required to understand this behavior at molecular level.

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References

- Mitzi DB. Templating and structural engineering in organic-inorganic perovskites. *J Chem Soc Dalton Trans.* 2001;1–12. doi: [10.1039/B007070J](https://doi.org/10.1039/B007070J).

- Sekine T, Okuno T, Awaga K. Observation of spontaneous magnetization in the layered perovskite ferromagnet. *Inorg Chem.* 1998;37:2129–33.
- Kaluza S, Suchanska M, Belka R, Lesniewski S. The phase transition in ferroelectric crystals of A₂MX₄ and AMX₃ type. *Ferroelectrics.* 2002;273:143–8.
- Nelson DJ, Chan K, Cervantes-Lee F, ter Haar LW. Magnetic phase transition in perovskite-type anilinium-based tetrachlorocuprates. *J Appl Phys.* 1996;79(8):4715–7.
- Ghalsasi PS, Inoue K. Distorted perovskite structured organic-inorganic hybrid compounds for possible multiferroic behavior. *Polyhedron.* 2009;28:1864–7.
- Belhouche M, Wamani W, Mhiri T. Synthesis, structure and spectroscopic investigations of two new organic-inorganic hybrids. *Mater Sci Eng.* 2010;13:12039–48.
- Dolling B, Gillon AL, Orpen AG, Starback J, Wang X-M. Homologous families of chloride-rich 4,4'-bipyridinium salt structures. *J Chem Soc Chem Commun.* 2001;6:567–8.
- Ishikawa J, Asaji T, Nakamura D. Chlorine-35 nuclear quadrupole resonance and phase transition. *J Magn Reson.* 1983;51:95–102.
- Horiuchi K. DSC studies on structural phase transitions and molecular motions in some A₂MX₄ compounds. *Phys Status Solidi A.* 2004;201(4):723–6.
- Vishwakarma AK, Ghalsasi P, Ghalsasi PS. Temperature-dependent Raman spectroscopy of anilinium chloride near phase transition. *Phys Status Solidi B.* 2011;1–5. doi: [10.1002/pssb.201046440](https://doi.org/10.1002/pssb.201046440).
- Vishwakarma AK, Ghalsasi PS, Navamoney A, Lan Y, Powell AK. Structural phase transition and magnetic properties of layered organic-inorganic hybrid compounds. *Polyhedron.* 2011. doi: [10.1016/j.poly.2011.03.025](https://doi.org/10.1016/j.poly.2011.03.025).
- Gibson EK, Winfield JM, Muir KW, Carr RH, Eaglesham A, Gavezzotti A, Lennon D. A structural and spectroscopic investigation of the hydrochlorination of 4,4'-methylene dianiline. *Phys Chem Chem Phys.* 2010;12:3824–33.
- Larsen KP. The crystal structure of anilinium tetrachlorocuprate(II). *Acta Chem Scand A.* 1974;28:194–200.
- Dupas A, Le Dang K, Renard J-P, Veillet P, Daoud A, Perret R. Magnetic properties of the nearly two-dimensional ferromagnets. *J Chem Phys.* 1976;65:4099.
- Purkayashtha A, Baruah JB. Tetra chlorocopper(II) chemistry: delineation of optical, thermal properties. *Thermochim Acta.* 2002;390:187–93.
- Textor M, Dubler E, Oswald HR. Crystal and molecular structure of tetraphenylphosphonium trichlorocuprate(II), a complex containing non planar dimetric trichlorocuprate(2⁻) units. *Inorg Chem.* 1974;13:1361–5.