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**Registry No.**  $[\text{Cu}_2(\text{Me}_3\text{dien})_2(\text{BiIm})](\text{BPh}_4)_2$ , 66810-56-8;  $[\text{Cu}_2(\text{Et}_3\text{dien})_2(\text{Im})](\text{ClO}_4)_3$ , 68152-09-0;  $[\text{Cu}_2(\text{Me}_3\text{dien})_2(\text{Im})](\text{ClO}_4)_3$ , 68152-11-4;  $[\text{Cu}_2(\text{dien})_2(\text{Im})](\text{ClO}_4)_3$ , 68152-13-6;  $[\text{Cu}_2(\text{dpt})_2(\text{Im})](\text{ClO}_4)_3$ , 68152-15-8.

**Supplementary Material Available:** Tables I (analytical data) and VIII–XI (calculated and observed magnetic susceptibility data) and listings of observed and calculated structure factors (45 pages). Ordering information is given on any current masthead page.

## References and Notes

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## Halocuprates(II) of the *N*-Phenylpiperazinium Mono- and Dications: Crystal and Molecular Structure of *N*-Phenylpiperazinium Tetrachlorocuprate(II). Correlation of the Electronic Spectrum vs. Distortion of the $\text{CuCl}_4^{2-}$ Anions from Tetrahedral Symmetry

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The X-ray structure of *N*-phenylpiperazinium tetrachlorocuprate(II),  $(\text{C}_{10}\text{H}_{16}\text{N}_2)\text{CuCl}_4$ , was determined by X-ray diffraction methods. Crystals are orthorhombic,  $P2_12_12_1$ , with  $a = 17.698$  (2) Å,  $b = 8.615$  (1) Å,  $c = 9.841$  (1) Å, and  $Z = 4$ . A final  $R$  value of 4.3 was obtained. The structure consists of  $[\text{CuCl}_4]^{2-}$  anions and *N*-phenylpiperazinium diprotonated cations. The  $[\text{CuCl}_4]^{2-}$  anions show a flattened tetrahedral geometry, the two larger Cl–Cu–Cl angles being 141.1 and 143.0°; the dihedral angle is 51.6°. The Cu–Cl distances range from 2.23 to 2.27 Å. All four chlorine atoms are involved in Cl···N interactions, which may be responsible for the large distortion of the  $[\text{CuCl}_4]^{2-}$  ion from the tetrahedral configuration. The *N*-phenylpiperazinium dication shows the usual "chair" configuration. The spectroscopic and magnetic results of the  $[\text{CuCl}_4]^{2-}$  and  $[\text{CuCl}_3\text{Br}]^{2-}$  anions are in agreement with a high distortion of these ions from tetrahedral symmetry. A study of the d–d transition maximum vs. the distortion of the  $\text{CuCl}_4$  chromophore from the  $T_d$  symmetry is also reported. Some compounds containing the monoprotonated amine such as  $(\text{NPhpipzH})_2\text{Cu}_2\text{X}_6$  ( $X = \text{Cl}, \text{Br}$ ) and  $(\text{NPhpipzH})_2\text{Cu}_2\text{Cl}_2\text{Br}_4$  are also studied. Their spectroscopic data suggest the presence of dimeric species in them with highly distorted tetrahedral symmetry.

## Introduction

The halocuprate(II) and, in particular, the tetrachlorocuprate(II) anions have been extensively investigated for the great ease with which they assume various geometries, ranging from square planar through tetrahedral and on to trigonal bipyramidal.<sup>2</sup> The geometry of the  $[\text{CuX}_4]^{2-}$  species in the solid state depends on many factors;<sup>2</sup> among them, the interactions due to crystal-packing forces and hydrogen bonding to cations are those on which the investigators may directly act.

Since cations like the piperidinium and morpholinium cations and the piperazinium dication have similar dimensions and therefore similar size effects, only the effect of the hy-

drogen bonding was recently investigated.<sup>3,4</sup>

In this paper the complexes formed between the *N*-phenylpiperazinium mono- and dication (hereafter abbreviated as NPhpipzH and NPhpipzH<sub>2</sub>, respectively) and the copper halides are considered. This cation, which is bulkier than the piperazinium dication but preserves almost the same NH···X hydrogen-bonding ability, exerted between two metal–halogen layers, enabled us to extend our study to the size effects on the tetrahalocuprate(II) geometry.

## Experimental Section

**Preparation of the *N*-Phenylpiperazinium Hydrohalides.** The *N*-phenylpiperazinium dihydrohalide salts were prepared by evaporating slowly and completely an aqueous amine solution neutralized

Table I. Conventional Chemical Analysis Results, Melting Points, and Magnetic Moments

compd	color	% C		% H		% N		% X		mp, °C	$\mu_{\text{eff}}, \mu_B$
		calcd	found	calcd	found	calcd	found	calcd	found		
(NPhpipzH)CuCl <sub>3</sub>	red	36.03	36.00	4.54	4.56	8.41	8.25	31.94	31.60	157-160	1.85
(NPhpipzH)CuClBr <sub>2</sub>	red-brown	28.44	28.40	3.58	3.50	6.64	6.45			187 dec	1.78
(NPhpipzH)CuBr <sub>3</sub>	brown	25.73	25.60	3.24	3.30	6.01	6.04			220 dec	1.94
(NPhpipzH <sub>2</sub> )CuCl <sub>4</sub>	yellow-green	32.49	32.57	4.36	4.41	7.58	7.60	38.38	37.80	185 dec	1.81
(NPhpipzH <sub>2</sub> )CuCl <sub>3</sub> Br	orange	29.06	29.41	3.66	3.88	6.79	6.76			195 dec	1.81
(NPhpipzH <sub>2</sub> )CuBr <sub>4</sub> <sup>a</sup>	black-violet	21.92	23.43	2.94	2.95	5.11	5.85				

<sup>a</sup> The magnetic moment of this compound cannot be measured as it rapidly decomposes.

with concentrated hydrogen halide. The salts were recrystallized from ethanol.

The *N*-phenylpiperazinium monohydrohalide salts were obtained by adding a stoichiometric amount of *N*-phenylpiperazine in ethanol to an ethanolic solution of the *N*-phenylpiperazinium dihydrohalide salt, by heating the mixture slowly until the *N*-phenylpiperazinium dihydrohalide salt was dissolved, and by adding diethyl ether. The compound was recrystallized from ethanol.

**Preparation of the Complexes.** (NPhpipzH<sub>2</sub>)CuCl<sub>4</sub> was obtained by adding drop by drop a hot methanolic *N*-phenylpiperazinium dihydrochloride solution to a hot methanolic CuCl<sub>2</sub>·2H<sub>2</sub>O solution, with a ligand to metal molar ratio of 1:1. By cooling, a yellow-green compound was separated. To obtain crystals useful for the structure analysis the compound was recrystallized from methanol and 2-propanol (1+1).

(NPhpipzH<sub>2</sub>)CuCl<sub>3</sub>Br was obtained by adding an ethanolic CuCl<sub>2</sub>·2H<sub>2</sub>O solution (4 mmol) to a hot ethanolic solution containing the *N*-phenylpiperazinium monohydrochloride salt (4 mmol) and HBr (48%) (4 mmol). An orange compound instantaneously precipitated.

(NPhpipzH)CuCl<sub>3</sub> was separated by concentrating an ethanolic solution containing CuCl<sub>2</sub>·2H<sub>2</sub>O (4 mmol) and *N*-phenylpiperazinium monohydrochloride salt (4 mmol). A red-brown compound instantaneously precipitated.

(NPhpipzH)CuClBr<sub>2</sub> was obtained by dissolving CuBr<sub>2</sub>·3H<sub>2</sub>O and *N*-phenylpiperazinium dihydrochloride in a 1:1 stoichiometric ratio in methanol and adding 2-propanol. The compound is red-brown.

(NPhpipzH<sub>2</sub>)CuBr<sub>4</sub> and (NPhpipzH)CuBr<sub>3</sub> were prepared by mixing CuBr<sub>2</sub>·3H<sub>2</sub>O with an excess of *N*-phenylpiperazine in ethanol and adding HBr (48%) until a violet solution was obtained and then concentrating the solution until a black-violet, impure (NPhpipzH<sub>2</sub>)CuBr<sub>4</sub> compound was obtained. This compound was dissolved in methylcellosolve, and from the concentrated solution standing for some days, red crystalline (NPhpipzH)CuBr<sub>3</sub> separated.

**Physical Measurements.** Electronic, infrared, and far-infrared spectra, magnetic measurements, and conductivities were recorded as previously reported.<sup>4</sup> Differential scanning calorimetric analysis was performed with a Perkin-Elmer DSC-1 instrument.

**Crystallographic Data Collection.** Crystallographic data were determined on a single-crystal diffractometer using Cu K $\alpha$  radiation ( $\lambda$  1.54178 Å). The unit cell dimensions, determined first from rotation and Weissenberg photographs and then refined by least squares using 10 high-angle reflections measured on the diffractometer, and other cell data are as follows:  $(C_{10}H_{16}N_2)CuCl_4$ , formula weight 369.6,  $a = 17.698$  (2) Å,  $b = 8.615$  (1) Å,  $c = 9.841$  (1) Å,  $V = 1500$  Å<sup>3</sup>,  $d_{\text{meas}} = 1.65$  g cm<sup>-3</sup> (by flotation),  $Z = 4$ ,  $d_{\text{calcd}} = 1.64$  g cm<sup>-3</sup>,  $F(000) = 740$ ,  $\mu = 81.6$  cm<sup>-1</sup> (Cu K $\alpha$ ), orthorhombic, space group  $P2_12_12_1$  (from systematic absences). Three-dimensional intensity data were collected at 20 °C using a prismatic crystal (0.13 × 0.13 × 0.56 mm<sup>3</sup>) mounted with the  $c$  axis along the  $\phi$  axis of a Siemens AED computer-controlled diffractometer. Nickel-filtered Cu K $\alpha$  radiation at a takeoff angle of 5° was employed. The pulse-height discriminator was set to accept 90% of the Cu K $\alpha$  peak. The moving counter-moving crystal scan technique was used with a drive speed related to the number of counts on the peaks, the maximum and minimum scan rate being 8 and 2°/min, respectively. The five-point technique was used for the intensity measurements. A standard reflection was remeasured every 20 reflections to check the instrument stability and the crystal stability and alignment: its intensity was practically constant. In his way 1619 reflections were collected using the  $\omega$ - $\theta$  scan technique in the interval  $0^\circ < 2\theta < 140^\circ$ ; 1464 of these, for which  $I > 2\sigma(I)$  ( $\sigma(I) = [\text{total counts} + (0.05 \times \text{intensity})]^{1/2}$ ), were employed in the analysis; the remaining 155 were considered "unobserved". The structure amplitudes were obtained after the usual

Lorentz and polarization reduction, and the absolute scale was established first by Wilson's method and then by least-squares refinement. No correction for absorption was applied.

**Solution and Refinement of the Structure.** The structure was solved by Patterson and Fourier methods using the heavy-atom technique, localizing first the copper atom from the Patterson synthesis and then the remaining nonhydrogen atoms from the successive Fourier maps.

The refinement was carried out by means of full-matrix least squares isotropically to  $R = 11.8$  and anisotropically to  $R = 5.0$  minimizing the function  $R = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ , where  $w$  is the weight calculated as  $w = K / ((\sum F_o)^2 + gF_o^2)$  ( $K = 1.3464$ ,  $g = 0.0027$ ). At this stage a  $\Delta F$  synthesis revealed all hydrogen atoms, which were refined with isotropic temperature factors: the improvement of the  $R$  index was to 4.3%. In the last stage of the refinement no parameter shifted by more than 0.5 times its estimated standard deviation. No evidence for secondary extinction was found. Scattering factors for Cu, Cl, N, and C were those of Cromer and Mann<sup>5</sup> and for hydrogen were those of Stewart, Davidson, and Simpson.<sup>6</sup> The effects of anomalous dispersion were corrected by including the values of  $f'$  and  $f''$  in the calculations for Cu and Cl atoms. The final positional parameters are given in Table II. A listing of the observed and calculated structure factors for the reflections used in the refinement with thermal parameters is available as supplementary material. All calculations were performed on the Cyber 7600 computer of the Centro di Calcolo dell'Italia Nord-Orientale Bologna.

**Analyses.** Nitrogen, carbon, and hydrogen were analyzed by Mr. Giuseppe Pistoni using a Perkin-Elmer 240 elemental analyzer. The halogen ions were determined gravimetrically as AgX.

## Results and Discussion

The conventional chemical analysis results are reported in Table I. All of the compounds are crystalline, stable in air, and soluble in polar organic solvents, except the (NPhpipzH<sub>2</sub>)CuBr<sub>4</sub> compound which is not pure and rapidly decomposes in air.

In the differential scanning calorimetric analysis the mixed-halo cuprates show only a sharp endothermic peak, corresponding to their melting point, like all the other complexes, which indicates that they are true compounds and not mixtures containing the  $[CuCl_4]^{2-}$  and  $[CuBr_3]^-$  or  $[CuBr_4]^{2-}$  species, as is suggested also by their powder spectra.

As the compounds contain diprotonated or monoprotonated amine, they are indicated as type a and type b complexes, respectively, and separately discussed.

**Type a Complexes. Crystal Structure of (NPhpipzH<sub>2</sub>)CuCl<sub>4</sub>.** The structure consists of *N*-phenylpiperazinium dication and discrete  $[CuCl_4]^{2-}$  anions which show a flattened tetrahedral geometry, since two Cl-Cu-Cl angles (143.0, 141.1°) are greater than tetrahedral, while the others are smaller (Table III). The Cu-Cl distances range from 2.23 to 2.27 Å, as found in several compounds in which discrete  $[CuCl_4]^{2-}$  ions are present.

The deformation from the tetrahedral geometry can be expressed by the  $(Cl(1)-Cu-Cl(4))-(Cl(2)-Cu-Cl(3)) = 51.6^\circ$  dihedral angle. In Table VI, dihedral angles in distorted  $[CuCl_4]^{2-}$  anions are compared (the extreme cases are tetrahedral (90°) and square-planar (0°) configuration). The network of N...Cl interactions (all distances less than 3.5 Å) is illustrated in Figure 1; the contacts are tabulated in Table IV with Cl...H-N angles; some of these are probably as-

**Table II.** Final Fractional Coordinates<sup>a</sup> and Esd's in Parentheses

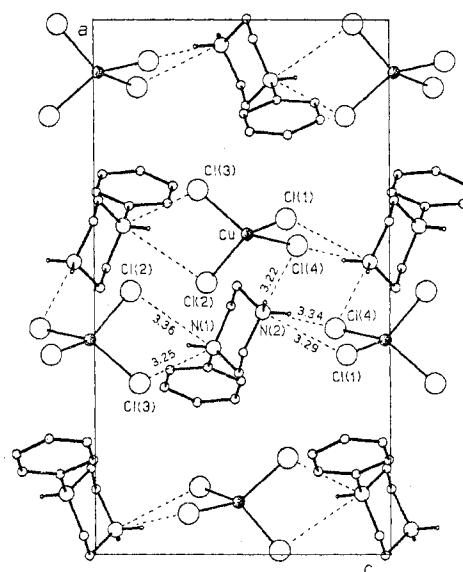
atom	<i>x/a</i> (σ)	<i>y/b</i> (σ)	<i>z/c</i> (σ)
Cu	-984 (1)	1017 (1)	159 (1)
Cl(1)	-1267 (1)	-1011 (2)	1471 (2)
Cl(2)	-78 (1)	1999 (2)	-1215 (2)
Cl(3)	-1807 (1)	499 (2)	-1503 (2)
Cl(4)	-770 (1)	2744 (2)	-1859 (2)
N(1)	-1139 (3)	2528 (6)	5982 (5)
N(2)	-469 (4)	139 (7)	4324 (6)
C(1)	-1506 (4)	4074 (8)	6182 (7)
C(2)	-1765 (5)	4879 (9)	5066 (9)
C(3)	-2100 (5)	6307 (10)	5271 (11)
C(4)	-2161 (4)	6904 (10)	6555 (12)
C(5)	-1879 (5)	6116 (10)	7657 (10)
C(6)	-1555 (5)	4646 (9)	7469 (8)
C(7)	-1612 (4)	1439 (8)	5140 (8)
C(8)	-1225 (4)	-99 (7)	4979 (8)
C(9)	17 (4)	1156 (9)	5193 (9)
C(10)	-355 (4)	2712 (8)	5396 (8)
H(1)	-109 (4)	224 (8)	682 (7)
H(2)	-167 (4)	438 (9)	426 (9)
H(3)	-215 (4)	697 (9)	434 (9)
H(4)	-242 (5)	791 (10)	677 (9)
H(5)	-194 (5)	660 (10)	850 (9)
H(6)	-141 (4)	407 (9)	818 (8)
H(7)	-209 (4)	127 (8)	530 (8)
H(8)	-169 (4)	206 (8)	427 (8)
H(9)	-119 (4)	-66 (9)	585 (8)
H(10)	-155 (4)	-78 (9)	446 (8)
H(11)	-29 (4)	-89 (9)	424 (8)
H(12)	-50 (4)	53 (9)	344 (8)
H(13)	9 (4)	59 (9)	588 (8)
H(14)	46 (4)	129 (8)	494 (8)
H(15)	-4 (4)	355 (8)	588 (8)
H(16)	-36 (4)	339 (8)	450 (8)

<sup>a</sup> Multiplied by 10<sup>4</sup> for nonhydrogen atoms and by 10<sup>3</sup> for hydrogen atoms.

**Table III.** Bond Distances (Å) and Angles (deg)

(a) [CuCl <sub>4</sub> ] <sup>2-</sup> Anion			
Cu-Cl(1)	2.230 (2)	Cu-Cl(3)	2.236 (3)
Cu-Cl(2)	2.262 (3)	Cu-Cl(4)	2.271 (2)
Cl(1)-Cu-Cl(2)	143.0 (3)	Cl(2)-Cu-Cl(3)	95.7 (1)
Cl(1)-Cu-Cl(3)	97.0 (1)	Cl(2)-Cu-Cl(4)	94.4 (1)
Cl(1)-Cu-Cl(4)	97.1 (1)	Cl(3)-Cu-Cl(4)	141.1 (3)
(b) N-Phenylpiperazinium Cation			
N(1)-C(1)	1.495 (9)	C(2)-C(3)	1.38 (1)
N(1)-C(7)	1.506 (9)	C(3)-C(4)	1.37 (2)
N(1)-C(10)	1.511 (9)	C(4)-C(5)	1.37 (1)
N(2)-C(8)	1.50 (1)	C(5)-C(6)	1.40 (1)
N(2)-C(9)	1.50 (1)	C(7)-C(8)	1.50 (1)
C(1)-C(2)	1.38 (1)	C(9)-C(10)	1.51 (1)
C(1)-C(6)	1.36 (1)		
C(1)-N(1)-C(7)	113 (1)	C(2)-C(3)-C(4)	120 (2)
C(1)-N(1)-C(10)	111 (1)	C(3)-C(4)-C(5)	121 (2)
C(7)-N(1)-C(10)	111 (1)	C(4)-C(5)-C(6)	119 (2)
C(8)-N(2)-C(9)	110 (1)	C(1)-C(6)-C(5)	118 (1)
N(1)-C(1)-C(6)	118 (1)	N(1)-C(7)-C(8)	111 (1)
N(1)-C(1)-C(2)	119 (1)	N(2)-C(8)-C(7)	109 (1)
C(2)-C(1)-C(6)	123 (1)	N(2)-C(9)-C(10)	110 (1)
C(1)-C(2)-C(3)	118 (1)	N(1)-C(10)-C(9)	111 (1)
(c) Involving Hydrogen Atoms			
N(1)-H(1)	0.87	C(8)-H(9)	0.99
C(2)-H(2)	0.91	C(8)-H(10)	0.97
C(3)-H(3)	1.08	N(2)-H(11)	0.95
C(4)-H(4)	1.00	N(2)-H(12)	0.93
C(5)-H(5)	0.93	C(9)-H(13)	0.84
C(6)-H(6)	0.90	C(9)-H(14)	0.83
C(7)-H(7)	0.87	C(10)-H(15)	1.03
C(7)-H(8)	1.02	C(10)-H(16)	1.06

sociated with bifurcated hydrogen bonds. As depicted in Figure 1, all four chlorine atoms are involved in Cl...H—N

**Figure 1.** Projection of the structure along [010].**Table IV.** Contacts Less Than 3.5 Å<sup>a</sup>

Cl...H—N, N, Å	Cl...H—N, deg	Cu—Cl, Å	N—H, Å	H—N...Cl, deg
Cl(1)···H(12)—N(2)	3.295	121	2.229	0.93 45
Cl(2)···H(1) <sup>t</sup> —N(1) <sup>t</sup>	3.368	142	2.226	0.87 29
Cl(3)···H(1) <sup>t</sup> —N(1) <sup>t</sup>	3.253	137	2.253	0.87 33
Cl(4)···H(11) <sup>i</sup> —N(2) <sup>i</sup>	3.228	138	2.271	0.95 31
Cl(4)···H(12)—N(2)	3.347	150	2.271	0.93 22

<sup>a</sup> t = *x, y, z* - 1; i =  $\bar{x}, y - 1/2, 1/2 - z$ .

hydrogen bonds. These Cl...N interactions may explain the large distortion of the [CuCl<sub>4</sub>]<sup>2-</sup> ion from the tetrahedral configuration, as they are probably the major contributors to the crystal-packing forces.

In fact, in Cs<sub>2</sub>CuCl<sub>4</sub>, in which hydrogen bonds or strong van der Waals interactions are not present, the geometry of the [CuCl<sub>4</sub>]<sup>2-</sup> ion is moderately flattened tetrahedral. In several compounds<sup>2</sup> in which the packing forces are more relevant, the [CuCl<sub>4</sub>]<sup>2-</sup> anion shows a large distortion toward a square-planar configuration.

The N-phenylpiperazinium dication shows the usual "chair" conformation, as indicated by the puckering parameters:<sup>7</sup> *q*<sub>2</sub> = 0.044 Å, *q*<sub>3</sub> = -0.580 Å, *φ*<sub>2</sub> = 337°, *Q* = 0.58 Å. The distances of the N atoms from the main plane through the carbon atoms are 0.65 and 0.70 Å, respectively; the phenyl ring forms an angle of 78.3° with this plane.

**Powder, Electronic, and Far-Infrared Spectra and Magnetic Moments.** The room-temperature powder X-ray and electronic ((Table V) two broad d-d transitions at 8900 and 10700 cm<sup>-1</sup>) spectra of the (NPhpipzH<sub>2</sub>)CuCl<sub>3</sub>Br complex are very similar to those of the corresponding tetrachloride, suggesting that these two complexes are isomorphous and isostructural. The values of the d-d bands are considerably higher than those normally found for flattened tetrahedral [CuCl<sub>4</sub>]<sup>2-</sup><sup>8-11</sup> and may be explained by the greater degree of distortion toward planarity which increases the overall splitting of the d-orbital energy levels.<sup>12</sup>

Recently some attempts have been made to correlate empirically the maximum of the d-d transition for several [CuCl<sub>4</sub>]<sup>2-</sup> salts with the amount of distortion from the T<sub>d</sub>

Table V. Electronic and Far-Infrared Spectra (cm<sup>-1</sup>) of the Solid Type a Complexes

		Electronic Spectrum		
		d-d bands		CT bands
(NPhpipzH <sub>2</sub> )CuCl <sub>4</sub>		8930, 10 750		23 810 sh, 27 030
(NPhpipzH <sub>2</sub> )CuCl <sub>3</sub> Br		8900, 10 700		23 810 sh, 25 640
(NPhpipzH <sub>2</sub> )CuBr <sub>4</sub>		6250, 6850, 9010		16 000, 18 870, 23 260 sh
		Far-Infrared Spectrum		
approx geom	$\nu(\text{Cu-Cl})$	$\nu(\text{Cu-Br})$	$\delta(\text{Cu-X})$	
NPhpipz(HCl) <sub>2</sub>			370 m, 315 m, 293 m, 266 m, 210 sh, 180 m, 148 m, 116 mb, 100 sh	
NPhpipz(HBr) <sub>2</sub>			370 ms, 316 sh, 306 m, 288 m, 258 m, 181 m, 140 ms, 100 mb	
(NPhpipzH <sub>2</sub> )CuCl <sub>4</sub>	D <sub>2h</sub>	300 vs, 278 w	172 s, 128 m, 87 w	377 s, 312 sh, 290 sh, 221 m
(NPhpipzH <sub>2</sub> )CuCl <sub>3</sub> Br	C <sub>2v</sub> <sup>a</sup>	300 vs, 280 sh	234 w	377 s, 312 sh, 290 s, 250 w, 191 sh
(NPhpipzH <sub>2</sub> )CuBr <sub>4</sub>	D <sub>2d</sub>		220 mb	374 m, 294 w, 250 sh

<sup>a</sup> Planar C<sub>2v</sub> symmetry predicts three IR-active Cu-Cl and one IR-active Cu-Br stretching modes.

Table VI. Found and Calculated Maxima of the d-d Transition and Dihedral Angles for a Number of Chlorocuprate(II) Complexes Containing the CuCl<sub>4</sub> Chromophore

	max d-d trans, cm <sup>-1</sup>		dihedral angle, deg
	calcd	found	
tetrahedron	6680		90
Cs <sub>2</sub> CuCl <sub>4</sub>	9060	9050 <sup>8-10</sup>	67.9 <sup>29</sup>
[C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> N(CH <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> CuCl <sub>4</sub>	9200	9250 <sup>8,10</sup>	66.6 <sup>30</sup>
[(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NH] <sub>2</sub> CuCl <sub>4</sub>	9510	9390 <sup>8</sup>	63.7 <sup>31</sup>
( <i>d</i> -mamph) <sub>2</sub> CuCl <sub>4</sub> <sup>a</sup>	10380	10200 <sup>12</sup>	55.5 <sup>12</sup>
(NPhpipzH <sub>2</sub> )CuCl <sub>4</sub>	10790	10750 <sup>b</sup>	51.6 <sup>b</sup>
(C <sub>13</sub> H <sub>19</sub> N <sub>2</sub> OS) <sub>2</sub> CuCl <sub>4</sub>	11010	10810 <sup>b</sup>	49.5 <sup>32</sup>
[Pt(en) <sub>2</sub> Cl <sub>2</sub> ] <sub>2</sub> CuCl <sub>4</sub>	12475	12990 <sup>c</sup>	35.7 <sup>33</sup>
[(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> CH <sub>3</sub> ] <sub>2</sub> CuCl <sub>4</sub>	16260	16100 <sup>28</sup>	0 <sup>28</sup>

<sup>a</sup> *d*-mamph = (+)-*N,N*-dimethylphenethylammonium. <sup>b</sup> This work. <sup>c</sup> This work on these crystals was kindly supplied by Professor H. Toftlund.<sup>33</sup>

symmetry as determined from X-ray crystal structure studies. Lamotte-Brasseur<sup>8</sup> correlated the electronic spectra with a distortion parameter based on the distances between the opposite edges of the tetrahedron, while Willett et al.<sup>13</sup> used as distortion parameter the average of the two larger Cl-Cu-Cl angles. Both methods suffer from some limitation, as recognized by Harlow et al.,<sup>12</sup> who also correlated the maximum d-d electronic spectra with the average of the two large Cl-Cu-Cl angles selecting accurately the suitable compounds, but using also compounds containing [Cu<sub>2</sub>Cl<sub>6</sub>]<sup>2-</sup> anion, probably for want of [CuCl<sub>4</sub>]<sup>2-</sup> anions. The [Cu<sub>2</sub>Cl<sub>6</sub>]<sup>2-</sup> anions exhibit intradimer ferromagnetic interactions<sup>14,15</sup> which play a dominant role in their magnetic properties and, consequently, in their spectroscopic properties.

Table VII. Electronic and Far-Infrared Spectra (cm<sup>-1</sup>) of the Solid Type b Complexes

		Electronic Spectrum		
		d-d bands		CT bands
(NPhpipzH) <sub>2</sub> Cu <sub>2</sub> Cl <sub>6</sub>		9710 sh, 11 110		19 050 sh, 24 390, 27 780 sh
(NPhpipzH) <sub>2</sub> Cu <sub>2</sub> Cl <sub>2</sub> Br <sub>4</sub>		10 750 sh, 11 910		18 870 sh, 27 000
(NPhpipzH) <sub>2</sub> Cu <sub>2</sub> Br <sub>6</sub>		10 870 sh, 12 050		18 180, 20 830 sh, 26 670
		Far-Infrared Spectrum		
approx geom	$\nu(\text{Cu-Cl})$	$\nu(\text{Cu-Br})$	$\delta(\text{Cu-X})$	
		terminal	bridging	
(NPhpipzH) <sub>2</sub> Cu <sub>2</sub> Cl <sub>6</sub>	D <sub>2h</sub>	292 vs, 276 s	258 s	166 m, 138 s, 68 w
(NPhpipzH) <sub>2</sub> Cu <sub>2</sub> Cl <sub>2</sub> Br <sub>4</sub>	C <sub>2v</sub> <sup>a</sup>	284 sh, 278 vs, b	245 sh	168 w, 138 mb, 85 w
(NPhpipzH) <sub>2</sub> Cu <sub>2</sub> Br <sub>6</sub>	D <sub>2h</sub>		220 mb	140 wb, 100 ms, 70 m

<sup>a</sup> Planar C<sub>2v</sub> symmetry predicts three IR-active Cu-Cl and one IR-active Cu-Br stretching modes.

Since during the elaboration of this paper the number of compounds having recent structures, with no disordering problems, in which the Cu atom is truly four-coordinate with spectral and structural data obtained at 25 °C, has increased, we have thought it convenient to correlate the maximum d-d electronic spectra vs. distortion expressed as Cl-Cu-Cl dihedral angle, hereafter abbreviated as  $\Delta$ . The choice of suitable compounds is therefore limited to those in which the deformation of the tetrahedron may be practically caused by the same effects, e.g., strong hydrogen-bonding or van der Waals interactions.

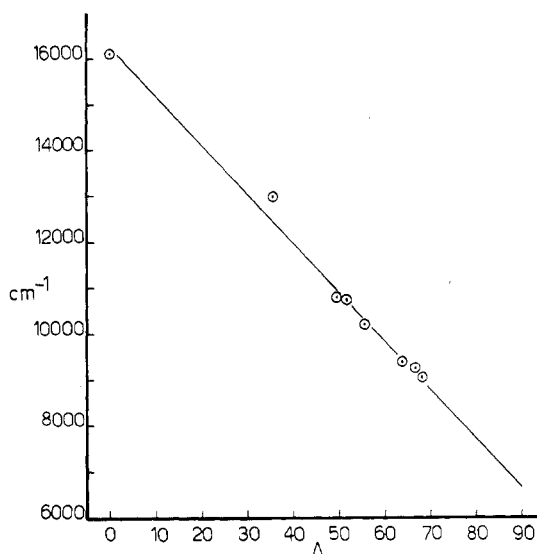
The value of the maximum d-d transition used for the correlation with the dihedral angle is that corresponding to the higher energy band of the electronic spectra of the [CuCl<sub>4</sub>]<sup>2-</sup> ions which generally show two d-d bands. These values and the dihedral angles of some [CuCl<sub>4</sub>]<sup>2-</sup> anions are reported in Table VI, together with the "calculated" maximum d-d transitions.

The graph of the maximum d-d transition vs.  $\Delta$  is reported in Figure 2. The least-squares equation for this line is (maximum d-d transition) = -106 $\Delta$  + 16260 with a correlation coefficient  $r^2 = 0.9906$ .

The straight-line approximation predicts that a [CuCl<sub>4</sub>]<sup>2-</sup> complex with a regular tetrahedral configuration should have a maximum d-d transition around 6680 cm<sup>-1</sup>, which appears reasonable.<sup>9,12</sup>

The electronic spectrum of the (NPhpipzH<sub>2</sub>)CuBr<sub>4</sub> complex shows d-d bands in the near-infrared region at 6250, 6850, and 9010 cm<sup>-1</sup> which agree with those reported for compounds containing [CuBr<sub>4</sub>]<sup>2-</sup> ions with D<sub>2d</sub> symmetry.<sup>3,4</sup>

The far-IR spectra of the solid compounds, reported in Table V, agree well with the proposed geometries. In particular the



**Figure 2.** Graphical representation of the maximum d-d transition ( $\text{cm}^{-1}$ ) vs. the dihedral angle (degrees) ( $\Delta$ ).

$b_2$  stretching band, expected at  $255\text{--}230\text{ cm}^{-1}$  for the  $D_{2d}$  symmetry<sup>16-18</sup> is absent.

The room-temperature magnetic moments of the solid type a complexes are in good agreement with the proposed configuration.<sup>19,20</sup>

**Type b Complexes.** We have also prepared and investigated some compounds containing monoprotonated amine, which are characterized by a cation:metal:halide molar ratio of 1:1:3.

Their room-temperature solid electronic spectra (Table VII) are very similar to one another and to those of  $[\text{Cu}_2\text{X}_6]^{2-}$  dimers, for which an approximately square-planar stereochemistry is found<sup>2,3,12,21</sup> and, in particular, show a new band appearing at  $18180\text{--}19650\text{ cm}^{-1}$ , which is probably a polarized charge-transfer band, thus accounting for its weak absorbance.<sup>9,22</sup> This band is characteristic of the  $\text{Cu}_2\text{X}_6$  dimers and justifies the formulation adopted for these complexes, as reported in the tables.

The size of the cation and the hydrogen-bonding interactions may also be considered as responsible for the distortion of the type b complexes. In these complexes the bridging of the halogen atom to a second copper atom also contributes to the reduction of the chlorine-chlorine repulsions.<sup>13</sup>

The type b complexes show a shift at higher energies of the d-d transitions in the sequence  $\text{Cu}_2\text{Cl}_6 < \text{Cu}_2\text{Cl}_2\text{Br}_4 < \text{Cu}_2\text{Br}_6$ , which suggests the possibility of tetragonal distortions, increasing in the same direction, due to interactions among  $[\text{Cu}_2\text{X}_6]^{2-}$  layers, as the hydrogen-bonding interactions between the cation and the anion decrease with the increase in number of bromine atoms in the anion.

The far-IR spectra of these complexes (Table VII) confirm the proposed geometries. The bands at  $258\text{ (s)}$  and  $245\text{ (sh)}$   $\text{cm}^{-1}$  in the  $[\text{Cu}_2\text{Cl}_6]^{2-}$  and  $[\text{Cu}_2\text{Cl}_2\text{Br}_4]^{2-}$  anions, respectively, are probably stretching frequencies involving bridging chlorines,<sup>23-26</sup> suggesting the presence of such bridges in the latter complexes.

**Hydrogen Bonding.** The IR spectra of the monohydro- and dihydrohalide salts show a complex series of absorption bands at  $2850\text{--}2450$  and  $3000\text{--}2400\text{ cm}^{-1}$ , respectively, which are attenuated and in part shifted to  $2350\text{--}1900\text{ cm}^{-1}$  on deuteration, indicating that the N-H motion is involved<sup>27</sup> and that

in the monoprotonated amine the nonprotonated nitrogen is involved in strong intermolecular hydrogen bonding.

The  $\text{NH}_2^+$  stretching vibrations in the IR spectra of the type b complexes are found at  $3100\text{--}3088$  and  $3040\text{--}3038\text{ cm}^{-1}$ , while those of the type a complexes appear lowered in energy about  $100\text{ cm}^{-1}$  ( $3025, 2952\text{--}2945\text{ cm}^{-1}$ ) confirming that the distortion of the type a complexes is mostly due to the presence of a strong hydrogen bonding between the cation and the  $[\text{CuCl}_4]^{2-}$  anion.

The other bands assignable to the N-H motion at energy lower than  $1600\text{ cm}^{-1}$  do not show significant shifts on comparison of type a and type b complexes.

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**Registry No.** (NPhpipzH)<sub>2</sub>Cu<sub>2</sub>Cl<sub>6</sub>, 68069-71-6; (NPhpipzH)<sub>2</sub>Cu<sub>2</sub>Cl<sub>2</sub>Br<sub>4</sub>, 68069-73-8; (NPhpipzH)<sub>2</sub>Cu<sub>2</sub>Br<sub>6</sub>, 68069-74-9; (NPhpipzH<sub>2</sub>)CuCl<sub>4</sub>, 68024-45-3; (NPhpipzH<sub>2</sub>)CuCl<sub>3</sub>Br, 68024-46-4; (NPhpipzH<sub>2</sub>)CuBr<sub>4</sub>, 68024-47-5; NPhpipz(HCl)<sub>2</sub>, 4004-95-9; NPhpipz(HBr)<sub>2</sub>, 36596-75-5.

**Supplementary Material Available:** Listings of the thermal parameters (with esd's) and observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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