

## The Crystal Structure of Bis-(2-ammonioethyl)ammonium Monochloride Tetrachlorocuprate(II)

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THE crystal structure of bis-(2-ammonioethyl)-ammonium monochloride tetrachlorocuprate(II)  $[(\text{NH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{NH}_2]\text{Cl}[\text{CuCl}_4]$ , has been determined by single crystal, X-ray diffraction analysis. When first prepared, the compound was formulated as a pentachlorocuprate(II).<sup>3</sup> Although other authors<sup>2,3</sup> retained this notation, our analysis reveals that the  $\text{CuCl}_5^{3-}$  formulation is incorrect.

Crystals prepared by the method of Jonassen *et al.*<sup>1</sup> were analyzed for copper and chloride ion to confirm the identity of the compound.  $[(\text{NH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{NH}_2]\text{Cl}[\text{CuCl}_4]$  is orthorhombic, with  $a = 7.117$ ,  $b = 23.78$ ,  $c = 7.342$  Å,  $Z = 4$ ,  $D_m = 1.87$ , and  $D_c = 1.85$ . Space group:  $Pnma$  or  $Pna$ ; the former (No. 62) was chosen on the basis of a statistical test,<sup>4</sup> and is borne out by structure

analysis, based on 287 independent reflexions ( $\text{Mo-K}\alpha$  radiation); refinement, by anisotropic, full-matrix least-squares, reduced  $R$  to 0.10, H-atoms being ignored.

$[(\text{NH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{NH}_2]\text{Cl}[\text{CuCl}_4]$  is a double salt which is characterized by the presence of square-planar tetrachlorocuprate(II) ions and additional chloride ions in a 1:1 ratio. Copper atoms are located at centres of symmetry, and are coordinated by two pairs of chlorine atoms; bond distances within the  $\text{CuCl}_4^{2-}$  ion are  $2.276 \pm 0.009$  and  $2.272 \pm 0.004$  Å, and the bond angle is  $90.5 \pm 0.2^\circ$ . Nearly perpendicular to the plane of each tetrachlorocuprate(II) ion, and at distances of 2.88 Å from the central copper atom, are two more chlorine atoms which belong to neighbouring  $\text{CuCl}_4^{2-}$  ions. The arrangement of  $\text{CuCl}_4^{2-}$  ions is similar to the network found in  $(\text{NH}_4)_2\text{CuCl}_4$ .<sup>5</sup> The bis-(2-ammonioethyl)ammonium ion exists linearly extended in the  $b$ -axis direction. Its terminal ammonium groups are found in cavities constructed from eight Cl atoms, two from each of four different  $\text{CuCl}_4^{2-}$  ions. Both the central nitrogen and the odd chloride ion lie on the mirror plane located at  $b/4$  in close proximity to each other. Packing features are illustrated in the Figure.

The absence of  $\text{CuCl}_5^{3-}$  ions from  $[(\text{NH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{NH}_2]\text{Cl}[\text{CuCl}_4]$  means that the e.s.r. spectrum of the double salt should be re-interpreted,<sup>2</sup> and accounts for differences observed when its far-infrared spectrum is compared with that of other pentachlorocuprate(II) salts.<sup>3</sup> The bis-(2-ammonioethyl)ammonium compound exhibits the same type of thermochromism reported by Willett for  $(\text{NH}_4)_2\text{CuCl}_4$  and other tetrachlorocuprate(II) salts,<sup>5</sup> *i.e.*, the colour changes from yellow at room temperature to pale green at lower temperatures;

its range of thermochromism extends above room temperature, for as the temperature is raised to  $100^\circ$ , the colour changes to orange-brown.

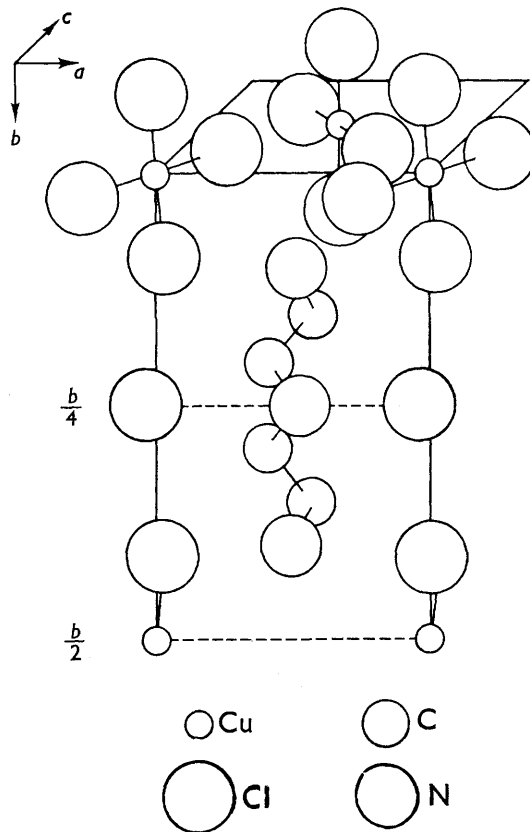


FIGURE. Some of the atoms located near the  $ab$  and  $ac$  faces in the unit cell of  $[(\text{NH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2)_2\text{NH}_2]\text{Cl}[\text{CuCl}_4]$ .

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