Spectroscopic and Structural Investigation of two *N*-Benzylpiperazinium Tetrachlorocuprates(II), one Hemihydrate and one Anhydrous: Two Compounds containing Unequally Flattened $[CuCl_4]^{2-}$ Tetrahedra

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Two compounds $[bzpipzn][CuCl_4]\cdot0.5H_2O$ (yellow) and $[bzpipzn][CuCl_4]$ (green) ($[bzpipzn]^{2+}$ = *N*-benzylpiperazinium dication) have been prepared and investigated by means of electronic and vibrational spectra, magnetic moments, d.s.c., and crystal-structure measurements. The crystal structures were determined by three-dimensional *X*-ray diffraction. The two compounds crystallize in the space groups $P2_1/a$ (yellow) and $P2_1$ (green) with unit-cell dimensions a = 17.015(1), b = 16.977(2), c = 11.377(2) Å, β = 97.156(4)°, Z = 8 and a = 12.075 7(3), b = 28.479 8(10), c = 9.925 8(9) Å, β = 109.54(1)°, Z = 8, for the yellow and green compounds respectively. The structures have been refined to R 0.036 and 0.067, respectively. The yellow complex consists of two crystallographically independent $[CuCl_4]^{2-}$ anions with moderately flattened tetrahedral geometry, two $[bzpipzn]^{2+}$ cations, and a water molecule of crystallization. The green complex consists of four independent discrete $[CuCl_4]^{2-}$ anions, unequally flattened, and four independent $[bzpipzn]^{2+}$ cations, which bridge the anions through hydrogen bonds involving their *N*-bonded H atoms. The role of hydrogen bonding in the flattening of the tetrahedral $[CuCl_4]^{2-}$ ions is discussed. The spectroscopic and magnetic properties of the complexes are explained in the light of their known crystal structures. The transformation of the yellow form to the green form by heating (quasi-irreversible thermochromism) is also discussed.

THE great interest in tetrachlorocuprates(II) derives from the fact that they may assume various structural geometries. A combination of size and hydrogen-bond effects of counter ions is of fundamental importance in determining the co-ordination geometry of the chlorocuprate(II) ions.[1,2] The use of dications as counter ions, although limited, has shown interesting results as in the case of the ethylenediammonium,[3,4] piperazinium, [5] and *N*-phenylpiperazinium ions.[6]

In the case of the *N*-benzylpiperazinium dication, $[bzpipzn]^{2+}$, although it should behave like the *N*-phenylpiperazinium dication since it has similar dimensions and almost similar hydrogen bonding ability, two tetrachlorocuprates(II), one green of formula $[bzpipzn][CuCl_4]$ and one yellow of formula $[bzpipzn][CuCl_4]\cdot0.5H_2O$ are separated at room temperature. In this paper their crystal structures and physical properties are investigated in order to clarify the factors determining their structural differences.

EXPERIMENTAL

Preparation of the Complexes.—The green compound $[bzpipzn][CuCl_4]$ was separated by mixing copper(II) chloride dihydrate in methanol and the amine in concentrated hydrogen chloride (Found: C, 34.45; H, 4.80; Cl, 36.90; N, 7.35. Calc. for $C_{11}H_{18}Cl_4CuN_2$: C, 34.40; H, 4.75; Cl, 37.00; N, 7.30%). The yellow compound $[bzpipzn][CuCl_4]\cdot0.5H_2O$ separated after the precipitation of the green form, by standing the same solution for several days at room temperature. The crystal selected for *X*-ray data collection was cut from a very large geminate crystal (Found: C, 33.70; H, 4.90; Cl, 36.70; N, 7.20. Calc. for $C_{11}H_{19}Cl_4CuN_2O_{0.5}$: C, 33.65; H, 4.90; Cl, 36.15; N, 7.15%).

Physical Measurements.—All physical measurements were performed as reported in ref. 6.

Crystallographic Data Collection.—The crystals selected for *X*-ray analysis were sealed on a glass fibre and directly mounted, in a random orientation, on a Philips PW 1100 automated four-circle diffractometer at 18—20 °C. Details specific to the *X*-ray diffraction data collection and processing are reported in Table 1.

For the yellow compound, the space group was determined unambiguously from a survey of systematic absences. For the green compound, inspection of the complete data set revealed the systematic absences $0k0$; $k = 2n + 1$. This condition is consistent with space groups $P2_1m$ (C_{2h}^2, no. 11) and $P2_1$ (C_2^2, no. 4). The latter was chosen as the correct space group, and confirmed by successful refinement, only on the basis of distribution of peaks in the Patterson function,[7] because the results of the *E*-statistic were intermediate between a centric and acentric prediction.

All data were corrected for Lorentz and polarization effects, but not for absorption in view of the small and almost isotropic crystal dimensions. The background time was 10 s at the beginning and end of the scan. Two standards every 120 reflections were collected, but no significant changes were observed.

Structure Determination and Refinement.—The analytical form [8a] of the scattering factors for Cu, Cl, O, N, C, and H was used throughout; both the real and imaginary components of anomalous dispersion [8b] were included for all non-hydrogen atoms. Refinement was by full-matrix least-squares with $\Sigma w(|F_o|-|F_c|)^2$ being minimized; discrepancy indices used below are $R = (\Sigma||F_o|-|F_c||)/\Sigma|F_c|$ and $R' = \Sigma w^{\frac{1}{2}}||F_o|-|F_c||/\Sigma w^{\frac{1}{2}}|F_o|$.

Major calculations were performed on the CYBER 76 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale at Bologna, by using the 'SHELX-76' system of programs [9] for direct methods, Fourier and least-squares calculations, and Johnson's ORTEP program [10] for drawing.

The structure of the yellow hemihydrate compound was determined by conventional heavy-atom methods and refined by full-matrix least-squares techniques to a final $R = 0.036$ and $R' = 0.038$ ($w = 1$). In the final least-squares cycles the Cu, Cl, O, and the phenyl C atoms were allowed to vibrate anisotropically; the thermal parameters of the hydrogen atoms, located from a Fourier-difference map, were held fixed. During the refinement zero weight was assigned to three strong low-order reflections, which may be affected by secondary absorption.

The structure of the green anhydrous compound was solved by direct methods; the best E-map, based on 452 $E(hkl)$ values >1.50, clearly showed the positions of all the Cu and the Cl atoms, and all the remaining non-hydrogen atoms were found from difference-Fourier maps. Blocked full-matrix least-squares refinements of structural parameters led to a final $R = 0.067$ and $R' = 0.070$ [$w = 1.31/\sigma^2(F_o) + 0.000\,024\,F_o^2$]; only the Cu and the Cl atoms were allowed to vibrate anisotropically, the four phenyl rings were treated as rigid groups, with mean isotropic thermal parameters, and the hydrogen atoms were added as fixed contributors, at their calculated positions. Two chlorine atoms appear to be slightly disordered, in view of their large B_{ij} values. No attempts were made to determine the chirality of the crystal.

TABLE 1

Summary of crystal-data collection [a]

	[bzpipzn][CuCl$_4$]·0.5H$_2$O	[bzpipzn][CuCl$_4$]
Radiation	Mo-K_α [b]	Cu-K_α [b]
λ/Å	0.710 69	1.541 78
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/a$ (C^5_{2h}, no. 14)	$P2_1$ (C^2_2, no. 4)
a/Å	17.015(1)	12.075 7(3)
b/Å	16.977(2)	28.479 8(10)
c/Å	11.377(2)	9.925 8(9)
β/°	97.156(4)	109.54(1)
U/Å^3	3 260.9	3 217.1
Z	8	8
M	392.64	383.53
D_c/g cm^{-3}	1.599	1.584
D_m/g cm^{-3} [c]	1.59	1.59
Reflections measured	$-h_{max.} \leqslant h \leqslant h_{max.}$ with k and $l \geqslant 0$	$-h_{max.} \leqslant h \leqslant h_{max.}$ with k and $l \geqslant 0$
Scan type	θ—2θ	ω—2θ
θ range/° ($d_{min.}$/Å)	2.50—24.00 (0.87)	3.0—55.0 (0.94)
Scan speed/° min^{-1}	3.0	3.6
Scan width/°	1.0	1.5
Collected reflections	5 298	4 089
Non-zero independent data	5 096	4 075
Observed reflections with $I > 3.0\sigma(I)$ [d]	3 132	2 176
Approximate crystal size/mm	0.29 × 0.19 × 0.16	0.10 × 0.10 × 0.09
Absorption coefficient/cm^{-1}	18.9	76.3 [e]
Absorption correction	not applied	not applied

[a] The unit-cell parameters and their e.s.d.s (estimated standard deviations) 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 (see user manual for Philips PW 1100) for a randomly oriented crystal. [b] Graphite monochromated. [c] By flotation in CCl$_4$. [d] $\sigma(I) = (\text{peak counts} + \text{total background counts})^{\frac{1}{2}}$. [e] The variation in transmittance was estimated to be ±3%.

For both structures final fractional atomic co-ordinates of the non-hydrogen atoms are given in Tables 2 and 3.

Temperature factors of these atoms, hydrogen-atom

TABLE 2

Atomic fractional co-ordinates for [bzpipzn][CuCl$_4$]·0.5H$_2$O

Atom	x	y	z
Cu(1)	0.101 7(1)	0.373 3(1)	0.954 0(1)
Cu(2)	0.272 3(1)	0.120 4(1)	0.445 1(1)
Cl(11)	0.010 2(1)	0.426 3(1)	0.818 4(2)
Cl(12)	0.174 6(1)	0.433 1(1)	1.115 7(2)
Cl(13)	0.201 4(1)	0.351 7(1)	0.851 0(2)
Cl(14)	0.025 0(1)	0.298 8(1)	1.054 8(2)
Cl(21)	0.149 7(1)	0.146 5(1)	0.347 7(2)
Cl(22)	0.335 7(1)	0.225 5(1)	0.384 1(2)
Cl(23)	0.361 3(1)	0.027 9(1)	0.407 9(2)
Cl(24)	0.239 4(1)	0.072 7(2)	0.613 8(2)
O	0.261 7(4)	0.264 1(3)	0.125 7(5)
N(1)	0.121 6(4)	0.417 8(4)	0.370 3(6)
C(2)	0.186 5(5)	0.359 4(5)	0.406 1(7)
C(3)	0.174 1(4)	0.320 1(5)	0.521 1(7)
N(4)	0.095 0(3)	0.280 5(3)	0.511 7(5)
C(5)	0.030 4(4)	0.340 4(5)	0.478 5(7)
C(6)	0.041 5(5)	0.381 2(5)	0.362 2(7)
C(7)	0.085 1(5)	0.237 2(5)	0.625 8(7)
H(11)	0.124(4)	0.440(4)	0.286(6)
H(12)	0.134(4)	0.461(4)	0.416(6)
H(21)	0.239(4)	0.392(4)	0.415(6)
H(22)	0.185(4)	0.321(4)	0.341(6)
H(31)	0.179(4)	0.353(4)	0.584(6)
H(32)	0.213(4)	0.279(4)	0.534(6)
H(41)	0.087(4)	0.245(4)	0.438(6)
H(51)	0.031(4)	0.370(4)	0.545(6)
H(52)	−0.032(4)	0.306(4)	0.466(6)
H(61)	−0.005(4)	0.428(4)	0.341(6)
H(62)	0.039(4)	0.339(4)	0.302(7)
H(71)	0.084(4)	0.271(4)	0.683(6)
H(72)	0.128(4)	0.204(4)	0.644(6)
H(91)	0.030(4)	0.106(4)	0.505(6)
H(101)	−0.082(4)	0.038(4)	0.520(6)
H(111)	−0.181(4)	0.062(4)	0.621(5)
H(121)	−0.153(4)	0.193(4)	0.749(6)
H(131)	−0.039(4)	0.264(4)	0.737(6)
H(01)	0.259(4)	0.308(4)	0.109(7)
C(8)	0.007 7(3)	0.193 9(3)	0.621 2(5)
C(9)	−0.006 7(4)	0.126 4(4)	0.553 4(6)
C(10)	−0.074 2(4)	0.083 2(4)	0.557 9(7)
C(11)	−0.129 7(4)	0.105 9(4)	0.631 3(6)
C(12)	−0.116 3(4)	0.172 2(5)	0.697 6(6)
C(13)	−0.047 6(4)	0.217 0(4)	0.693 8(6)
C(28)	0.101 1(3)	0.029 3(3)	0.960 5(5)
C(29)	0.075 3(4)	0.026 1(4)	0.841 4(6)
C(30)	0.055 3(5)	−0.043 7(5)	0.786 2(7)
C(31)	0.060 0(4)	−0.113 2(5)	0.849 4(8)
C(32)	0.084 4(4)	−0.110 0(4)	0.969 1(8)
C(33)	0.104 0(4)	−0.039 9(4)	1.024 3(6)
N(21)	0.371 8(3)	0.101 3(3)	0.988 1(5)
C(22)	0.321 7(5)	0.156 9(5)	0.911 9(8)
C(23)	0.234 7(4)	0.132 4(5)	0.904 2(7)
N(24)	0.210 1(3)	0.126 8(4)	1.026 0(5)
C(25)	0.261 6(4)	0.068 5(4)	1.100 7(7)
C(26)	0.348 5(4)	0.093 0(5)	1.110 1(6)
C(27)	0.121 7(4)	0.106 8(5)	1.020 9(7)
H(211)	0.419(4)	0.112(4)	1.014(5)
H(212)	0.375(3)	0.053(4)	0.955(5)
H(221)	0.332(4)	0.210(5)	0.942(7)
H(222)	0.345(4)	0.151(4)	0.825(7)
H(231)	0.193(4)	0.173(4)	0.858(6)
H(232)	0.222(4)	0.076(5)	0.867(7)
H(241)	0.216(4)	0.181(4)	1.067(6)
H(251)	0.257(4)	0.014(4)	1.069(6)
H(252)	0.244(4)	0.059(4)	1.182(6)
H(261)	0.382(4)	0.049(4)	1.165(6)
H(262)	0.362(4)	0.146(4)	1.158(7)
H(271)	0.110(4)	0.101(4)	1.111(7)
H(272)	0.094(4)	0.152(4)	0.970(6)
H(291)	0.071(4)	0.072(4)	0.804(6)
H(301)	0.039(4)	−0.047(4)	0.706(7)
H(311)	0.053(4)	−0.164(4)	0.816(6)
H(321)	0.084(4)	−0.154(4)	1.003(6)
H(331)	0.120(4)	−0.037(4)	1.109(6)
H(02)	0.280(4)	0.264(5)	0.192(7)

TABLE 3

Atomic fractional co-ordinates for [bzpipzn][CuCl$_4$]

Atom	*x*	*y*	*z*
Cu(1)	0.564 2(4)	0.250 0	0.149 5(4)
Cu(2)	0.364 3(4)	0.068 2(2)	0.575 2(4)
Cu(3)	0.365 4(3)	0.422 8(2)	0.654 6(4)
Cu(4)	0.850 6(4)	0.104 2(2)	0.911 6(4)
Cl(11)	0.425 5(6)	0.223 0(3)	−0.051 3(7)
Cl(12)	0.586 1(7)	0.308 7(3)	0.303 8(8)
Cl(13)	0.701 5(8)	0.267 8(3)	0.053 6(8)
Cl(14)	0.532 3(7)	0.193 7(3)	0.295 3(8)
Cl(21)	0.270 8(8)	0.108 7(4)	0.375 6(9)
Cl(22)	0.280 4(9)	0.115 0(4)	0.695 1(9)
N(1)	0.607 9(19)	0.213 5(8)	0.756 6(23)
C(2)	0.509 6(27)	0.188 1(11)	0.648 6(30)
C(3)	0.408 9(23)	0.221 6(10)	0.580 1(28)
N(4)	0.447 7(19)	0.262 9(7)	0.512 3(23)
C(5)	0.548 1(24)	0.286 3(10)	0.632 9(29)
C(6)	0.651 2(24)	0.255 3(10)	0.692 1(29)
C(7)	0.355 0(24)	0.298 7(10)	0.454 1(29)
C(8) *	0.249 0(16)	0.284 7(8)	0.332 0(20)
C(9)	0.252 9(16)	0.255 7(8)	0.220 3(20)
C(10)	0.149 5(16)	0.244 5(8)	0.110 1(20)
C(11)	0.042 2(16)	0.262 2(8)	0.111 5(20)
C(12)	0.038 3(16)	0.291 1(8)	0.223 2(20)
C(13)	0.141 7(16)	0.302 4(8)	0.333 4(20)
N(21)	0.388 8(21)	0.117 1(9)	0.018 2(24)
C(22)	0.470 9(28)	0.083 9(12)	0.121 3(33)
C(23)	0.415 7(21)	0.037 0(9)	0.120 4(25)
N(24)	0.298 5(19)	0.042 1(8)	0.138 0(22)
C(25)	0.218 4(23)	0.069 9(10)	0.028 4(27)
C(26)	0.268 9(32)	0.120 3(13)	0.022 5(38)
C(27)	0.256 4(28)	−0.007 6(12)	0.160 5(34)
C(28) *	0.231 3(16)	−0.037 8(6)	0.031 7(16)
C(29)	0.319 5(16)	−0.070 4(6)	0.039 4(16)
C(30)	0.304 1(16)	−0.103 0(6)	−0.070 2(16)
C(31)	0.200 5(16)	−0.103 1(6)	−0.187 4(16)
C(32)	0.112 3(16)	−0.070 5(6)	−0.195 1(16)
C(33)	0.127 7(16)	−0.037 9(6)	−0.085 6(16)
Cl(23)	0.514 3(9)	0.046 7(4)	0.505 9(12)
Cl(24)	0.371 6(18)	0.010 8(6)	0.725 1(20)
Cl(31)	0.215 0(6)	0.445 1(3)	0.449 4(7)
Cl(32)	0.317 6(6)	0.476 5(3)	0.802 4(7)
Cl(33)	0.499 2(6)	0.410 8(3)	0.565 7(8)
Cl(34)	0.380 6(8)	0.361 7(3)	0.802 9(8)
Cl(41)	0.704 8(9)	0.125 5(4)	0.988 4(10)
Cl(42)	0.850 0(14)	0.165 6(5)	0.783 1(20)
Cl(43)	0.942 9(8)	0.060 1(3)	1.108 3(9)
Cl(44)	0.932 9(9)	0.056 9(4)	0.789 6(9)
N(41)	0.386 1(18)	0.462 9(7)	0.255 2(22)
C(42)	0.438 0(25)	0.421 9(11)	0.192 0(30)
C(43)	0.347 8(24)	0.385 0(10)	0.128 7(28)
N(44)	0.239 1(16)	0.404 8(7)	0.019 0(20)
C(45)	0.189 9(24)	0.447 8(10)	0.080 4(28)
C(46)	0.283 3(23)	0.481 1(10)	0.144 7(27)
C(47)	0.149 1(24)	0.368 5(10)	−0.036 7(29)
C(48) *	0.041 8(14)	0.384 1(7)	−0.155 0(18)
C(49)	−0.068 4(14)	0.373 6(7)	−0.146 2(18)
C(50)	−0.170 0(14)	0.385 2(7)	−0.259 0(18)
C(51)	−0.161 3(14)	0.407 2(7)	−0.380 5(18)
C(52)	−0.051 1(14)	0.417 7(7)	−0.389 3(18)
C(53)	0.050 4(14)	0.406 2(7)	−0.276 6(18)
N(61)	0.823 0(21)	0.053 8(8)	0.476 9(24)
C(62)	0.744 6(28)	0.086 7(11)	0.371 1(32)
C(63)	0.796 6(27)	0.134 4(11)	0.364 6(32)
N(64)	0.909 3(17)	0.128 0(7)	0.340 9(20)
C(65)	0.990 5(24)	0.098 5(10)	0.454 4(28)
C(66)	0.933 6(22)	0.050 9(9)	0.456 8(26)
C(67)	0.963 4(26)	0.174 9(11)	0.318 8(30)
C(68) *	0.978 4(19)	0.209 7(7)	0.441 0(19)
C(69)	0.895 5(19)	0.243 4(7)	0.444 3(19)
C(70)	0.918 6(19)	0.273 7(7)	0.560 8(19)
C(71)	1.024 5(19)	0.270 4(7)	0.673 9(19)
C(72)	1.107 5(19)	0.236 7(7)	0.670 7(19)
C(73)	1.084 4(19)	0.206 4(7)	0.554 1(19)

* Phenyl rings were treated as rigid groups of D_{6h} idealized geometry with C–C distances of 1.395 Å.

parameters, tables of all bond lengths, angles, hydrogen-bonding distances and angles, and lists of observed and calculated structure factors are in Supplementary Publication No. SUP 23070 (12 pp.).*

Analyses.—N, C, and H were analysed by Mr. G. Pistoni with a Carlo Erba Elemental Analyser model 1106. Halides were directly determined in an aqueous solution of the complexes using the Volhard method.

RESULTS AND DISCUSSION

Description of the Structures.—The structure of the yellow hydrate form consists of two crystallographically independent [CuCl$_4$]$^{2-}$ anions, with an essentially D_{2d} symmetry, two [bzpipzn]$^{2+}$ cations, and a water molecule of crystallization (Figure 1). All the discrete moieties are linked in an infinite three-dimensional network by hydrogen-bonding interactions (Figure 2).

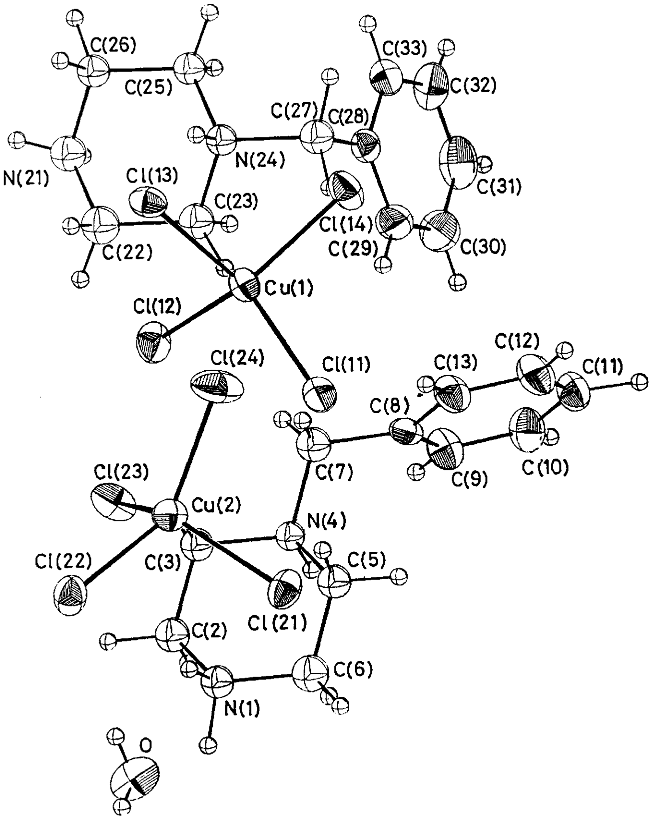

FIGURE 1 ORTEP drawing of [bzpipzn][CuCl$_4$]·0.5H$_2$O showing the atom numbering. Non-hydrogen atoms are represented by 40% probability ellipsoids, and hydrogen atoms by spheres of 0.1 Å radius

The structure of the green anhydrous form consists of four crystallographically independent flattened tetrahedral [CuCl$_4$]$^{2-}$ anions with nearly idealized D_{2d} symmetry, and four independent [bzpipzn]$^{2+}$ cations, linked to the anions through their *N*-bonded hydrogen atoms (Figure 3 and 4). Selected bond distances and angles for both the complexes appear in Table 4.

As a criterion to evaluate the extent of distortion from T_d symmetry of the [CuCl$_4$]$^{2-}$ chromophores, we have

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

chosen the average of the two largest (greater than 109.5°) Cl–Cu–Cl angles, defined as θ.[11] The mean values of the two Cl–Cu–Cl angles in the yellow form are 132.2(1) and 133.8(1)°, respectively. In the green complex the four crystallographically independent units present values of 137.8 and 135.3° respectively for the anions I and III (by assigning to anions the numbering of their Cu atoms), indicating high and quite similar tetragonal distortions, and of 151.8 and 150.9° for the anions II and IV respectively, which are closest to the value of the square-planar limit, rather than to the tetrahedral one. These θ values are within the rather wide range (125.6—159.2°) previously found [2,6,12] for many chlorocuprates(II) containing discrete $[CuCl_4]^{2-}$ anions having D_{2d} symmetry.

The most notable structural feature of the green compound is the presence in the same phase of very unequally flattened $[CuCl_4]^{2-}$ tetrahedra, as previously found only for $[H_3\overset{+}{N}CH_2CH_2(\overset{+}{N}HCH_2CH_2\overset{+}{N}H_3CH_2CH_2)]_4[Cu_5Cl_{22}]$,[12] which contains one $[Cu_3Cl_{14}]^{8-}$ and two $[CuCl_4]^{2-}$ with flattening angles θ of 125.64(5), and 141.82(5)°, respectively. However, the different extent of tetrahedral flattening in the latter compound was considered as depending on crystal packing forces, while in the present case it appears to be due to hydrogen-bonding effects, as later reported. The values of individual and mean Cu–Cl bond distances of the two least flattened anions are within the ranges (2.18—2.28 Å) found previously for non-planar $[CuCl_4]^{2-}$

TABLE 4

Bond distances (Å), bond angles (°) and e.s.d.s within the $[CuCl_4]^{2-}$ anions

(*a*) $[bzpipzn][CuCl_4]\cdot 0.5H_2O$			
Cu(1)–Cl(11)	2.239(2)	Cu(2)–Cl(21)	2.280(2)
Cu(1)–Cl(12)	2.321(2)	Cu(2)–Cl(22)	2.240(2)
Cu(1)–Cl(13)	2.209(2)	Cu(2)–Cl(23)	2.258(2)
Cu(1)–Cl(14)	2.234(2)	Cu(2)–Cl(24)	2.218(3)
Cl(11)–Cu(1)–Cl(12)	128.9(1)	Cl(21)–Cu(2)–Cl(22)	98.2(1)
Cl(11)–Cu(1)–Cl(13)	102.4(1)	Cl(21)–Cu(2)–Cl(23)	129.7(1)
Cl(11)–Cu(1)–Cl(14)	100.4(1)	Cl(21)–Cu(2)–Cl(24)	100.2(1)
Cl(12)–Cu(1)–Cl(13)	97.1(1)	Cl(22)–Cu(2)–Cl(23)	97.8(1)
Cl(12)–Cu(1)–Cl(14)	97.4(1)	Cl(22)–Cu(2)–Cl(24)	137.9(1)
Cl(13)–Cu(1)–Cl(14)	135.6(1)	Cl(23)–Cu(2)–Cl(24)	98.9(1)
(*b*) $[bzpipzn][CuCl_4]$			
Cu(1)–Cl(11)	2.266(7)	Cu(3)–Cl(31)	2.268(7)
Cu(1)–Cl(12)	2.223(9)	Cu(3)–Cl(32)	2.273(9)
Cu(1)–Cl(13)	2.229(11)	Cu(3)–Cl(33)	2.212(10)
Cu(1)–Cl(14)	2.278(9)	Cu(3)–Cl(34)	2.235(10)
Cu(2)–Cl(21)	2.243(9)	Cu(4)–Cl(41)	2.225(13)
Cu(2)–Cl(22)	2.241(13)	Cu(4)–Cl(42)	2.165(18)
Cu(2)–Cl(23)	2.228(14)	Cu(4)–Cl(43)	2.276(9)
Cu(2)–Cl(24)	2.194(19)	Cu(4)–Cl(44)	2.252(13)
Cl(11)–Cu(1)–Cl(12)	138.0(3)	Cl(31)–Cu(3)–Cl(32)	97.8(3)
Cl(11)–Cu(1)–Cl(13)	97.9(3)	Cl(31)–Cu(3)–Cl(33)	97.9(3)
Cl(11)–Cu(1)–Cl(14)	95.1(3)	Cl(31)–Cu(3)–Cl(34)	134.6(4)
Cl(12)–Cu(1)–Cl(13)	100.9(3)	Cl(32)–Cu(3)–Cl(33)	136.0(3)
Cl(12)–Cu(1)–Cl(14)	95.6(3)	Cl(32)–Cu(3)–Cl(34)	96.2(3)
Cl(13)–Cu(1)–Cl(14)	137.7(3)	Cl(33)–Cu(3)–Cl(34)	101.2(4)
Cl(21)–Cu(2)–Cl(22)	88.9(4)	Cl(41)–Cu(4)–Cl(42)	97.7(6)
Cl(21)–Cu(2)–Cl(23)	95.1(4)	Cl(41)–Cu(4)–Cl(43)	94.2(4)
Cl(21)–Cu(2)–Cl(24)	151.2(6)	Cl(41)–Cu(4)–Cl(44)	152.9(4)
Cl(22)–Cu(2)–Cl(23)	152.4(4)	Cl(42)–Cu(4)–Cl(43)	148.9(5)
Cl(22)–Cu(2)–Cl(24)	90.3(7)	Cl(42)–Cu(4)–Cl(44)	94.7(6)
Cl(23)–Cu(2)–Cl(24)	98.7(7)	Cl(43)–Cu(4)–Cl(44)	87.4(4)

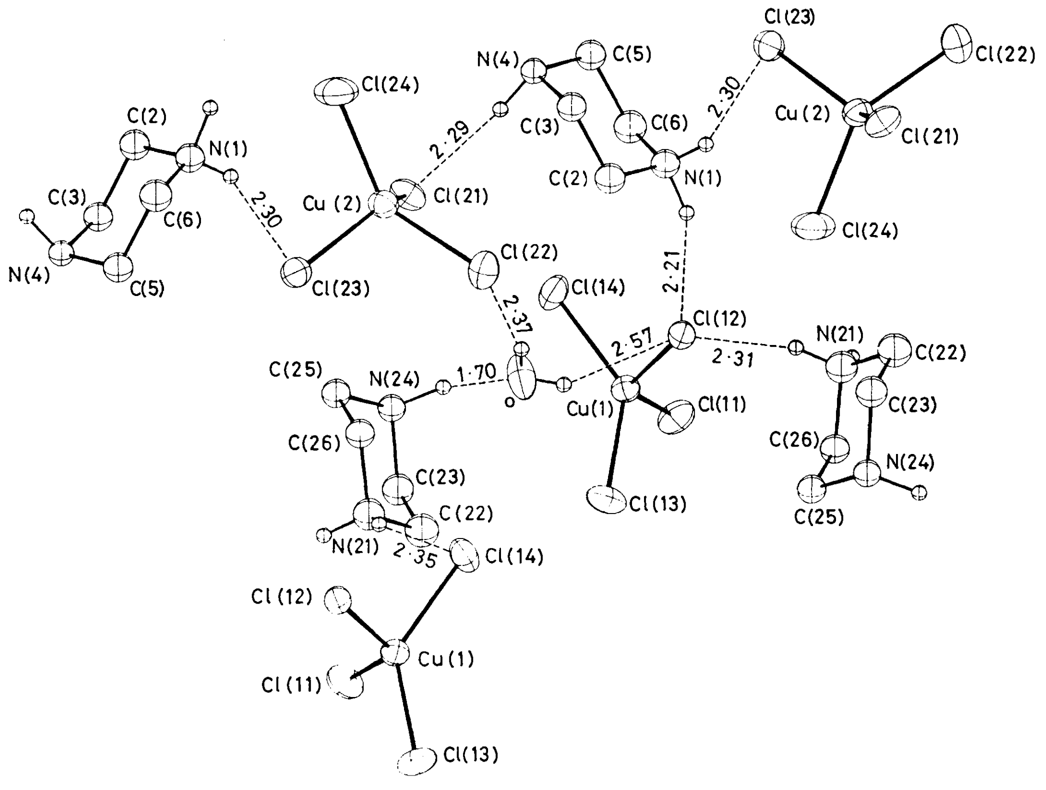

FIGURE 2 Hydrogen bonds (dashed lines) and distances (Å) in $[bzpipzn][CuCl_4]\cdot 0.5H_2O$. Benzyl groups and C-bonded H atoms have been omitted for clarity

anions, while for the two most flattened $[CuCl_4]^{2-}$ tetrahedra, two Cu–Cl bond lengths [Cu(2)–Cl(24) = 2.194(19) and Cu(4)–Cl(42) = 2.165(18) Å], related to the Cl atoms which appear to be slightly disordered, are artificially shortened due to the large thermal motion of the chlorine atoms.

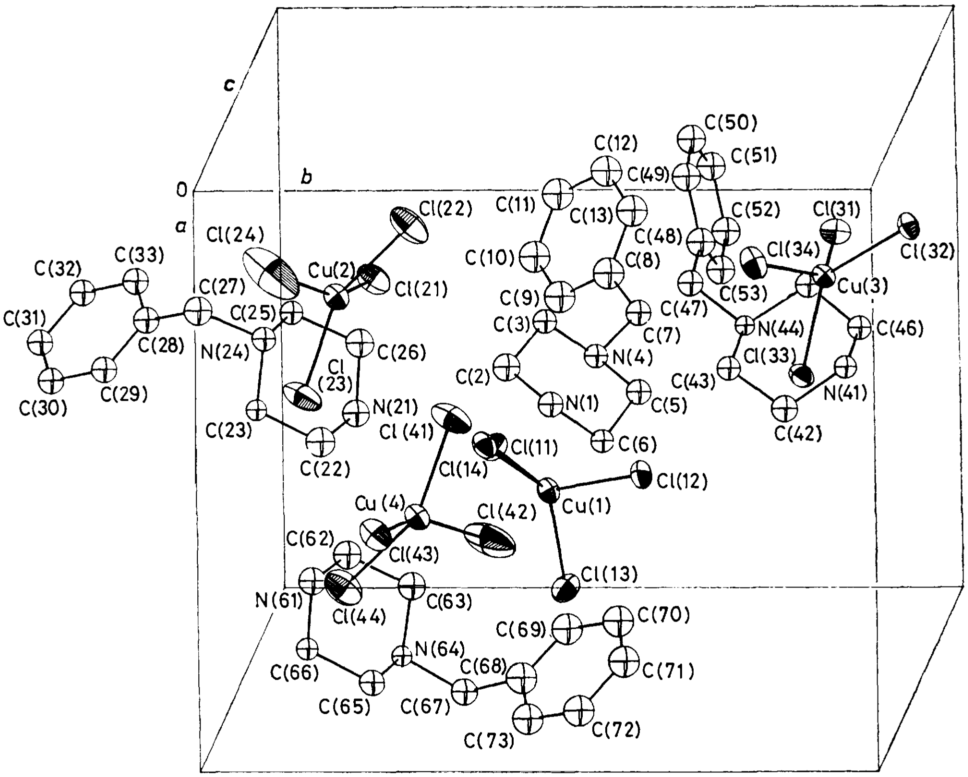

Figure 3 ORTEP drawing of the half unit cell (to *b*/2) of [bzpipzn]$[CuCl_4]$ showing the atom numbering scheme and thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity

The network of N–H · · · Cl interactions of the green compounds on which the crystal packing depends is reported in Figure 4. The three N-bonded H atoms of each cation are involved in strong interactions with Cl atoms belonging to three distinct $[CuCl_4]^{2-}$ anions, two of which are related by a unit-cell translation along the *c* axis. Similarly, each anion bridges, through hydrogen-bonding interaction, three $[bzpipzn]^{2+}$ cations, two of which are again related by a cell translation along the *c* axis. However, in the most flattened $[CuCl_4]^{2-}$ tetrahedra there are three Cl atoms involved in hydrogen bonding, while one Cl atom of both the least flattened anions is hydrogen-bonded to two $[bzpipzn]^{2+}$ cations, so that only two Cl atoms in both the anions are involved in this type of interaction. Thus, to the different dispositions of the hydrogen bonds we attribute the different extent of tetragonal distortion between the unequally flattened $[CuCl_4]^{2-}$ anions, for which no other short interionic contacts were found.

In [bzpipzn]$[CuCl_4]\cdot 0.5H_2O$ the hydrogen-bonding ability of the dication toward the Cl atoms appears diminished, with respect to the green anhydrous form, owing to the presence of water of crystallization. The O–H · · · Cl interactions, which replace $\overset{+}{N}$–H · · · Cl hydrogen bonds, and the formation of a triple hydrogen bond to a Cl atom led to a lower reduction of the fractional charges at the Cl atoms, whose electrostatic repulsion makes a slightly flattened tetrahedral geometry preferential.[2] It is interesting to note that the degree of distortion of the tetrahedron at Cu(2) [θ = 133.8(1)°] is very close to that found in [*cyclo*-$(NPMe_2)_5H_2$-1,5]-$[CuCl_4]\cdot H_2O$ [13] [θ = 133.5(1)°], where three Cl atoms are similarly involved in two N–H · · · Cl and one O–H · · · Cl hydrogen-bonding interactions. Also, the unusually long bond distance of 2.321(2) Å, related to the Cl atom involved in three hydrogen bonds, is a clear confirmation of the strong influence of the hydrogen bonding on bond lengths, as well as on bond angles.

Present results indicate that cation size and hydrogen bonding are the major contributors to the factors which determine the preferred co-ordination geometry about the copper atom in chlorocuprates(II).[2,6,11,12,14,15] The $[bzpipzn]^{2+}$ cation appears sufficiently bulky to prevent the inter-anion contacts which, for smaller cations and in the presence of strong hydrogen bonds, lead to polymeric layer or ribbon structures [2] with five- or six-co-ordination about the copper atom.

In both the complexes bond distances and angles in the [bzpipzn]$^{2+}$ cations, whose piperazine ring exhibits the usual ' chair ' conformation, are in the normal range within the limits of precision of the structure analysis.

Electronic and Far-i.r. Spectra, D.S.C., and Magnetic Measurements.—The electronic absorption spectrum of [bzpipzn][CuCl$_4$]·0.5H$_2$O, which shows two *d–d* bands, at 6 350 and 9 390 cm^{-1}, strictly agrees with the structural results and with those normally found for similarly flattened tetrahedral [CuCl$_4$]$^{2-}$ (D_{2d} symmetry) anions.[2,6,16-19]

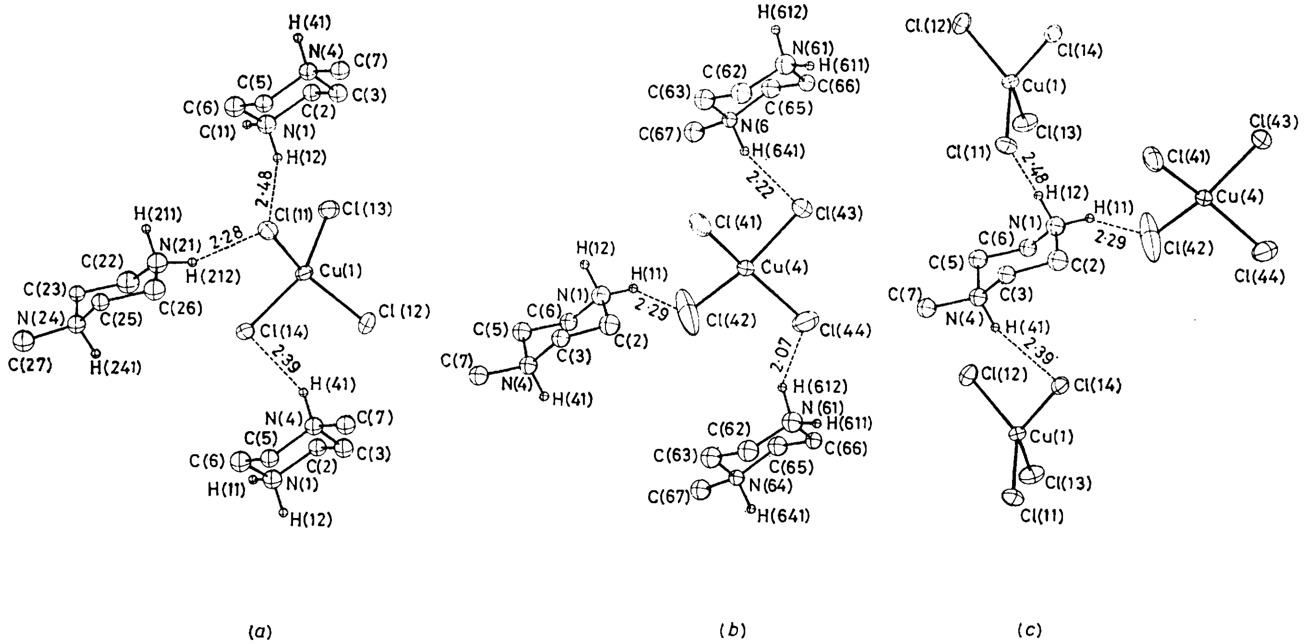

FIGURE 4 Hydrogen bonds (dashed lines) and distances (Å) involving (*a*) a ' least-flattened ' [CuCl$_4$]$^{2-}$ anion, (*b*) a ' flattest ' [CuCl$_4$]$^{2-}$ anion, (*c*) a [bzpipzn]$^{2+}$ cation. Phenyl rings and C-bonded H atoms have been omitted for clarity

The room-temperature electronic spectrum of the green compound in the solid state consists of an unresolved band envelope in the near-i.r. region centred at 10 250 cm^{-1} with a not-well resolved shoulder around 12 500 cm^{-1}, arising from *d–d* transitions. The presence of four unequally flattened [CuCl$_4$]$^{2-}$ anions in the unit cell does not permit rationalization of this spectrum.

The shift to lower energies of the *d–d* bands in the yellow complex with respect to the green one depends on the fact that the former complex contains [CuCl$_4$]$^{2-}$ anions having less distorted tetrahedral geometries than the latter. Since this fact is directly associated with the presence of hydrogen bonds in the yellow form weaker than in the green, it is very surprising that upon heating the yellow form converts to the green form with a consequent shift of the *d–d* bands to higher energies. This fact is also evidenced by differential scanning calorimetric (d.s.c.) analysis of the yellow complex which shows an endothermic peak in the temperature range 87—120 °C.

The thermochromism of some [CuCl$_4$]$^{2-}$ anions is well known, but it has always been associated with a change in the co-ordination geometry which is favoured by a weakening of the hydrogen-bonding network as a result of the increasing disorder due to the thermal motion.[5,11,13,20,21]

The apparent inconsistency in our complex, in which higher temperatures seem to favour a more ordered geometry (green form), is due to the thermal extrusion of the water molecules which permits a strengthening of the hydrogen bonding between the anions and the cations. From exposure to moisture the green form slowly reconverts to the yellow form over several months.

The room-temperature magnetic moment of 1.86 B.M.* for both the complexes excludes the presence of any type of exchange interactions among the copper ions.

The far-i.r. spectra of the solid compounds, showing a broad very strong band at 310 (yellow form) and 300 cm^{-1} (green form), agree well with the structures.[5,6,20,22-25] Some differences are observed between the yellow and the green form, regarding not only the positions of ν(Cu–Cl) at higher energies in the former than in the latter, but also the presence of a strong band at 264 cm^{-1}, assignable to the b_2 stretching vibration, only in the yellow form, which is always present in tetrachlorocuprates(II) having D_{2d} symmetry.[5,6,20,22-25]

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* Throughout this paper: 1 B.M. = 9.274×10^{-24} A m^2.

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