

# The Crystal Structure of Anilinium Tetrachlorocuprate(II)

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Anilinium tetrachlorocuprate(II),  $(C_6H_5NH_3)_2CuCl_4$ , is monoclinic, space group  $P2_1/c$  with  $a = 15.050 \text{ \AA}$ ,  $b = 7.443 \text{ \AA}$ ,  $c = 7.180 \text{ \AA}$ ,  $\beta = 100.7^\circ$  and  $Z = 2$ . The structure has been determined from three-dimensional X-ray data and refined by the method of least squares to a conventional  $R$ -value of 0.033. The coordination around the copper atom consists of an approximately square planar arrangement of chlorine atoms, with an average Cu-Cl distance of 2.29  $\text{\AA}$ . These units are linked together through longer chlorine bonds from neighbouring complexes, thus constituting the typical 4+2 coordination around the copper atom.

Complexes of the type  $CuCl_n^{(n-2)-}$ ,  $n = 3, 4, 5$  are known to exist in various geometries, more or less dependent on the cation employed. Reviews have been given by Hathaway and Billing<sup>1</sup> and Hatfield and Whyman.<sup>2</sup> Some of these complexes exist in the crystal as isolated units; this is the case in  $Cs_2CuCl_4$  where  $CuCl_4^{2-}$  shows approximately  $D_{2d}$  symmetry.<sup>3</sup> In  $[Cr(NH_3)_6][CuCl_6]$  the  $CuCl_6^{3-}$  ion, which has regular  $D_{3h}$  symmetry,<sup>4</sup> also forms discrete species. Complexes containing isolated  $CuCl_6^{4-}$  ions do not, however, seem to have been reported in the literature. The compound investigated,  $(C_6H_5NH_3)_2CuCl_4$ , is the product obtained from a synthesis described by Dubský and Wagenhofer<sup>5</sup> who claimed to have prepared the complex  $(CuCl_6) \cdot H_4 \cdot \text{aniline}_4 \cdot 2H_2O$ .

## EXPERIMENTAL

**Chemistry.** 1.70 g  $CuCl_2 \cdot 2H_2O$  and 7.77 g  $C_6H_5NH_3Cl$  corresponding to a 1:6 molar ratio was dissolved in 200 ml conc. HCl. The mixture was boiled and depending on the cooling rate, crystals of different shapes were formed: (a) thin yellow-brownish quadratic plates (predominant), (b) yellow-brownish quadratic prisms.

The crystals of type (a) were shown to be twins of the (b)-form. The density was measured by the flotation technique in a mixture of  $CHBr_3$  and  $CCl_4$ .

**X-Ray technique.** Lattice type and space group were determined from Weissenberg and precession photographs using Cu and Mo radiation ( $\lambda_{Cu} = 1.5418 \text{ \AA}$ ,  $\lambda_{Mo} = 0.7109 \text{ \AA}$ ). Lattice parameters were obtained from a least squares refinement of setting angles for 18 reflections with  $20^\circ \leq 2\theta \leq 45^\circ$ . Three dimensional intensity data were collected with an automatic Picker four-circle instrument using graphite monochromatized  $MoK\alpha$  radiation. The crystal employed which had the linear dimensions  $0.30 \times 0.40 \times 0.25 \text{ mm}^3$  and was bounded by {100} and {011}, was mounted along [011]. Data were collected up to  $\sin \theta/\lambda = 0.7$ , yielding 2469 independent reflections of which 1993 had  $F_{obs}^2 \geq 2\sigma(F_{obs}^2)$ . The linear absorption coefficient for  $MoK\alpha$  radiation was  $20.9 \text{ cm}^{-1}$ . Data processing was performed with the program DATAPP<sup>6</sup> and included absorption correction using a  $6 \times 4 \times 4$  grid. The transmission factor varied between 0.5348 and 0.6299.

## CRYSTAL DATA

Crystal system: monoclinic ( $b$ -axis unique).  
Unit cell:  $a = 15.050(2) \text{ \AA}$ ,  $b = 7.443(1) \text{ \AA}$ ,  $c = 7.180(1) \text{ \AA}$ ,  $\beta = 100.71(1)^\circ$ ,  $Z = 2$ ,  $d_{calc} = 1.654 \text{ g/cm}^3$ ,  $d_{obs} = 1.650 \text{ g/cm}^3$ .  
Systematic absences:  $h0l: l = 2n + 1$ .  
 $0k0: k = 2n + 1$ .

Space group:  $P2_1/c$ .

## STRUCTURE DETERMINATION

With two molecules per unit cell the Cu atom had to be in a special position. This was confirmed by the three-dimensional Patterson function from which the chlorine positions were also determined. A Fourier map calculated with the signs determined from copper and the two

Table 1. Atomic coordinates and their standard deviations  $\times 10^5$ . For hydrogen standard deviations  $\times 10^4$  and isotropic  $B$  values ( $\text{\AA}^2$ ) with standard deviations  $\times 10$  are given.

Atom	$x$	$\sigma(x)$	$y$	$\sigma(y)$	$z$	$\sigma(z)$	$B$	$\sigma(B)$
Cu	0.00000	(0)	0.00000	(0)	0.00000	(0)		
Cl <sub>1</sub>	0.02237	(4)	0.29064	(7)	0.27751	(7)		
Cl <sub>2</sub>	0.15241	(4)	-0.04141	(7)	0.88166	(8)		
N	0.14957	(14)	-0.02748	(31)	0.54458	(33)		
C <sub>1</sub>	0.24762	(14)	-0.00803	(28)	0.60750	(29)		
C <sub>2</sub>	0.27999	(18)	0.11263	(34)	0.74825	(37)		
C <sub>3</sub>	0.37231	(19)	0.12543	(42)	0.81044	(42)		
C <sub>4</sub>	0.43052	(19)	0.01868	(40)	0.73438	(43)		
C <sub>5</sub>	0.39680	(17)	-0.10016	(38)	0.59154	(42)		
C <sub>6</sub>	0.30473	(16)	-0.11462	(33)	0.52837	(36)		
H <sub>1</sub>	0.2395	(18)	0.1759	(36)	0.7945	(36)	4.6	(6)
H <sub>2</sub>	0.3945	(21)	0.2122	(44)	0.9084	(41)	6.5	(8)
H <sub>3</sub>	0.4951	(18)	0.0207	(34)	0.7741	(38)	4.5	(6)
H <sub>4</sub>	0.4391	(17)	-0.1727	(35)	0.5449	(38)	4.6	(6)
H <sub>5</sub>	0.2787	(17)	-0.1880	(36)	0.4445	(37)	4.6	(7)
H <sub>6</sub>	0.1192	(21)	0.0424	(40)	0.6144	(44)	5.8	(8)
H <sub>7</sub>	0.1313	(21)	-0.1316	(46)	0.5630	(44)	7.1	(9)
H <sub>8</sub>	0.1444	(26)	-0.0125	(49)	0.4038	(64)	10.2	(2)

Table 2. Mean square vibration amplitudes,  $u_{ij}$ , with standard deviations (both in  $\text{\AA}^2 \times 10^4$ ).

Atom	$u_{11}$	$\sigma(u_{11})$	$u_{22}$	$\sigma(u_{22})$	$u_{33}$	$\sigma(u_{33})$	$u_{12}$	$\sigma(u_{12})$	$u_{13}$	$\sigma(u_{13})$	$u_{23}$	$\sigma(u_{23})$
Cu	250	(2)	233	(2)	228	(2)	12	(1)	43	(1)	62	(1)
Cl <sub>1</sub>	406	(3)	270	(3)	271	(3)	26	(2)	68	(2)	-74	(2)
Cl <sub>2</sub>	254	(3)	378	(3)	394	(3)	36	(2)	42	(2)	33	(2)
N	298	(10)	369	(11)	407	(12)	-8	(9)	38	(9)	11	(9)
C <sub>1</sub>	269	(10)	305	(10)	290	(10)	7	(9)	27	(8)	56	(9)
C <sub>2</sub>	429	(14)	427	(14)	447	(14)	-48	(11)	111	(12)	-95	(12)
C <sub>3</sub>	500	(17)	699	(20)	512	(17)	-177	(15)	10	(14)	-178	(15)
C <sub>4</sub>	304	(13)	728	(20)	581	(17)	-60	(14)	-27	(12)	44	(16)
C <sub>5</sub>	336	(13)	543	(16)	612	(17)	98	(12)	123	(13)	20	(14)
C <sub>6</sub>	372	(13)	394	(13)	414	(14)	5	(10)	56	(11)	-65	(11)

chlorine atoms showed clearly all the atoms in the aniline molecule. The scattering factors used were those given by Cromer and Mann<sup>7</sup> for the heavy atoms and by Stewart, Davidson and Simpson<sup>8</sup> for hydrogen. The structure was refined isotropically with the full matrix least squares program LINUS<sup>9</sup> to an  $R$ -value of 0.102. Further refinement with anisotropic temperature factor coefficients and reflections weighted by  $w = 1/[\mu(F)]^2$ , where  $\mu(F) = \{\sigma(F^2)_{\text{count}} + 1.01F_{\text{obs}}^2\}^{1/2} - |F_{\text{obs}}|$  lowered  $R$  to 0.042. The approximate positions of the hydrogen atoms belonging to the benzene ring were calculated and included with isotropic tempera-

ture factor coefficients. A difference Fourier synthesis showed the remaining hydrogen atoms (N-H) and no further features. Including isotropic extinction a final conventional  $R$ -value of 0.033 was obtained. The extinction parameter was 0.0120(7), and the correction factor varied from 1.00 down to 0.71 for a few low order reflections. Coordinates and isotropic temperature factor parameters are given in Table 1, anisotropic temperature factor parameters for heavy atoms in Table 2, and a list of observed and calculated structure factors is given in Table 3.



Table 3. Continued.

Table with multiple columns of numerical data, likely representing crystallographic coordinates or parameters. The table is organized in a grid-like structure with columns for different axes or parameters.

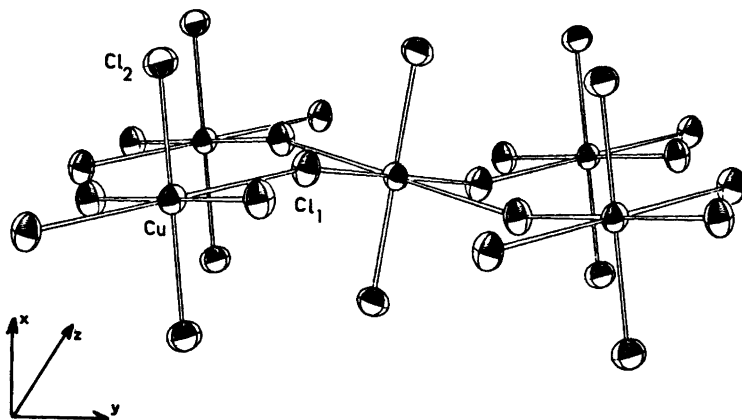


Fig. 1. Coordination around Cu in  $(C_6H_5NH_3)_2CuCl_4$ . Thermal ellipsoids enclose 50 % probability. (ORTEP II).<sup>10</sup>

#### DESCRIPTION OF THE STRUCTURE

The coordination around the  $Cu^{2+}$  ion which is located on a centre of symmetry, is the normal tetragonally distorted octahedron or 4 + 2 coordination often found in Cu-complexes. In this compound this is established through a two dimensional network in the  $b-c$  plane consisting of  $CuCl_4^{2-}$  units linked together through chlorine bonds as shown in Fig. 1.

This gives the three unique Cu-Cl distances shown in Table 4 which also includes the corresponding angles.

The observed bond lengths are in agreement with previously obtained Cu-Cl distances mentioned in the discussion. Apart from the

Table 4. Interatomic distances and angles with standard deviations in parentheses, calculated with the program ORFFE<sup>11</sup> including variance-covariance matrix and cell parameter errors.

Distance	Å
Cu - Cl <sub>1</sub>	2.9178(5)
Cu - Cl <sub>2</sub> <sup>(i)</sup>	2.3007(5)
Cu - Cl <sub>3</sub>	2.2804(6)
Angle	Degrees
Cu - Cl <sub>1</sub> - Cu <sup>(ii)</sup>	164.38(2)
Cl <sub>2</sub> - Cu - Cl <sub>2</sub>	86.66(2)
Cl <sub>1</sub> <sup>(i)</sup> - Cu - Cl <sub>2</sub>	90.01(2)
Cl <sub>1</sub> <sup>(ii)</sup> - Cu - Cl <sub>1</sub>	92.36(1)

(i) Symmetry operation  $\bar{x} y - \frac{1}{2} \frac{1}{2} - z$

(ii) Symmetry operation  $x \frac{1}{2} - y \frac{1}{2} + z$

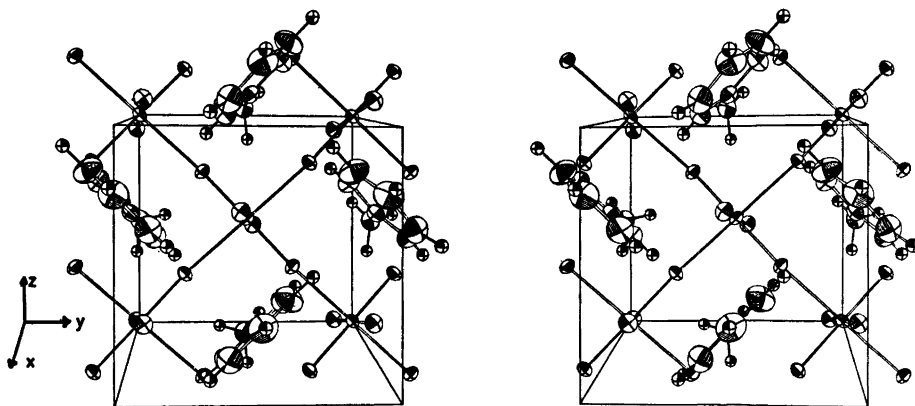


Fig. 2. Stereoscopic drawing of the packing in  $(C_6H_5NH_3)_2CuCl_4$ . Only half the unit cell is shown for clarity. Thermal ellipsoids enclose 50 % probability. All hydrogen atoms have been given the same temperature parameter. (ORTEP II).<sup>10</sup>

Table 5. Interatomic distances and angles with standard deviations in parentheses.

Distance	Å	Distance	Å
N—C <sub>1</sub>	1.468(3)	H <sub>1</sub> —C <sub>2</sub>	0.88(3)
C <sub>1</sub> —C <sub>2</sub>	1.372(3)	H <sub>2</sub> —C <sub>3</sub>	0.97(3)
C <sub>2</sub> —C <sub>3</sub>	1.381(4)	H <sub>3</sub> —C <sub>4</sub>	0.96(3)
C <sub>3</sub> —C <sub>4</sub>	1.369(4)	H <sub>4</sub> —C <sub>5</sub>	0.94(3)
C <sub>4</sub> —C <sub>5</sub>	1.378(4)	H <sub>5</sub> —C <sub>6</sub>	0.85(3)
C <sub>5</sub> —C <sub>6</sub>	1.380(3)	H <sub>6</sub> —N	0.90(3)
C <sub>6</sub> —C <sub>1</sub>	1.368(3)	H <sub>7</sub> —N	0.84(3)
		H <sub>8</sub> —N	1.00(5)
Angle	Degrees	Angle	Degrees
N—C <sub>1</sub> —C <sub>2</sub>	119.4(2)	C <sub>2</sub> —C <sub>3</sub> —C <sub>4</sub>	120.7(3)
N—C <sub>1</sub> —C <sub>6</sub>	119.2(2)	C <sub>3</sub> —C <sub>4</sub> —C <sub>5</sub>	119.7(3)
C <sub>2</sub> —C <sub>1</sub> —C <sub>6</sub>	121.4(2)	C <sub>4</sub> —C <sub>5</sub> —C <sub>6</sub>	120.2(3)
C <sub>1</sub> —C <sub>2</sub> —C <sub>3</sub>	118.8(2)	C <sub>5</sub> —C <sub>6</sub> —C <sub>1</sub>	119.2(2)

small deviations from right angles in the CuCl<sub>4</sub><sup>2-</sup> unit, the bond lengths also violate the regular *D<sub>4h</sub>* symmetry. The angle Cu—Cl<sub>1</sub>—Cu<sup>(ii)</sup> also indicates that the packing which is shown in Fig. 2 is determined not only by the Cu—Cl network, but also by interaction between the chlorine ions and the anilinium ion. The following short Cl...H distances were found (standard deviations in parentheses):

Cl <sub>1</sub> <sup>(ii)</sup> ...H <sub>6</sub>	2.38(3) Å
Cl <sub>2</sub> <sup>(ii)</sup> ...H <sub>7</sub>	2.46(3) Å
Cl <sub>2</sub> ...H <sub>8</sub>	2.35(5) Å

The bond lengths and angles in the anilinium molecule, listed in Table 5, are in agreement with the geometry of the benzene ring.

## DISCUSSION

CuCl<sub>n</sub><sup>(n-2)-</sup> complexes containing ammonium or substituted ammonium ions as cations are known in several different geometries. NH<sub>4</sub>CuCl<sub>3</sub> contains planar Cu<sub>2</sub>Cl<sub>6</sub><sup>2-</sup> dimers<sup>12</sup> with Cu—Cl distances ranging from 2.25 Å to 2.32 Å. The stacking of these dimers completes the 4+2 coordination with two Cu—Cl bonds of 2.99 Å and 3.19 Å. A square pyramidal coordination is found in (CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>CuCl<sub>3</sub> (Ref. 13). The Cu—Cl distances in the base are 2.25 Å—2.33 Å, the fifth 2.73 Å, while the sixth position is empty out to 3.78 Å. In [(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>NH]<sub>2</sub>CuCl<sub>4</sub> the coordination figure is a distorted tetrahedron<sup>14</sup> with four nearly equal distances of 2.24 Å. The 4+2 coordination is also adopted

in (C<sub>2</sub>H<sub>5</sub>NH<sub>3</sub>)<sub>2</sub>CuCl<sub>4</sub> (Ref. 15) which resembles the structure of (C<sub>6</sub>H<sub>5</sub>NH<sub>3</sub>)<sub>2</sub>CuCl<sub>4</sub> very much although the former crystallises in space group *Pbca*. The observed Cu—Cl distances<sup>15</sup> were 2.28 Å and 2.98 Å, but a close resemblance is also to be expected due to the cations.

In all these compounds, hydrogen bonding seems to be of importance in affecting the geometries adopted by the CuCl<sub>n</sub> units. This might explain the small deviations from the regular geometries (*T<sub>d</sub>*, *O<sub>h</sub>*, *D<sub>4h</sub>*, *C<sub>4v</sub>*, etc.), which are found in bond lengths and angles. An explanation of the non-regularity is also offered by the Jahn-Teller effect, which should be operative in the 3d<sup>9</sup> system, Cu<sup>2+</sup>. But it is difficult to determine which of these is the governing factor.

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