

# Crystal structures and thermal behavior of bis[dibenzyltrimethylammonium]CuBr<sub>4</sub>, bis[dibenzyltrimethylammonium]CuCl<sub>4</sub> and bis[diethyl(2-phenylethyl)ammonium]CuBr<sub>4</sub> crystallized from acetonitrile and dilute HX (X = Cl or Br) solutions

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## Abstract

Bis[dibenzyltrimethylammonium]CuBr<sub>4</sub>, bis[dibenzyltrimethylammonium]CuCl<sub>4</sub> and bis[diethyl(2-phenylethyl)ammonium]CuBr<sub>4</sub> were crystallized from acetonitrile and/or dilute HX solutions. Five different kinds of single crystals were obtained. In the case of bis[dibenzyltrimethylammonium]CuX<sub>4</sub> (X = Br or Cl), the acetonitrile molecules cocrystallized into the crystal structure when acetonitrile solution was used. As a result, the isomorphous structures of Bis[dibenzyltrimethylammonium]CuX<sub>4</sub>·0.5 CH<sub>3</sub>CN (X = Br or Cl) in monoclinic space group *P*2<sub>1</sub>/*n* were obtained. When a dilute HX solution was used, the bis[dibenzyltrimethylammonium]CuX<sub>4</sub> (X = Br or Cl) crystallized without solvent molecules. The formed crystals were not isomorphous with each other as the tetrabromocuprate structure crystallized in triclinic space group and the tetrachlorocuprate structure in monoclinic space group. The third compound, bis[diethyl(2-phenylethyl)ammonium]CuBr<sub>4</sub>, crystallized without solvent molecules from an acetonitrile solution and no measurable single crystals were obtained from a dilute HX solution. Elemental analysis and powder diffraction analysis were performed to verify the structural similarities of all formed single crystals. The powder diffraction measurements also showed that the compounds have the same structure at room temperature and at a temperature of –100 °C. The thermal behaviour of the compounds was studied by using TG/DTA and DSC measurements; the compounds decomposed in two stages. No phase transitions were observed between room temperature and the melting point. In addition, these crystals showed to be very stable in the air at room temperature as they could be kept in the air for several weeks without any marks of the decomposition.

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## 1. Introduction

The A<sub>2</sub>MX<sub>4</sub> structures have been of interest for a long time because of their structural properties, phase transitions and thermochromic behavior in the solid state. A<sub>2</sub>MX<sub>4</sub> compounds exhibit phase transitions at subambient and above ambient temperatures [1–9]. The thermochromic behavior of copper(II) chloride complexes (tetrachlorocuprates) can be divided at least into two classes. In one class the compounds show a phase transition involving a change in the coordination geometry

around the copper ion. In the other class the thermochromism is associated only with the temperature dependence of the line widths of the electronic absorption bands [1]. It has been observed that the *trans* Cl–Cu–Cl angle is less than 132° when there is no possibility of hydrogen bonding between the cation and the CuCl<sub>4</sub><sup>2–</sup> anion. When N–H···Cl<sup>–</sup> hydrogen bonding exists, the *trans* Cl–Cu–Cl angle is greater than 132° [1]. In some cases the angle can be so large that the anion can have a planar configuration (Cl–Cu–Cl angle of 180°) [5–9].

Many of the copper(II) chloride complexes are yellow or yellow-orange at room temperature or a little above room temperature, but turn pale green on cooling and darken significantly on heating. In most cases it is not clear whether any definite phase changes are involved [1,9]. Willett et al. have found an endothermic transition at a temperature of 43 °C in the DTA curve of (Et<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>CuCl<sub>4</sub>. The crystals of

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(EtNH<sub>3</sub>)<sub>2</sub>CuCl<sub>4</sub> are bright green at room temperature and turn yellow when heated above 43 °C [1]. Harlow et al. found the bis(*N*-methylphenethylammonium)CuCl<sub>4</sub>(II) to be green at room temperature (25 °C) and a transition at 80 °C yielded the yellow phase [6]. The same kind of phase change has also been observed for (Me<sub>2</sub>CHNH<sub>3</sub>)<sub>2</sub>CuCl<sub>4</sub> [1]. In the first two cases, the room temperature coordination of CuCl<sub>4</sub><sup>2-</sup> anion is square-planar and after the phase transition the copper atom has a distorted tetrahedral coordination [1,6]. In the case of (Me<sub>2</sub>CHNH<sub>3</sub>)<sub>2</sub>CuCl<sub>4</sub> three chemically distinct CuCl<sub>4</sub><sup>2-</sup> anions are found in the crystal structure: one with planar geometry, one with a moderate tetrahedral distortion (the average *trans* Cl–Cu–Cl angle 159°) and the third with a larger distortion (the average *trans* Cl–Cu–Cl angle 152°) [1,6,9].

Place and Willett have also compared the tetrabromocuprate and tetrachlorocuprate anions with each other, for example the bis(*N*-methylphenethylammonium)CuBr<sub>4</sub>(II) salt with the above-mentioned low-temperature phase of the tetrachlorocuprate salt [10]. In the tetrabromocuprate(II) anion a geometry of the Cu is intermediate between tetrahedral and square planar (the *trans* Br(1)–Cu–Br(2) angle is 142.1° and the dihedral angle is 51.6°); the room-temperature phase of the tetrachlorocuprate(II) salt of the CuCl<sub>4</sub><sup>2-</sup> is square planar with the dihedral angle 0° in low-temperature phase. The tetrabromo-cuprate(II) anion has been expected to have a larger dihedral angle than the tetrachlorocuprate(II) anion because of the distortion towards a tetrahedral geometry will lessen ligand–ligand repulsions for the larger Br atom [10].

Willett et al. have also reported the structural properties and phase transitions in the [(Et<sub>n</sub>Me<sub>4-n</sub>)N]<sub>2</sub>CuX<sub>4</sub> family [11]. The room temperature phases of the (EtMe<sub>3</sub>N)<sub>2</sub>CuX<sub>4</sub> salts crystallize in the polar *P*2<sub>1</sub>*cn* space group and two phase transitions exist below room temperature (about –18 and +20 °C for X=Cl and –16 and +14 °C for X=Br). For the (Et<sub>2</sub>Me<sub>2</sub>N)<sub>2</sub>CuX<sub>4</sub> salts, the room temperature space group is *P*2<sub>1</sub>/*n* and a single phase transition exists just above room temperature [11,12].

The new R<sub>2</sub>R'<sub>2</sub>N<sup>+</sup>X<sup>-</sup> type quaternary ammonium halides [13–16] have enabled us to synthesize and characterize

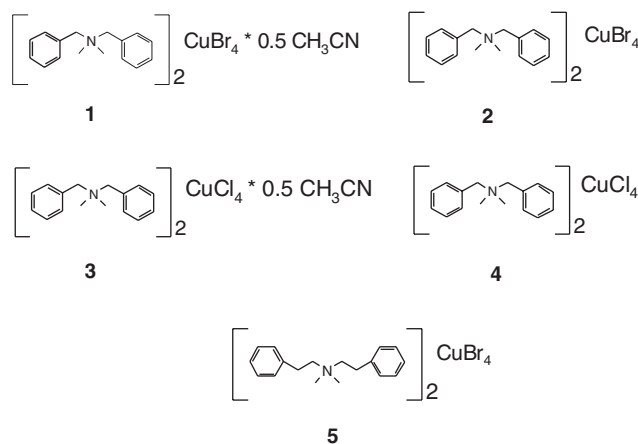
a new kind of (R<sub>2</sub>R'<sub>2</sub>N)<sub>2</sub>MX<sub>4</sub> compounds and examine their thermal behavior in the solid state. In this paper, we present the structural properties of bis[dibenzylidimethylammonium]CuBr<sub>4</sub>, bis[dibenzylidimethylammonium]CuCl<sub>4</sub> and bis[dimethylidi(2-phenylethyl)ammonium]CuBr<sub>4</sub> crystallized from acetonitrile and/or a dilute HX solution. In all crystals the CuX<sub>4</sub> anion showed to have a distorted tetrahedral geometry as the average of the two large X–Cu–X angles was about 124–133° depending on the structure. Thermal analysis (TG/DTA and DSC methods) together with powder diffraction analysis showed that these crystals are exceptionally stable compounds having no phase transitions between –100 °C and the melting point. Thus, these crystals showed no thermochromic behavior in contrast to the general behavior of the similar compounds described above and besides of the stability against heating, the crystals described in this article could be stored in the air for several weeks without any changes in their crystal structures.

## 2. Experimental section

### 2.1. Synthesis and elemental analysis

The molecular structures of compounds **1–5** are presented in Scheme 1. Compounds **1**, **3** and **5** were crystallized from acetonitrile solution and compounds **2** and **4** from dilute HX/H<sub>2</sub>O solution. In both cases the solution contained a stoichiometric amount (2:1) of the desired (R<sub>2</sub>Me<sub>2</sub>N)X salt with either anhydrous CuBr<sub>2</sub> or CuCl<sub>2</sub>. Purple crystals of (R<sub>2</sub>Me<sub>2</sub>N)<sub>2</sub>CuBr<sub>4</sub> and yellow crystals of (R<sub>2</sub>Me<sub>2</sub>N)<sub>2</sub>CuCl<sub>4</sub> were obtained.

The acetonitrile molecules cocrystallized into the crystal structure of compounds **1** and **3**, but the crystal structure of **5** was obtained from acetonitrile solution without solvent molecules. When using a dilute aqueous HX solution no solvent molecules cocrystallized into single crystal structures of **2** and **4**. In addition to single crystals of compound **4**, small amounts of yellow powder were observed among the single crystals. Furthermore, a small endothermic peak was noticed in DSC measurement before the main melting, suggesting the existence



Scheme 1. Molecular structures of the compounds **1–5**.

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