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The Effect of Hydrogen Bonding on the Chlorocuprate(II) Geometry. A Compound Containing an Unusual Copper/Chlorine Ratio of 1:6. Crystal and Molecular Structure of Bis(N-benzylpiperaziniumchloride)tetrachlorocuprate(II)

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A compound of the type $(NBzpipzH_2)_2CuCl_6$ *(*$NBzpipzH_2$ *= N-benzylpiperazinium dication) was prepared and characterized by means of X-ray, electronic, differential scanning calorimetric and magnetic measurements. Crystals of the compound are monoclinic, space group Pc, with* a = *21.954(2)* Å, b = *7.0889(5)* Å, c = *9.1391(9)* Å, β = *97.054(8)°, and* Z = *2. Intensities were obtained from* $\theta-2\theta$ *scan with a Philips PW 1100 automatic four-circle diffractometer using graphite-monochromated Mo K*α *radiation. The structure was solved by conventional heavy-atom methods, and least-squares refinement of structural parameters led to a conventional* R *factor of 0.049 for 1508 reflections having* $I > 3\sigma(I)$*. The crystal consists of a* $CuCl_4^{2-}$ *anion, two lattice* Cl^- *ions, and two* $(NBzpipzH_2)^{2+}$ *cations. The* $CuCl_4^{2-}$ *ion shows a slight tetrahedral distortion superimposed to the basic square-planar geometry, but may be also regarded as an example of an extremely flattened tetrahedron. The strong hydrogen bonds formed by the N-bonded H atoms of the cations, which bridge the* $CuCl_4^{2-}$ *anions and link the* Cl^- *ions, were considered responsible for the unusual geometry of the* $CuCl_4^{2-}$ *chromophore. The electronic spectra are discussed and assigned on the basis of the known crystal structure.*

Introduction

The great interest in the copper(II) chloride systems stems from the fact that they show a great variety of coordination numbers and geometries [1, 2]. However there are few precedents in the literature for species containing a copper/chlorine ratio of 1:6. One of these is Tl_4CuCl_6 which has been little studied [3]; another is $[Pt(en)_2Cl_2][CuCl_4]$, obtained in an attempt to prepare a $[Pt(en)_3][CuCl_6]$ species, which contains $CuCl_4^{2-}$ units having a strongly distorted tetrahedral configuration with a dihedral angle of 35.7(2)° (4). Others include $(piperazinium)_2CuCl_6$ [5a] and $(1\text{-Methylpiperazinium})_2CuCl_6$ [5b] complexes (which, it has been suggested on the basis of electronic and far-infrared spectra, contain approximately square-planar $CuCl_4^{2-}$ ions), and the latest $(adeninium)_2CuCl_6$, for which a structure similar to that of piperazinium complex has been tentatively assigned, as their color and formula are very similar [6].

As the dications seem to facilitate the existence of compounds containing an uncommon copper/chlorine ratio of 1:6, by using the N-benzylpiperazinium a compound of formula $(NBzpipzH_2)_2CuCl_6$ has been now isolated and investigated in order to rationalize the formation conditions and configurations of these species.

Further interest also derives from the fact that the compound now investigated is the third chlorocuprate(II) obtained with the same dication. The structural results of the other two compounds, one yellow hemihydrate and one green anhydrous of formula $[NBzpipzH_2][CuCl_4]\cdot\frac{1}{2}H_2O$ and $[NBzpipzH_2][CuCl_4]$, have been previously reported elsewhere [7].

Experimental

Preparation of the Bis(N-benzylpiperazinium-chloride)tetrachlorocuprate(II)

A green compound slowly precipitated by mixing a methanolic $CuCl_2\cdot 2H_2O$ (1 m*M*) solution with a methanolic $NBzpipz\cdot(HCl)_2$ (4 m*M*) solution. Single crystals suitable for X-ray analysis were obtained after repeated recrystallization in methanol. *Anal.* Calcd. for $C_{22}H_{36}CuN_4Cl_6$: C, 41.73; H, 5.74; N,

TABLE I. Summary of Crystal Data Collection[a] for $(NBzpipzH_2 \cdot Cl)_2CuCl_4$.

Diffractometer	Philips PW 1100
Radiation	graphite-monochromated Mo Kα (λ = 0.71069 A)
Temp, °C	20 ± 2
Crystal system	monoclinic
Space group	Pc (C_s^2, No. 7)
a, A	21.954(2)
b, A	7.0889(5)
c, A	9.1391(9)
β, deg	97.054(8)
V, A^3	1411.5
Z	2
Molecular weight	632.602
ρ(calcd), g/cm^3	1.488
ρ(obsd), g/cm^3	1.48 (by flotation in $CHCl_3$)
Reflections measd	$-h_{max} \leqslant h \leqslant + h_{max}$ with k and $l \geqslant 0$
Scan type	coupled θ (crystal)–2θ (counter)
2θ range, deg	5–48
Scan speed	2.7°/min in 2θ
Scan width, deg	0.9
Background time	10 s at beginning and end of 2θ scan
Standards	2 every 180 reflections (no significant changes)
Collected reflections	2428, yielding 2225 nonzero independent data
Obsd reflections	1508 with $I > 3\sigma(I)$ [$\sigma(I)$ = (peak counts + total background counts)$^{1/2}$]
Crystal size, mm	~0.22 × 0.20 × 0.06
Absorption coefficient, cm^{-1}	12.7
Absorption correction	not applied

[a] The unit cell parameters and their esds were obtained from least-squares refinement of the setting angles of 24 strong high-angle reflections, by using the standard control program of the PW 1100 system [10] for a randomly oriented crystals.

8.86; Cl, 33.63. Found: C, 41.65; H, 5.74; N, 8.81; Cl, 33.24. Color: green. M.p. 202–6 °C.

Physical Measurements

The electronic spectrum of the solid compound was recorded as mull transmission spectrum with a Shimadzu MPS 50L spectrophotometer. The differential scanning calorimetric analysis was performed with a Perkin Elmer DSC 1 instrument. The room-temperature magnetic moment was measured with the Gouy method by using $Ni(en)_3S_2O_3$ as calibrant and correction for diamagnetism by the appropriate Pascal constants.

Collection and Processing of the X-ray Diffraction Data

The crystal selected for X-ray analysis was sealed on a glass fiber and data were collected at room-temperature on a Philips PW 1100 automatic four-circle diffractometer using graphite-monochromated Mo Kα radiation. Details specific to the X-ray diffraction data collection and processing are reported in Table I.

An examination of the complete data set revealed systematic extinctions h0l for l = 2n + 1.

Possible space groups are the noncentrosymmetric monoclinic space group Pc (C_s^2, no. 7) and the centrosymmetric monoclinic space group P2/c (C_{2h}^4, no. 13). The former was chosen as the correct group on the basis of distribution of peaks in the Patterson function [8], and because the statistics on E factors clearly indicated a non centric space group, as is confirmed by the subsequent refinement. All data were corrected for Lorentz and polarization effects, but not for absorption in view of the small crystal size and absorption coefficient. Of the 2225 independent nonzero reflections, 1508 for which $I > 3\sigma(I)$ were denoted observed and used in the structure analysis.

Solution and Refinement of the Structure

Scattering factors for Cu^{2+} and Cl^- ions and for N and C atoms (including real and imaginary terms of anomalous dispersion) and for H atoms were taken from published Tables [9]. The function minimized during least-squares refinements was $\Sigma w(|F_o|-|F_c|)^2$; discrepancy indices used below are $R = (\Sigma||F_o|-|F_c||)/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ where w is the weighting factor. All calculations were performed on the CDC Cyber 76 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale at Bologna, by using the programs detailed in ref. 10. An approximate absolute scale factor and an overall thermal parameter were obtained from a Wilson plot. A three-dimensional Patterson synthesis revealed the approximate location of the tetrahedral $CuCl_4^{2-}$ ion; all the remaining non hydrogen atoms were easily located in a subsequent Fourier-difference map. The starting set of parameters gave R = 0.137. Least-squares refinement of atomic positional and isotropic thermal parameters, using units weights, leads to a convergence at R = 0.078 and R_w = 0.083. At this stage 36 H atoms were introduced as fixed contributors at their calculated positions assuming a N–H bond length of 0.95 Å and C–H bond length of 1.0 Å; the isotropic thermal parameter assigned to hydrogen atom was 1.0 Å^2 greater than the bonded atom.

TABLE II. Atomic Positional and Temperature Parameters for $(\mathrm{NBzpipzH_2 \cdot Cl})_2\mathrm{CuCl_4}$.[a]

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu[b]	½	0.7228(2)	¾	2.90(6)	2.17(6)	3.13(7)	0.08(9)	0.43(5)	0.28(7)
Cl(1)	0.6026(2)	0.7044(6)	0.8054(4)	2.9(2)	2.7(2)	3.4(1)	0.1(1)	0.4(1)	0.2(1)
Cl(2)	0.3975(2)	0.7020(6)	0.7433(4)	2.9(2)	3.0(2)	3.3(2)	0.3(1)	−0.1(1)	−0.1(1)
Cl(3)	0.4997(2)	1.0001(5)	0.8877(4)	3.1(1)	2.2(1)	4.7(2)	0.1(1)	0.6(1)	0.5(1)
Cl(4)	0.5008(2)	0.5054(7)	0.5733(5)	4.7(2)	5.4(2)	6.1(2)	−0.2(2)	0.4(2)	3.4(2)
Cl(5)	0.7576(2)	0.8129(6)	0.7933(4)	4.2(2)	2.2(1)	4.5(2)	−0.2(1)	0.5(1)	−0.1(1)
Cl(6)	0.2424(2)	0.8155(5)	0.6428(4)	4.0(2)	2.3(1)	4.2(2)	0.3(1)	0.3(1)	−0.2(1)

Atom	x	y	z	B, A^2	Atom	x	y	z	B, A^2
N(1)	0.6106(6)	0.2550(18)	0.8197(13)	3.4(2)	N(21)	0.3877(5)	0.2543(17)	0.7589(12)	3.0(2)
C(2)	0.6603(6)	0.2247(19)	0.9450(13)	2.7(2)	C(22)	0.3371(7)	0.2225(21)	0.8504(14)	3.2(3)
C(3)	0.7194(6)	0.3123(20)	0.9180(14)	3.1(3)	C(23)	0.2798(6)	0.3109(19)	0.7842(13)	2.4(2)
N(4)	0.7403(4)	0.2373(14)	0.7816(11)	1.9(2)	N(24)	0.2604(5)	0.2396(15)	0.6302(11)	2.4(2)
C(5)	0.6913(6)	0.2727(21)	0.6556(15)	3.2(3)	C(25)	0.3099(6)	0.2767(20)	0.5408(14)	3.1(2)
C(6)	0.6318(6)	0.1852(19)	0.6815(14)	2.7(2)	C(26)	0.3704(6)	0.1863(19)	0.6052(14)	2.7(2)
C(7)	0.8010(7)	0.3161(21)	0.7477(16)	3.6(3)	C(27)	0.1995(6)	0.3229(19)	0.5600(15)	3.1(3)
C(8)	0.8513(8)	0.2939(28)	0.8792(17)	4.0(3)	C(28)	0.1476(8)	0.3032(28)	0.6483(18)	4.1(3)
C(9)	0.8753(9)	0.1259(28)	0.9271(22)	5.5(4)	C(29)	0.1273(8)	0.4522(24)	0.7227(18)	4.5(3)
C(10)	0.9193(11)	0.1194(34)	1.0491(25)	7.5(5)	C(30)	0.0799(10)	0.4321(32)	0.8094(24)	7.0(5)
C(11)	0.9411(9)	0.2792(34)	1.1190(23)	7.1(5)	C(31)	0.0526(12)	0.2593(38)	0.8167(27)	8.7(6)
C(12)	0.9193(10)	0.4490(31)	1.0642(23)	6.8(5)	C(32)	0.0709(12)	0.1120(41)	0.7433(29)	9.1(6)
C(13)	0.8728(9)	0.4632(26)	0.9445(20)	5.0(3)	C(33)	0.1198(10)	0.1194(33)	0.6560(22)	6.8(5)

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [b] The origin of the unit cell was arbitrarily defined by assigning the values ½ and ¾ to the x and z coordinates, respectively, of the Cu atom.

TABLE III. Interatomic Distances and Esd's (Å) for $(\mathrm{NBzpipzH_2 \cdot Cl})_2\mathrm{CuCl_4}$.

a) Within Anions

Cu–Cl(1)	2.252(4)	Cl(1)···Cl(2)	4.469(6)
Cu–Cl(2)	2.249(4)	Cl(1)···Cl(3)	3.238(5)
Cu–Cl(3)	2.334(4)	Cl(1)···Cl(4)	3.212(5)
Cu–Cl(4)	2.234(4)	Cl(2)···Cl(3)	3.242(5)
		Cl(2)···Cl(4)	3.220(6)
Cu···Cl(3′)	3.849(4)	Cl(3)···Cl(4)	4.536(6)
Cu···Cu′	6.027(2)	Cl(1)···Cl(5)	3.505(5)
Cu···Cl(4″)	3.367(4)	Cl(2)···Cl(6)	3.509(5)
Cu···Cu″	5.555(2)		

b) Within $(\mathrm{NBzpipzH_2})^{2+}$ Cations

N(1)–C(2)	1.50(2)	N(21)–C(22)	1.50(2)
N(1)–C(6)	1.48(2)	N(21)–C(26)	1.49(2)
C(2)–C(3)	1.48(2)	C(22)–C(23)	1.47(2)
C(3)–N(4)	1.48(2)	C(23)–N(24)	1.51(2)
N(4)–C(5)	1.50(2)	N(24)–C(25)	1.46(2)
N(4)–C(7)	1.51(2)	N(24)–C(27)	1.53(2)
C(5)–C(6)	1.49(2)	C(25)–C(26)	1.53(2)
C(7)–C(8)	1.54(2)	C(27)–C(28)	1.48(2)
C(8)–C(9)	1.35(2)	C(28)–C(29)	1.36(2)
C(8)–C(13)	1.40(2)	C(28)–C(33)	1.44(3)
C(9)–C(10)	1.38(3)	C(29)–C(30)	1.39(2)
C(10)–C(11)	1.36(3)	C(30)–C(31)	1.37(3)
C(11)–C(12)	1.37(3)	C(31)–C(32)	1.33(3)
C(12)–C(13)	1.41(2)	C(32)–C(33)	1.41(3)

[a] Superscripts refer to the following transformations of the reference coordinates: ′ x, 2 – y, z – ½. ″ x, 1 – y, ½ + z.

Final full-matrix least-squares refinement, in which the Cu and Cl atoms were allowed to vibrate anisotropically, leads to convergence at R = 0.049 and R_w = 0.051. Unit weights were used also in the final cycles of refinement because the quantity $w(|F_o|-|F_c|)^2$ showed no serious dependence on $|F_o|$ or on $(\sin\theta)/\lambda$, and the resulting weighting scheme was better than that based on the counting statistics, previously tested. In the final least-squares cycle the shifts in all parameters were less than 0.1 of an esd.

A final electron density map was featureless, with no peaks greater than 0.45e $\mathrm{Å}^{-3}$. Correction for secondary extinction was not deemed necessary. The final structural parameters appear in Table II. A list of final $10|F_o|$ and $10|F_c|$ is available [11].

TABLE IV. Interatomic Angles and Esd's (deg) for $(NBzpipzH_2 \cdot Cl)_2 CuCl_4$.[a]

a) Within Anions			
Cl(1)–Cu–Cl(2)	166.6(1)	Cl(3)–Cu···Cl(3')	92.0(2)
Cl(1)–Cu–Cl(3)	89.8(2)	Cl(4)–Cu···Cl(3')	74.3(2)
Cl(1)–Cu–Cl(4)	91.5(2)	Cu···Cl(3')–Cu'	155.3(1)
Cl(2)–Cu–Cl(3)	90.0(2)	Cl(1)–Cu···Cl(4")	83.0(2)
Cl(2)–Cu–Cl(4)	91.8(2)	Cl(2)–Cu···Cl(4")	83.7(2)
Cl(3)–Cu–Cl(4)	166.3(2)	Cl(3)–Cu···Cl(4")	86.1(2)
		Cl(4)–Cu···Cl(4")	107.6(2)
Cl(1)–Cu···Cl(3')	96.8(2)	Cu···Cl(4")–Cu"	165.1(1)
Cl(2)–Cu···Cl(3')	96.5(2)	Cl(3')···Cu···Cl(4")	178.0(2)
b) Within $(NBzpipzH_2)^{2+}$ Cations			
C(6)–N(1)–C(2)	109(1)	C(26)–N(21)–C(22)	111(1)
N(1)–C(2)–C(3)	112(1)	N(21)–C(22)–C(23)	111(1)
C(2)–C(3)–N(4)	111(1)	C(22)–C(23)–N(24)	112(1)
C(3)–N(4)–C(5)	109(1)	C(23)–N(24)–C(25)	109(1)
N(4)–C(5)–C(6)	112(1)	N(24)–C(25)–C(26)	112(1)
C(5)–C(6)–N(1)	112(1)	C(25)–C(26)–N(21)	110(1)
C(3)–N(4)–C(7)	114(1)	C(23)–N(24)–C(27)	113(1)
C(5)–N(4)–C(7)	110(1)	C(25)–N(24)–C(27)	112(1)
N(4)–C(7)–C(8)	112(1)	N(24)–C(27)–C(28)	115(1)
C(7)–C(8)–C(9)	124(1)	C(27)–C(28)–C(29)	121(1)
C(7)–C(8)–C(13)	115(2)	C(27)–C(28)–C(33)	118(2)
C(13)–C(8)–C(9)	121(2)	C(33)–C(28)–C(29)	121(2)
C(8)–C(9)–C(10)	120(2)	C(28)–C(29)–C(30)	121(2)
C(9)–C(10)–C(11)	121(2)	C(29)–C(30)–C(31)	119(2)
C(10)–C(11)–C(12)	118(2)	C(30)–C(31)–C(32)	121(2)
C(11)–C(12)–C(13)	122(2)	C(31)–C(32)–C(33)	124(3)
C(12)–C(13)–C(8)	117(2)	C(32)–C(33)–C(28)	115(2)

[a] Superscripts refer to the symmetry transformations of Table III.

Results and Discussion

For the preparation of the title compound, which is very stable in air and which shows a melting point indicating a predominantly inorganic character, the presence of methanol as solvent is of fundamental importance. In fact in strong acidic media two other compounds with the same dication of formula $(NBzpipzH_2)CuCl_4$ (green) and $(NBzpipzH_2)CuCl_4 \cdot ½H_2O$ (yellow) have been separated and previously investigated [7]. Other $(LH_2)_2CuCl_6$ complexes [5a and b] require the simultaneous presence of methanol as solvent and an excess of counterion.

Description of the Structure

Interatomic distances and angles are reported in Tables III and IV, respectively, with atoms numbered as in Fig. 1.

The crystal structure analysis established the chemical formula to be best represented by $(NBzpipzH_2Cl)_2CuCl_4$ as consisting of a discrete $CuCl_4^{2-}$ anion, two lattice chloride ions, and two $(NBzpipzH_2)^{2+}$ cations hydrogen-bonded to the anions.

The coordination geometry about the Cu atom shows a slight tetrahedral distortion superimposed on the basic square-planar configuration. In addition, two Cl atoms from neighbouring $CuCl_4^{2-}$ units occupy the octahedral sites of the $CuCl_4^{2-}$ chromophore; nevertheless their distances from the Cu atom (3.367(4) and 3.849(4) Å, respectively) are much longer (in particular the latter) than those of 2.793–3.257 Å previously found in polymeric chlorocuprates(II) with the (4 + 2) elongated octahedral geometry or the (4 + 1) square-pyramidal coordination [2], and they were therefore assumed to be only weak interactions.

In view of its idealized geometry, The $CuCl_4^{2-}$ ion may also be regarded as an extremely flattened, tetrahedron with D_{2d} symmetry. Its distortion from T_d symmetry, expressed by a flattening angle θ of 166.4(2)° (where θ is the mean value of the two Cl–Cu–Cl angles greater than the tetrahedral one), seems to be the most pronounced so far reported, and falls in the gap existing between the value of 159.2(3)° found in $(Me_2CHNH_3)_2CuCl_4$ [12] and the square-planar limit, as in $(PhCH_2CH_2NMeH_2)_2CuCl_4$ [13] (low-temperature form) or in creatininium tetrachlorocuprate(II) [14].

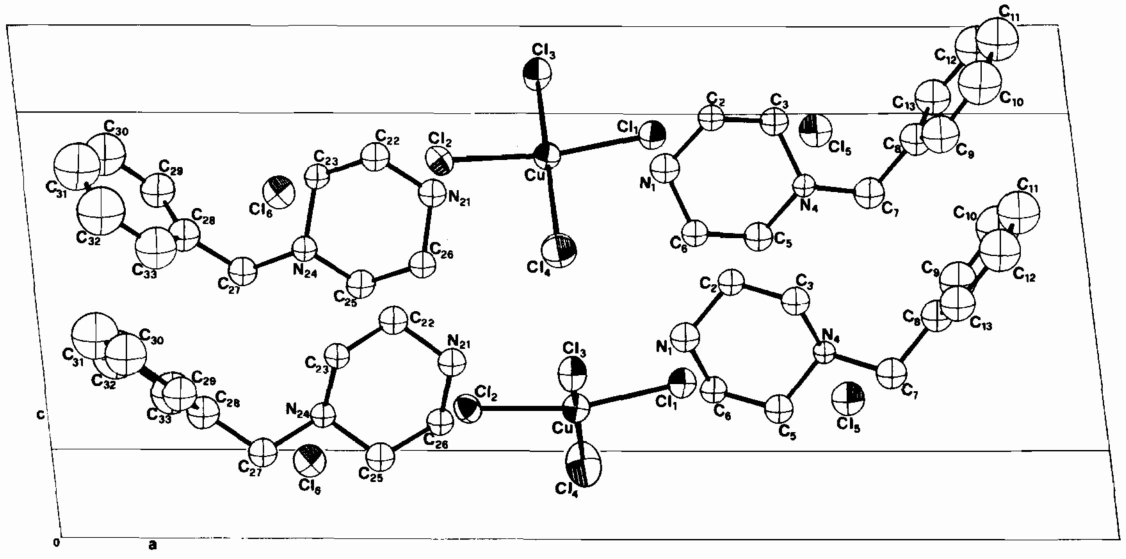

Fig. 1. ORTEP drawing of the unit cell contents of $(NBzpipzH_2 \cdot Cl)_2CuCl_4$, showing the labeling scheme and vibrational ellipsoids at the 45% probability level. The H atoms have been omitted for the sake of clarity.

TABLE V. Hydrogen Bonding Distances (Å) and Angles (deg) for $(NBzpipzH_2 \cdot Cl)_2CuCl_4$.[a]

Atoms	H···Cl	N···Cl	⟨N–H···Cl
N(1)–H(11)···Cl(1)	2.26	3.192	167
N(1)–H(12)···Cl(3′)	2.21	3.154	173
N(4)–H(41)···Cl(5′)	2.09	3.033	173
N(21)–H(211)···Cl(3′)	2.21	3.157	172
N(21)–H(212)···Cl(2)	2.25	3.185	170
N(24)–H(241)···Cl(6′)	2.09	3.036	178

[a] Superscript refers to the symmetry transformation x, y − 1, z.

It is probably hydrogen bonding, rather than crystal packing forces or the cation bulk, which accounts for the unusual geometry of the $CuCl_4^{2-}$ ion in the present compound. The four strong, nearly linear hydrogen bonds, which involve three of the Cu-bonded chlorine atoms (see Table V and Fig. 2), may produce such a reduction of the ligand–ligand electrostatic repulsion to allow a nearly square-planar geometry, favoured by the crystal field stabilization [2].

The decisive role of hydrogen bonding in determining the tetrahedral flattening of the $CuCl_4^{2-}$ ion is clearly confirmed by comparing the present results with those obtained from a previous structural analysis of two tetrachlorocuprates(II) of the same dication, $(NBzpipzH_2)CuCl_4$ and $(NBzpipzH_2)CuCl_4 \cdot ½H_2O$, which contain, respectively, four and two unequally flattened $CuCl_4^{2-}$ chromophores, whose θ values range from 132.2° to 151.8° [7]. Such a comparison strongly suggests that the number, the disposition and the nature of the hydrogen bonding interactions act as decisive contributors to the factors which determine the tetrahedral flattening of the $CuCl_4^{2-}$ ion.

Hydrogen bonding is likely to affect bond lengths as well as bond angles [2]. The shortest Cu–Cl bond (2.234(4) Å) is related to the only Cl atom not engaged in hydrogen bonding, while an unusually long bond distance (2.334(4) Å) was found for the Cl atom involved in two strong hydrogen bond interactions.

The two lattice Cl^- ions, strongly hydrogen-bonded to the cations, are separated by normal Van der Waals distances from Cu-bonded Cl atoms (see Table III).

Quite similar are the structural features of the two crystallographically independent $(NbzpipzH_2)^{2+}$ cations, whose piperazine rings show the usual 'chair' conformation with torsion angles ranging from 54.1° to 57.8°, respectively. In spite of the rather large esd s (as absolute values, from 54.4 to 58.0), the shortening of the C–C bond distances and the lengthening of the C–N bond distances, with respect to their expected values, appear to be significant and in agreement with previous results for the $(N(2amet)pipzH_3)^{3+}$ trication [15].

Both the $(NBzpipzH_2)^{2+}$ cations form three strong hydrogen bonds (see Table V and Fig. 2) through their N-bonded H atoms, bridging two $CuCl_4^{2-}$ ions in a nearly planar arrangement (see Table VI) and linking the lattice Cl^- ions. As a result, infinite chains running along the crystallo-

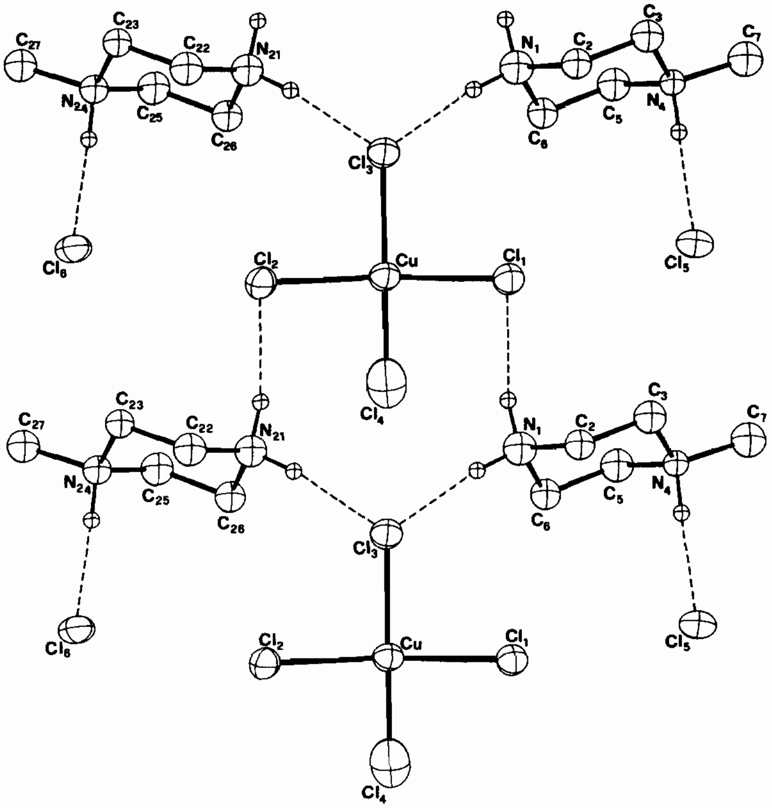

Fig. 2. Hydrogen bonds (dashed lines) in $(NBzpipzH_2 \cdot Cl)_2CuCl_4$. C-bonded H atoms and phenyl rings have been omitted for clarity. Equivalent atoms are related by unit cell translation along the *b* axis.

TABLE VI. Selected Least-Squares Planes and Atomic Deviations (Å) derived Therefrom.[a]

Atom	Dev	Atom	Dev
1. Equation:[b] $-0.0949x + 0.6335y + 0.7738z = 1.9646$			
Cl(1)	0.267	Cl(4)	−0.269
Cl(2)	0.266	Cu*	0.006
Cl(3)	−0.264		
2. Equation: $-0.4292x + 0.9020y + 0.0059z = -4.7340$			
C(2)	−0.001	C(6)	0.001
C(3)	0.001	N(1)*	0.655
C(5)	−0.001	N(4)*	−0.683
3. Equation: $-0.7878x - 0.0535y + 0.7057z = -9.1832$			
C(8)	0.019	C(11)	0.018
C(9)	−0.023	C(12)	−0.023
C(10)	0.005	C(13)	0.004
	Dihedral angle between 2 and 3: 74.9°		
4. Equation: $0.4263x + 0.9005y + 0.0323z = 4.8307$			
C(22)	−0.004	C(26)	0.004
C(23)	0.004	N(21)*	0.645

(continued on facing page)

TABLE VI. *(continued)*

Atom	Dev	Atom	Dev
C(25)	−0.004	N(24)*	−0.678
5. Equation: $0.5633x - 0.2322y + 0.7178z = 5.5792$			
C(28)	0.000	C(31)	0.002
C(29)	−0.008	C(32)	−0.011
C(30)	0.007	C(33)	0.009
Dihedral angle between 4 and 5: 84.3°			
6. Equation: $-0.1127x + 0.1615y + 0.9868z = 6.3874$			
Cu	−0.033	Cl(3)^c	0.382
Cl(1)	0.192	H(211)	0.009
H(11)	−0.125	N(21)	−0.211
N(1)	−0.213	H(212)	−0.102
H(12)	−0.037	Cl(2)	0.137

[a] Atoms not used in calculating the plane are marked with an asterisk. [b] x, y, z are fractional crystal coordinates. [c] Symmetry transformation: x, y − 1, z.

graphic *b* axis are produced; the shortest interactions between these chains are due to the Cl atoms in 'pseudooctahedral' locations.

Electronic and Magnetic Properties

The electronic spectrum of the $(NBzpipzH_2)_2CuCl_6$ shows d–d bands at 14450, 12802 and 10530 cm^{-1}. Tetrachlorocuprate(II) anions, having tetragonally distorted octahedral geometry, present the highest energy d–d bands around 13000 cm^{-1} [16, 17], which may split as the ligands on the *z*-axis are gradually withdrawn, the limiting case being reached in the four-coordinate square-planar arrangement, as found in the green form of bis(N-methylphenetylammonium)tetrachlorocuprate(II) which shows distinct peaks at 16100, 13600 and 11500 cm^{-1} [13, 18]. The presence of three d–d bands (although not-well resolved) and their positions indicate that our compound may be considered as truly four coordinate, in agreement with the above suggestions that the Cu–Cl distances of 3.367(4) and 3.849(4) Å are too large to be considered as some type of bonding interactions. Then the shift toward lower energies of the d–d bands in our complex with respect to those of the (N-methylphenethylammonium) tetrachlorocuprate(II) [13] takes into account the lower distortion from tetrahedral geometry.

However, the d–d bands may be assigned to $^2A_{2g}(x^2 - y^2) \rightarrow {}^2A_g(z^2)$ (14450 cm^{-1}), $\rightarrow {}^2B_{3g}(yz)$ (12820 cm^{-1}) and $\rightarrow {}^2B_{2g}(xz)$ (10530 cm^{-1}) transitions, in agreement to those of the (N-methylphenethylammonium)tetrachlorocuprate(II) [18].

In a previous paper a linear dependence of the higher energy band of the electronic spectrum from the dihedral angle of truly four-coordinate compounds was observed [19]. The d–d band maximum (14450 cm^{-1}) and dihedral angle (19°) of the present compound agree perfectly with the above correlation, filling the gap of dihedral angles between 35.5° and 0°. This further confirms that our compound must be treated as truly four coordinate.

The role and strength of hydrogen bonding in stabilizing an approximately square-planar configuration is also demonstrated by the fact that no structural change is observed in the compound on heating between 20 °C and the melting point. In this case the increasing disorder due to the thermal motion does not weaken the hydrogen bonding network.

The room-temperature magnetic moment of 1.91 B.M. of the complex excludes the presence of interactions between the copper ions.

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References

1 W. E. Hatfield and R. Whyman, *Transition Met. Chem., 5,* 147 (1969).

2 D. W. Smith, *Coord. Chem. Rev., 21,* 93 (1976).

3 M. S. Golubova, R. D. Sidakova, *Fiz. Khim. Analiz. Solevykh. Sistem. SB,* 189 (1962).

4 K. P. Larsen, R. G. Hazell, H. Toftlund, P. R. Andersen, P. Bisgard, K. Edlund, M. Eliasen, C. Herskind, T. Laursen and P. M. Pedersen, *Acta Chem. Scand. Sec A, 29,* 499 (1975).

5 a) G. Marcotrigiano, L. Menabue and G. C. Pellacani, *Inorg. Chem., 15,* 2333 (1976).
b) G. Marcotrigiano, L. Menabue and G. C. Pellacani, *J. Coord. Chem., 9,* 141 (1979).

6 D. B. Brown, J. W. Hall, H. M. Helis, E. G. Walton, D. J. Hodgson and W. E. Hatfield, *Inorg. Chem., 16,* 2675 (1977).

7 L. Antolini, L. Menabue, G. C. Pellacani, M. Saladini, G. Marcotrigiano and W. Porzio, *J. Chem. Soc. Dalton Trans.,* 1753 (1981).

8 M. J. Buerger, 'Vector Space', Wiley, New York, 1959.

9 'International Tables for X-Ray Crystallography', Vol. IV, Kynoch Press, Birmingham, England, 1974, pp. 99–101, 149–150.

10 G. M. Sheldrick, 'SHELX-76 Program for Crystal Structure Determination', Cambridge, England, 1976.

11 See paragraph at the end of paper regarding supplementary material.

12 D. L. Anderson and R. D. Willett, *Inorg. Chim. Acta, 8,* 167 (1974).

13 R. L. Harlow, W. J. Wells, 111, G. W. Watt and S. H. Simonsen, *Inorg. Chem., 13,* 2106 (1974).

14 M. R. Udupa and B. Krebs, *Inorg. Chim. Acta, 33,* 241 (1979).

15 L. Antolini, G. Marcotrigiano, L. Menabue and G. C. Pellacani, *J. Am. Chem. Soc., 102,* 5506 (1980).

16 W. E. Hatfield and T. S. Piper, *Inorg. Chem., 3,* 841 (1964).

17 R. D. Willett, O. L. Liles and C. Michelson, *Inorg. Chem., 6,* 1885 (1967).

18 M. A. Hitchman and P. J. Cassidy, *Inorg. Chem., 18,* 1745 (1979).

19 L. P. Battaglia, A. Bonamartini Corradi, G. Marcotrigiano, *L. Menabue and G. C. Pellacani, Inorg. Chem., 18,* 148 (1979).