Les atomes de carbone et d’azote de l’ion pentane-diammonium-l,5 sont tous situés dans le plan \( x = 0 \) ou dans le plan \( x = \frac{1}{2} \). En outre, cet ion admet, pour plan de symétrie, le plan \( y = 0 \) et, pour axe de symétrie, l’axe \( Oz \) ou l’axe intersection des plans \( x = 0 \) et \( x = \frac{1}{2} \). Les longueurs des liaisons \( C-C \) [1,501 (6) et 1,512 (5) Å] et de la liaison \( C(2)\text{-}N(1) \) [1,480 (5) Å] sont compatibles, compte tenu des incertitudes, avec les longueurs trouvées pour les mêmes liaisons dans le chlorure de propanediammonium-l,3 (Brisson & Brisse, 1982) [\( C-C: 1,515 (4) \), \( C-N: 1,484 (4) \) Å] ou dans l’hydrogénophosphate de putrescinium dihydraté (Jaskoński, Alejska & Wiewiórowski, 1986) [\( C-C: 1,511 (5) \), \( C-N: 1,488 (1) \) Å]. Il en est de même pour les angles \( N-C-C \) et \( C-C-C \) (Tableau 2). Dans le dernier composé cité, leurs homologues mesurent respectivement 113 (1) et 111,7 (8) °.

La Fig. 1 montre que les cations \([C_5H_{16}N_2]^2+\) forment des couches qui zigzaguent au voisinage des plans \( z = \pm \frac{1}{4} \) et \( z = \pm \frac{1}{2} \). Deux couches consécutives de cations sont séparées tantôt par une couche d’anions \( Cl^- \), tantôt par une couche d’anions \([PtCl_6]^{2-}\). Les premiers sont situés dans les plans \( z = \pm \frac{1}{4} \) et les seconds ont pour positions moyennes les plans \( z = 0 \) et \( z = \frac{1}{2} \).

La cohésion de la structure fait intervenir les liaisons hydrogène \( N(1)\text{-}H(N1)\ldots Cl(1 \text{iii}) \) [3,173 (2) Å, 168°] et \( N(1)\text{-}H'(N1)\ldots Cl(3 \text{iv}) \) [3,274 (3) Å, 137°] \([\text{iii}]: 1-x, y, z \) et \([\text{iv}]: \frac{1}{2}+x, \frac{1}{2}+y, z \).

Références


Structure of Bis(2-amino-5-methylpyridinium) Tetrachlorocuprate(II) and Bis(2-amino-5-methylpyridinium) Tetrabromocuprate(II)

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(Received 25 March 1986; accepted 13 January 1987)

Abstract. 2C_6H_9N_2+.CuCl_2-, \( M_r=423.7 \), monoclinic, \( \text{C2/c} \), \( a = 13.377 (4) \), \( b = 8.344 (3) \), \( c = 15.941 (4) \) Å, \( \beta = 93.38(2) \) °, \( V = 1776.2 (1) \) Å³, \( Z = 4 \), \( D_x = 1.58 \) g cm⁻³, \( \lambda (\text{Mo Kα}) = 0.71069 \) Å, \( \mu = 18.30 \) cm⁻¹, \( F(000) = 860 \), \( T = 293 \) K, final \( R = 0.0545 \) for 701 unique observed reflections. The structure consists of discrete CuCl_2⁻ anions and 2-amino-methylpyridinium cations. The CuCl_2⁻ ions lie on a twofold axis and have approximate \( D_{2d} \) symmetry with \( Cu-Cl \text{(average)} = 2.240 \) Å and \( \text{trans} \) \( C-\text{Cu}-Cl \text{(average)} = 140.0 \) °. 2C_6H_9N_2+.CuBr_2-, \( M_r=601.5 \), monoclinic, \( \text{C2/c} \), \( a = 13.715 (2) \), \( b = 8.7162 (2) \), \( c = 16.013 (4) \) Å, \( \beta = 93.79(2) \) °, \( V = 1910.1 (6) \) Å³, \( Z = 4 \), \( D_x = 1.58 \) g cm⁻³, \( \lambda (\text{Mo Kα}) = 0.71069 \) Å, \( \mu = 18.30 \) cm⁻¹, \( F(000) = 1148 \), \( T = 293 \) K, final \( R = 0.0521 \) for 658 unique observed reflections. The tetrabromide structure is isomorphous with the tetrachloride structure. Cu-Br(average) = 2.376 Å and \( \text{trans} \) Br-Cu-Br(average) = 137.1 °.

Introduction. A central interest in this laboratory has been the study of the magnetic and structural characteristics of quasi-planar Cu$_m$X$_{2m+2}$ and Cu$_m$X$_{2m-2}$ \( (X = Cl^- \) or Br⁻) oligomers (Geiser, Willett, Lindbeck & Emerson, 1986; O’Brien, Gaura, Landee, Ramakrishna & Willett, 1987). These form bridged species, which are essentially fragments of the anhydrous CuCl (Wells, 1947) and CuBr (Helmholz, 1947) structures. It has been found (Grigereit, 1986) that the 2-amino-n-methylpyridinium cation, where \( n = 3, 4, 5 \),
or 6, can form salts which contain \( \text{Cu}_{m}X_{2m+2}^{2-} \) anions \((m = 3 \text{ or } 4)\). In the preparation of the \( n = 5 \) salt, a yellow crystalline impurity was formed in addition to the desired oligomeric salt. In order to devise an improved method for obtaining pure samples of the oligomeric salt for magnetic studies, a crystal structure analysis of the impurity was performed. The results indicated that the impurity had the formulation \((2\text{-amino-5-methylpyridinium})_{3}\text{CuCl}_{4}\).

A series of copper bromide salts analogous to the known copper chlorides have been sought with the 2-amino-\( n \) -methylpyridinium anions. In an attempt to make the 2-amino-5-methylpyridinium copper bromide oligomer the only crystals collected turned out to be the tetrabromide.

**Experimental.** For the tetrabromide salt, small yellow plate-like crystals separated out as a minor impurity upon crystallization of a solution of 2-amino-5-methylpyridinium hydrochloride and anhydrous copper(II) chloride (approximately 1:4 stoichiometry) in \( n \)-propyl alcohol which yielded primarily fine straw-colored needles of \((C_{6}N_{2}H_{9})_{2}\text{CuBr}_{4}\). A crystal approximately \(0.1 \times 0.2 \times 0.2 \text{ mm} \) was selected for data collection. Data were collected with an \( \omega \) scan on a Nicolet R3m/E diffractometer system with Mo K\( \alpha \) radiation and a graphite monochromator (Campana, Shepherd & Litchman, 1980). Agreement between equivalent reflections: \( R = 0.0145 \). The monoclinic cell and orientation matrix were defined by least-squares refinement of 25 reflections in the \( 2\theta \) range 20–22°. Space group \( C2/c \) (extinctions \( hkl, h + k \) odd; \( h0l, l \) odd). Empirical absorption corrections \((\mu = 94.46 \text{ cm}^{-1}) \) assuming an ellipsoidal-shaped crystal (minimum transmission = 0.67, maximum transmission = 0.81). Data were collected for \( h \geq 0, k \geq 0 \) and all \( l \) (maximum \( h, k, l = 12, 7 \) and 14, respectively). Three standards were monitored every 100 reflections with variation within counting statistics. Scan speeds ranged from 4.00° min\(^{-1}\) to 29.30° min\(^{-1}\), 940 total reflections (out to \( 2\theta = 40° \)), with 892 unique reflections and 658 reflections with \( F > 3\sigma(F) \). The structure was solved via direct methods yielding the bromine and copper positions. The pyridinium ring was found on the subsequent difference map. Final refinement on \( F \) for all observed reflections with anisotropic thermal parameters for the non-hydrogen atoms with hydrogen atoms again fixed at calculated positions gave \( R = 0.052 \) and \( wR = 0.049 \) based on 96 least-squares parameters with an average \( \Delta/\sigma = 0.001 \). Weighting scheme as above. The goodness of fit was 1.326. The largest residual on the difference map was \(-0.6 \text{ e Å}^{-3}\) near the Cu(1) atom, the largest negative residual being \(-0.6 \text{ e Å}^{-3}\). Final positional parameters for the two compounds are given in Tables 1 and 2 with selected bond distances and angles reported in Tables 3 and 4.*

**Discussion.** The chloride salt contains discrete 2-amino-5-methylpyridinium cations (Fig. 1a) and isolated \( \text{CuCl}_{4}^{2-} \) anions (Fig. 1b). N–H···Cl hydrogen bonds bind the ions together in the lattice, as seen in Fig. 2. Distances and angles within the cations are normal. The pyridine N–H moiety forms a short hydrogen bond with Cl(2), H(1)–Cl(2) = 2.84 (1) \( \text{Å} \), N(1)–Cl(2) = 3.25 (1) \( \text{Å} \), while the amino hydrogens form bifurcated hydrogen bonds to surrounding Cl(1)

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43723 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
and Cl(2) atoms; H—Cl distances range from 2.78 to 3.02 Å, N(7)—Cl distances range from 3.54 (1) to 3.62 (1) Å.

Within the CuCl$_4^{2-}$ anion, the Cu—Cl bond distances average 2.240 Å. The anion has approximate $D_{2d}$ symmetry, and assumes a geometry intermediate between tetrahedral and square planar. The extent of distortion can be characterized by the trans Cl—Cu—Cl angles, $\theta$, which average 140° in this salt (cf. 109.5° in tetrahedral geometry, 180° in square-planar geometry), or by the dihedral angle, $\beta$, between CuCl$_2$

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\AA^2 \times 10^3$) for the tetrachlorocuprate

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\AA^2 \times 10^3$) for the tetrabromocuprate

Table 3. Bond distances (Å) and angles (°) for the CuCl$_4^{2-}$ anion

Table 4. Bond distances (Å) and angles (°) for the CuBr$_4^{2-}$ anion

Fig. 1. (a) The 2-amino-5-methylpyridinium cation in (C$_6$H$_9$N$_2$)$_2$CuCl$_4$ with selected bond distances (Å). (b) The CuCl$_4^{2-}$ anion. (c) The CuBr$_4^{2-}$ anion in the bromide salt.

Fig. 2. Packing diagram of the structure of (C$_6$H$_9$N$_2$)$_2$CuCl$_4$. For clarity, only the hydrogens bonded to the nitrogen atoms are shown. The $a$ axis is horizontal and the $c$ axis vertical.
planes which is 54.5° (90° for tetrahedral, 0° for square planar). Previously studied CuCl$_2$ anions have shown a variable range of values from $\theta = 124^\circ$ and $\beta = 67.9^\circ$ in Cs$_2$CuCl$_4$ (Helmholz & Kruh, 1952) to $\theta = 180^\circ$ and $\beta = 0^\circ$ in bis(N-methylphenethyl-ammonium)CuCl$_4$ (Harlow, Wells, Watt & Simonsen, 1974). This distortion of geometry has been associated with a monotonic variation in the $d-d$ transition energies (Willett, Haugen, Lebsack & Morrey, 1974; Battaglia, Bonamartini-Corradi, Marcotrigiano, Menabue & Pellacani, 1979) and the electronic structure of the ion (Solomon, Hare, Dooley, Dawson, Stephens & Gray, 1980). The role of hydrogen bonding in stabilizing the square-planar configuration through removal of charge from the chloride ion has been argued (Geiser & Willett, 1984). Thus, with weak hydrogen bonding electrostatic forces dominate, yielding a geometry close to tetrahedral, while with strong hydrogen bonding the crystal field stabilization energy dominates, giving a geometry closer to square planar.

The tetrabromide structure is analogous to that of the tetrachloride (Fig. 1c). The cation bond angles and distances were within two standard deviations of those obtained for the chloride salt. The only significant difference lies in the Cu—Br vs Cu—Cl distance (average) of 2.377 (1) A vs 2.240 (1) A and the trans Br—Cu—Br angle vs the Cl—Cu—Cl angle of 137 (1) vs 140 (1)^\circ. The compression of the coordination sphere towards tetrahedral geometry is as expected upon replacement of the chloride ions by the larger bromide ion.


**Structure of cis-Dichlorobis(dimethylphenylphosphine)platinum(II)**

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(Received 23 October 1986; accepted 26 January 1987)

Abstract. [PtCl$_2$(C$_8$H$_{11}$P)$_2$], $M_e$ = 542.3, triclinic, $P\overline{1}$, $a = 9.127$ (2), $b = 10.286$ (3), $c = 10.890$ (2) A, $\alpha = 74.40$ (2), $\beta = 70.24$ (2), $\gamma = 88.23$ (2)^\circ, $V = 924.7$ (4) A$^3$, $Z = 2$, $D_x = 1.947$ g cm$^{-3}$, $\lambda$(Mo Ka) = 0.7107 A, $\mu = 81.2$ cm$^{-1}$, F(000) = 520, $T = 294$ K, R = 0.026 for 4693 unique observed reflections. The average Pt—P and Pt—Cl distances are 2.244 (2) and 2.357 (3) A, respectively.

Introduction. During investigation of insertion reactions in Pt$^{111}$ $\sigma$-allyl complexes, we had the opportunity of obtaining crystals of the title compound. The structure was determined in order to obtain further insight into the electronic and steric effects of phosphine ligands.

**Experimental.** Crystal approximately 0.11 x 0.32 x 0.50 mm. Weissenberg and precession photographs indicated the crystal to be triclinic. Nonius CAD-4 diffractometer, graphite-monochromated Mo Ka radiation; lattice parameters refined by least-squares fit of 25 reflections in the range 17 < $\theta$ < 21^\circ. Intensity data measured by the $\omega/2\theta$ scan technique, $\omega$ scan angle = (1.3 + 0.35tan$\theta$)^\circ; variable scan rate, 0.9—5^\circ min$^{-1}$. Three standard reflections (744, 740, 745), monitored every 3000 s, showed no decay throughout.

The authors acknowledge the support of NSF grants DMR-8219430 and INT-8219425. In addition, the X-ray diffraction facility was established through funds supplied by NSF grant CHE-8408407 and by The Boeing Company.

References


