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Crystal and Molecular Structure of Bis[(+)-*N*,α-dimethylphenethylammonium] Tetrachlorocuprate(II). Relationship between the Electronic Spectrum and the Distortion of the CuCl4 Chromophore from Tetrahedral Symmetry

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Investigation of the crystal structure of bis[(+)-*N*,α-dimethylphenethylammonium] tetrachlorocuprate(II), $[C_6H_5CH_2CH(CH_3)NH_2CH_3]_2CuCl_4$, was prompted when its maximum d–d transition, 10,200 cm^{-1}, was noted as being considerably greater in energy than that reported for other D_{2d} tetrachlorocuprate(II) complexes. Crystals of the compound are triclinic, space group $P1$, with $a = 12.115$ (3) Å, $b = 12.968$ (2) Å, $c = 8.741$ (2) Å, $\alpha = 106.64$ (1)°, $\beta = 100.25$ (2)°, $\gamma = 98.88$ (2)°, $Z = 2$ (two crystallographically independent $CuCl_4^{2-}$ anions per asymmetric unit), $d_x = 1.329$ g cm^{-3}, and $d_m = 1.330$ g cm^{-3}. Intensities were obtained from θ–2θ scans with a four-circle automatic diffractometer using graphite-monochromatized Mo Kα radiation. A total of 3190 reflections [$I > 3\sigma(I)$] were used in the full-matrix least-squares refinement; the phenyl groups were refined as rigid bodies. The positions of the hydrogen atoms could not be located unambiguously and were not included in the refinement. The conventional and weighted agreement indices are $R = 0.074$ and $R_w = 0.053$. The $CuCl_4^{2-}$ anions are found to be highly distorted from T_d symmetry in agreement with the spectral results; the average of the two large Cl–Cu–Cl angles is 138.3°. The average Cu–Cl bond distance is 2.238 Å. The $CuCl_4^{2-}$ anions are bridged by a network of hydrogen bonds involving the $-NH_2-$ groups of the cations. A study of the maximum d–d transition vs. the distortion of the $CuCl_4$ chromophore from T_d symmetry is also reported. The transition energy appears to be a smooth function of the distortion but more data points are needed to complete the curve.

Introduction

Recent investigations of the chemistry of methamphetamine (*N*,α-dimethylphenethylamine) and derived salts produced two compounds with novel chlorocuprate(II) coordination geometries as determined by single-crystal X-ray analysis.[1,2] Unusual spectral properties initiated the structure determinations of these compounds and prompted a more careful examination of the d–d electronic spectra of a number of tetrachlorocuprates(II).

One of the most common geometries found for the $CuCl_4^{2-}$ anion is that often referred to as the "flattened" tetrahedron with nearly or exactly D_{2d} symmetry. That it is intrinsically more stable than a complex with either T_d (regular tetrahedron) or D_{4h} (square plane) symmetry has been shown by various theoretical calculations.[3-5] Of the discrete (purely four-coordinate) $CuCl_4^{2-}$ anions studied by X-ray crystallographic methods, only one with nearly T_d symmetry[6] and one square-planar complex have been reported,[1] while at least 12 structural studies,[1,7-16] including the present work, have revealed anions with nearly D_{2d} symmetry (deviations from precise D_{2d} symmetry are quite small).

It has been predicted theoretically that the electronic absorption spectrum of any D_{2d} $CuCl_4^{2-}$ complex should be sensitive to the amount of "flattening", or distortion, that has occurred. In particular, the maximum d–d transition should increase in energy as the geometry distorts from a regular tetrahedron toward a square plane.[4] This was shown to be the case in two recent studies of several $CuCl_4^{2-}$ salts in which the maximum d–d absorption was correlated with a distortion parameter based on X-ray results.[17,18]

We report here the crystal structure of bis[(+)-*N*,α-dimethylphenethylammonium] tetrachlorocuprate(II), hereafter abbreviated (d-mampH)$_2$CuCl$_4$, which was undertaken because its maximum d–d transition was found to be greater than that for other D_{2d} tetrachlorocuprate(II) complexes that have been studied. In addition, the relationship between the distortion of the tetrahedral geometry and the electronic spectra for eight compounds containing the $CuCl_4$ chromophore is discussed.

Experimental Section

Electronic Spectra. The electronic spectra were measured as described previously.[1]

Crystallographic Data Collection. The bright yellow crystal selected for the measurement of lattice parameters and intensity data had dimensions of 0.24 × 0.24 × 0.32 × 0.29 mm perpendicular to (100), (11$\bar{1}$), (010), and (110), respectively. A preliminary study of the crystal was carried out on a Syntex $P2_1$ diffractometer and showed the crystal to be triclinic. Because the cation was present only as the (+) enantiomer, the space group was unambiguously assigned as $P1$. The least-squares refinement of the Bragg angles (Cu Kα_1, λ 1.54050 Å) for 18 high-angle reflections ($85° < 2\theta < 104°$) produced the following unit cell parameters: $a = 12.115$ (3) Å, $b = 12.968$ (2) Å, $c = 8.741$ (2) Å, $\alpha = 106.64$ (1)°, $\beta = 100.25$ (2)°, $\gamma = 98.88$ (2)°, and $V = 1263.8$ Å^3. With a formula weight of 505.85 and $Z = 2$, the calculated density is 1.329 g cm^{-3} which agrees well with the measured value of 1.330 g cm^{-3}. With $Z = 2$, of course, each unit cell must contain two crystallographically independent $CuCl_4^{2-}$ ions and four d-mampH$^+$ cations.

Intensity data were collected on the Syntex diffractometer with Mo Kα radiation monochromatized by a graphite crystal. The θ–2θ scan technique was employed with each scan ranging 1.0° in 2θ below and beyond the Kα_1 and Kα_2 peaks, respectively. The scan rate varied from 2.0 to 5.0° min^{-1} depending in a direct manner on the number of counts obtained in a rapid preliminary scan of the peak. Background counts were taken at both ends of the scan range, each for a time equal to half the scan time. A total of 4436 unique reflections

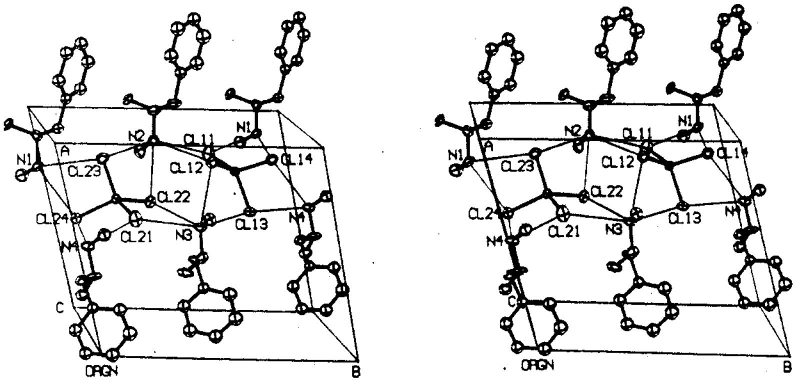

Figure 1. Packing diagram for $(d\text{-mampH})_2CuCl_4$.

of the type $h,\pm k,\pm l$ were measured in the range $4° < 2\theta < 50°$. The intensities of four standard reflections were measured after every 96 reflections; these intensities dropped by an average of 2% over the period of data collection and a correction factor, as a function of exposure time, was applied. Coincidence losses were corrected via direct knowledge of the counting system's dead time. Absorption corrections based on crystal shape were applied ($\mu = 13.25\ cm^{-1}$, Mo $K\alpha$) with transmission coefficients ranging from 0.65 to 0.78. Lorentz and polarization corrections completed the conversion from intensities to structure amplitudes. Standard deviations in the intensities, $\sigma(I)$, and in the structure amplitudes, $\sigma(F_o)$, were derived directly from counting statistics.

Solution and Refinement of the Structure. The structure was solved by a combination of the Patterson heavy-atom method and Fourier syntheses. The solution was complicated in the initial stages by a false center of symmetry which relates the two crystallographically independent $CuCl_4^{2-}$ ions, as well as relating atoms N, C(8), and C(10) of cation 1 to those of cation 4 and those of cation 2 to those of cation 3. The false symmetry was eventually overcome by the inclusion of one benzyl group which allowed the remaining carbon atom positions to be unequivocally determined.

Only the 3190 reflections for which $I > 3\sigma(I)$ were used in the full-matrix least-squares refinement of the structure. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where w is the weight calculated as $1/\sigma^2(F_o)$. All of the Cu, Cl, N, and C atoms, except those C atoms in the phenyl groups, were refined with anisotropic thermal parameters. The phenyl groups were treated as rigid groups with C–C distances of 1.392 Å, C–H distances of 1.00 Å, and all angles of 120.0°; each of these carbon atoms had a variable isotropic thermal parameter while each hydrogen atom was assigned an isotropic thermal parameter consistent with the overall thermal motion of the group. Many of the remaining hydrogen atoms could not be located unambiguously from various difference maps and hence were not included in the refinement.

During the refinement it was necessary to confirm well-documented chemical evidence that the d-mampH$^+$ cation has the S configuration. In the initial stages of the refinement, the imaginary component, $\Delta f''$, of the Cu and Cl scattering factors was omitted. At this point, the refinement had converged to a conventional $R = \sum||F_o| - |F_c||/\sum|F_o|$ of 0.076 and a weighted $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$ of 0.058. With the inclusion of $\Delta f''$ for Cu and Cl, the S-mampH structure then refined to $R = 0.074$ and $R_w = 0.053$; the corresponding values for the R-mampH structure were 0.075 and 0.054. The small differences in agreement indices for the two cation configurations made necessary a study of the intensity ratios of several Bijvoet pairs. Assuming the S configuration to be correct, intensity ratios were then calculated for all Bijvoet pairs (in this case, Friedel pairs). Seventeen pairs, for which ratios quite different from 1.0 were calculated and for which the intensity was sufficient to provide reasonable counting statistics, were measured experimentally. A comparison of the calculated and observed intensity ratios indicated that the d-mampH, or (+)-mampH, cation does indeed have the S configuration.

The final positional and thermal parameters are given in Table I. One reflection, $11\bar{1}$, was eliminated from the refinement when it was found to be in error for some unknown reason. Extinction did not prove to be a problem. The largest peak in the final difference map, 0.7 e $Å^{-3}$, was located near atom Cl(14). The atomic scattering factors for Cu, Cl, N, and C were those of Cromer and Waber;[19] the anomalous dispersion corrections for Cu and Cl were those of Cromer.[20] For H, the scattering factors of Stewart, Davidson, and Simpson[21] were used.

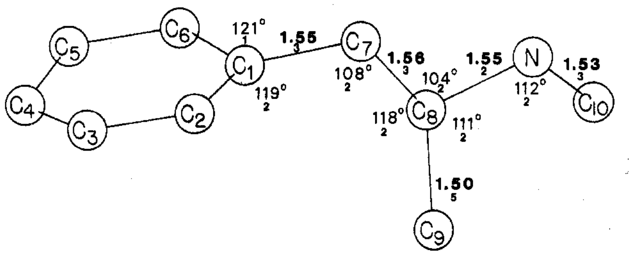

Figure 2. Bond distances and angles for the (d-mampH) cation as averaged over the four independent moieties.

Computer programs used to solve and refine the structure include the following: SYSABS, a local version of ORABS by W. R. Busing and H. A. Levy as modified by J. M. Williams, for absorption correction; RFOUR, Fourier synthesis, by S. T. Rao, modified by R. E. Davis; NUCLS, full-matrix least-squares refinement, ORFLS as modified by J. A. Ibers; DAESD, distances, angles, and their estimated standard deviations, by D. R. Harris, modified by R. E. Davis; ORTEP, by C. K. Johnson.

Discussion

Crystal Structure of $(d\text{-mampH})_2CuCl_4$. The bond distances and angles for the two crystallographically independent $CuCl_4^{2-}$ moieties are listed in Table II; most of these values are within the ranges found previously for $CuCl_4^{2-}$ anions. The atom-numbering scheme for the anions is as follows: all Cl atoms associated with Cu(1) of anion 1 have 10 added to their value, while Cl atoms of anion 2 have 20 added; atoms across the pseudocenter of symmetry have been assigned the same basic number such that Cl(11) is related to Cl(21), etc. The scheme and pseudocenter are well illustrated in Figure 1. The positions of cations 1–4 are also shown in this figure as indicated by the number attached to the N atoms.

The average bond distances and angles for the four cations are given in Figure 2. The associated standard deviations are based on the spread of the four independent measurements. The carbon atom numbering scheme used in Table I was derived by adding 100 to atoms in cation 1, 200 to those in cation 2, etc. Because of the large standard deviations brought about by the large number of heavy atoms in the structure and because the pertinent hydrogen atoms were not included in the refinement causing shifts in the carbon and nitrogen atom positions to compensate in part for the hydrogen atom electron density, the bond distances and angles of the cation are not particularly accurate and warrant no further discussion.

The network of N–Cl interactions (all distances less than 3.9 Å) is illustrated in Figure 1; the distances are tabulated in Table III. Contacts less than 3.15 Å undoubtedly represent strong, nearly linear hydrogen bonds, while many of the other contacts are probably associated with bifurcated hydrogen

Table I. Final Positional and Thermal Parameters[a] for (d-mampH)$_2$CuCl$_4$ with Esd's in Parentheses

Atom	*x*	*y*	*z*	*B*, Å^2
		Anion 1		
Cu(1)[b]	0.7500 (2)	0.7500 (2)	0.7500 (3)	
Cl(11)	0.7979 (6)	0.6831 (5)	0.9547 (7)	
Cl(12)	0.8247 (4)	0.6434 (4)	0.5659 (6)	
Cl(13)	0.5905 (5)	0.7544 (5)	0.5736 (7)	
Cl(14)	0.7816 (4)	0.9253 (4)	0.9049 (6)	
		Anion 2		
Cu(2)	0.6893 (2)	0.2143 (2)	0.3195 (3)	
Cl(21)	0.6433 (6)	0.2521 (5)	0.0843 (8)	
Cl(22)	0.6457 (5)	0.3616 (4)	0.4865 (7)	
Cl(23)	0.8460 (5)	0.2099 (5)	0.4947 (7)	
Cl(24)	0.6145 (4)	0.0329 (4)	0.2208 (6)	
		Cation 1		
N(1)	0.8432 (11)	0.9318 (12)	0.2757 (19)	
C(101)[c]	0.1430 (6)	0.1085 (7)	0.3563 (12)	5.2 (3)
C(102)[c]	0.2338 (9)	0.0900 (7)	0.2820 (9)	7.1 (4)
C(103)[c]	0.3453 (8)	0.1483 (8)	0.3637 (13)	6.9 (4)
C(104)[c]	0.3659 (7)	0.2252 (8)	0.5196 (12)	7.4 (4)
C(105)[c]	0.2750 (9)	0.2438 (7)	0.5938 (9)	7.7 (4)
C(106)[c]	0.1635 (8)	0.1854 (8)	0.5122 (12)	6.5 (4)
C(107)	0.0221 (12)	0.0461 (11)	0.2621 (15)	
C(108)	0.9737 (14)	0.9634 (13)	0.3483 (20)	
C(109)	0.0257 (13)	0.8611 (13)	0.3285 (21)	
C(110)	0.7838 (17)	0.8717 (16)	0.3722 (25)	
H(102)[c]	0.2191 (14)	0.0348 (9)	0.1701 (11)	8.0
H(103)[c]	0.4106 (10)	0.1350 (12)	0.3104 (18)	8.0
H(104)[c]	0.4459 (8)	0.2672 (11)	0.5783 (18)	8.0
H(105)[c]	0.2897 (14)	0.2990 (9)	0.7058 (10)	8.0
H(106)[c]	0.0982 (10)	0.1987 (12)	0.5655 (18)	8.0
		Cation 2		
N(2)	0.8871 (12)	0.4539 (11)	0.7772 (18)	
C(201)[c]	0.1907 (7)	0.6251 (9)	0.8685 (13)	6.3 (4)
C(202)[c]	0.2783 (11)	0.5922 (7)	0.7963 (11)	8.3 (5)
C(203)[c]	0.3918 (9)	0.6477 (10)	0.8693 (14)	9.1 (5)
C(204)[c]	0.4176 (8)	0.7361 (9)	0.0146 (14)	8.0 (4)
C(205)[c]	0.3297 (11)	0.7690 (7)	0.0867 (11)	10.2 (5)
C(206)[c]	0.2161 (9)	0.7135 (10)	0.0137 (14)	8.4 (5)
C(207)	0.0649 (12)	0.5765 (15)	0.7734 (20)	
C(208)	0.0154 (16)	0.4909 (17)	0.8597 (25)	
C(209)	0.0642 (13)	0.3951 (13)	0.8680 (21)	
C(210)	0.8172 (16)	0.4005 (14)	0.8711 (20)	
H(202)[c]	0.2598 (16)	0.5287 (10)	0.6920 (13)	10.0
H(203)[c]	0.4550 (12)	0.6241 (14)	0.8175 (21)	10.0
H(204)[c]	0.4991 (8)	0.7760 (13)	0.0670 (21)	10.0
H(205)[c]	0.3482 (16)	0.8324 (10)	0.1911 (13)	10.0
H(206)[c]	0.1530 (13)	0.7371 (14)	0.0656 (20)	10.0
		Cation 3		
N(3)	0.5698 (12)	0.5158 (12)	0.2897 (18)	
C(301)[c]	0.2618 (7)	0.4882 (10)	0.3487 (11)	5.8 (4)
C(302)[c]	0.1797 (10)	0.3914 (7)	0.3119 (12)	7.2 (5)
C(303)[c]	0.0643 (9)	0.3952 (8)	0.2992 (12)	8.4 (5)
C(304)[c]	0.0311 (7)	0.4956 (11)	0.3233 (12)	8.6 (5)
C(305)[c]	0.1132 (11)	0.5923 (8)	0.3602 (12)	9.1 (5)
C(306)[c]	0.2286 (9)	0.5886 (8)	0.3729 (12)	8.6 (5)
C(307)	0.3914 (13)	0.4805 (14)	0.3783 (19)	
C(308)	0.4368 (17)	0.4911 (16)	0.2222 (23)	
C(309)	0.3963 (13)	0.3987 (14)	0.0731 (20)	
C(310)	0.6325 (14)	0.5454 (13)	0.1644 (18)	
H(302)[c]	0.2035 (16)	0.3193 (9)	0.2945 (18)	10.0
H(303)[c]	0.0052 (12)	0.3257 (10)	0.2727 (18)	10.0
H(304)[c]	0.9482 (8)	0.4983 (16)	0.3142 (17)	10.0
H(305)[c]	0.0894 (16)	0.6645 (9)	0.3775 (18)	10.0
H(306)[c]	0.2877 (13)	0.6581 (10)	0.3993 (18)	10.0
		Cation 4		
N(4)	0.5775 (11)	0.0211 (11)	0.7761 (15)	
C(401)[c]	0.2734 (7)	0.9925 (9)	0.8358 (11)	5.2 (3)
C(402)[c]	0.1799 (10)	0.9034 (6)	0.7823 (11)	7.4 (5)
C(403)[c]	0.0691 (8)	0.9213 (8)	0.7768 (11)	7.0 (4)
C(404)[c]	0.0519 (7)	0.0285 (10)	0.8248 (12)	8.1 (5)
C(405)[c]	0.1454 (10)	0.1177 (7)	0.8783 (12)	9.1 (5)
C(406)[c]	0.2562 (8)	0.0997 (7)	0.8838 (11)	7.4 (4)
C(407)	0.3998 (12)	0.9741 (13)	0.8550 (19)	
C(408)	0.4465 (13)	0.0156 (17)	0.7236 (23)	
C(409)	0.4022 (13)	0.9423 (13)	0.5418 (17)	

Table I (*Continued*)

Atom	x	y	z	B, Å^2
		Cation 4 (*Continued*)		
C(410)	0.6496 (16)	0.0855 (15)	0.6877 (24)	
H(402)[c]	0.1923 (15)	0.8264 (7)	0.7479 (16)	10.0
H(403)[c]	0.0019 (10)	0.8573 (11)	0.7384 (16)	10.0
H(404)[c]	0.9723 (8)	0.0414 (15)	0.8208 (18)	10.0
H(405)[c]	0.1330 (15)	0.1947 (8)	0.9128 (17)	10.0
H(406)[c]	0.3234 (11)	0.1638 (10)	0.9223 (17)	10.0

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	64 (2)	75 (2)	141 (5)	20 (2)	23 (3)	39 (3)
Cl(11)	232 (9)	147 (6)	241 (12)	71 (6)	90 (8)	104 (7)
Cl(12)	109 (5)	106 (4)	199 (9)	36 (4)	28 (5)	31 (5)
Cl(13)	83 (5)	108 (5)	272 (13)	7 (4)	−13 (7)	43 (7)
Cl(14)	111 (5)	120 (5)	208 (10)	33 (4)	6 (5)	30 (5)
Cu(2)	71 (2)	64 (2)	162 (5)	16 (2)	21 (3)	29 (3)
Cl(21)	245 (9)	130 (6)	228 (11)	29 (6)	70 (8)	74 (7)
Cl(22)	122 (6)	97 (5)	297 (11)	39 (4)	33 (6)	56 (6)
Cl(23)	106 (6)	120 (6)	267 (13)	46 (5)	43 (7)	20 (7)
Cl(24)	112 (5)	87 (4)	279 (11)	19 (4)	77 (6)	45 (5)
N(1)	71 (13)	127 (15)	325 (34)	48 (11)	53 (17)	113 (18)
C(107)	74 (14)	106 (15)	109 (24)	21 (11)	37 (15)	47 (15)
C(108)	100 (17)	87 (15)	185 (34)	0 (13)	17 (20)	62 (19)
C(109)	114 (18)	96 (15)	391 (43)	68 (14)	51 (23)	87 (21)
C(110)	120 (22)	160 (25)	349 (54)	14 (19)	76 (29)	163 (30)
N(2)	89 (14)	104 (15)	227 (32)	29 (12)	49 (18)	69 (18)
C(207)	61 (15)	193 (23)	292 (39)	2 (15)	−3 (19)	159 (26)
C(208)	72 (19)	172 (23)	310 (49)	24 (17)	28 (26)	127 (29)
C(209)	108 (18)	109 (17)	403 (46)	51 (14)	1 (23)	114 (23)
C(210)	170 (26)	94 (17)	241 (39)	39 (16)	99 (27)	2 (20)
N(3)	70 (14)	137 (16)	210 (31)	−6 (12)	−22 (18)	69 (18)
C(307)	88 (17)	154 (20)	252 (37)	−29 (14)	−1 (20)	113 (23)
C(308)	116 (21)	148 (22)	238 (42)	34 (17)	33 (25)	124 (26)
C(309)	93 (17)	153 (20)	222 (35)	2 (15)	−32 (20)	−72 (21)
C(310)	120 (2)	114 (17)	198 (33)	18 (15)	95 (22)	58 (19)
N(4)	79 (13)	131 (15)	144 (24)	1 (11)	6 (14)	56 (15)
C(407)	72 (15)	128 (17)	296 (38)	34 (13)	72 (19)	116 (21)
C(408)	44 (14)	215 (26)	248 (41)	16 (15)	10 (20)	138 (28)
C(409)	112 (17)	125 (17)	165 (29)	24 (14)	2 (19)	26 (18)
C(410)	101 (20)	118 (20)	292 (45)	29 (16)	83 (26)	54 (24)

[a] Anisotropic thermal parameters are of the form $\exp[-(\beta_{11}h^2 + \ldots + 2\beta_{23}kl) \times 10^{-4}]$. [b] The coordinates of the Cu(1) atom were fixed during refinement; the assigned esd's are those of atom Cu(2). [c] These atoms make up the four phenyl groups which were refined as rigid bodies. The hydrogen atoms were assigned isotropic thermal parameters consistent with the overall motion of the group.

Table II. Bond Distances (A) and Angles (deg) for the Two $CuCl_4^{2-}$ Anions

Atoms (anion 1)	Dist	Atoms (anion 2)	Dist
Cu(1)–Cl(11)	2.229 (7)	Cu(2)–Cl(21)	2.243 (7)
Cu(1)–Cl(12)	2.225 (6)	Cu(2)–Cl(22)	2.247 (6)
Cu(1)–Cl(13)	2.267 (6)	Cu(2)–Cl(23)	2.237 (6)
Cu(1)–Cl(14)	2.221 (6)	Cu(2)–Cl(24)	2.237 (6)
Atoms (anion 1)	**Angle**	**Atoms (anion 2)**	**Angle**
Cl(11)–Cu(1)–Cl(12)	98.4 (2)	Cl(21)–Cu(2)–Cl(22)	98.0 (2)
Cl(11)–Cu(1)–Cl(13)	139.3 (3)	Cl(21)–Cu(2)–Cl(23)	139.0 (3)
Cl(11)–Cu(1)–Cl(14)	96.6 (2)	Cl(21)–Cu(2)–Cl(24)	97.9 (2)
Cl(12)–Cu(1)–Cl(13)	97.5 (2)	Cl(22)–Cu(2)–Cl(23)	96.9 (2)
Cl(12)–Cu(1)–Cl(14)	139.1 (2)	Cl(22)–Cu(2)–Cl(24)	135.6 (2)
Cl(13)–Cu(1)–Cl(14)	95.4 (2)	Cl(23)–Cu(2)–Cl(24)	97.7 (2)

Table III. N–Cl Contacts (Å)

Atoms	Dist	Atoms	Dist
N(1)–Cl(11)	3.51 (2)	N(3)–Cl(12)	3.40 (2)
N(1)–Cl(14)	3.17 (2)	N(3)–Cl(13)	3.31 (2)
N(1)–Cl(23)	3.56 (2)	N(3)–Cl(21)	3.70 (2)
N(1)–Cl(24)	3.26 (2)	N(3)–Cl(22)	3.13 (2)
N(2)–Cl(11)	3.37 (2)	N(4)–Cl(13)	3.45 (2)
N(2)–Cl(12)	3.56 (2)	N(4)–Cl(14)	3.11 (2)
N(2)–Cl(22)	3.31 (2)	N(4)–Cl(21)	3.28 (2)
N(2)–Cl(23)	3.31 (2)	N(4)–Cl(24)	3.79 (2)

bonds. Although the exact nature of the hydrogen bonding could not be determined, there is no doubt that it is a major contributor to the crystal-packing forces.

Electronic Spectra of (*d*-mampH)$_2$CuCl$_4$. The solid-state electronic spectrum of (*d*-mampH)$_2$CuCl$_4$ shows a broad d–d transition band at 10,200 cm^{-1} at 25° which shifts and resolves into two components at 77°K: 10,800 and 7500 cm^{-1}. These values are considerably higher than those normally found for flattened tetrahedral $CuCl_4^{2-}$ anions (see Table IV for some examples). This is easily explained by the greater degree of distortion toward planarity which increases the overall splitting of the d-orbital energy levels. This is further discussed in the following section in relation to a number of compounds containing a CuCl$_4$ chromophore.

Absorption Spectrum vs. Distortion. Before discussion of the distortion of CuCl$_4$ chromophores from T_d symmetry can be meaningful, the extent of distortion must be quantified. Three methods have been utilized in previous investigations: (1) the average of the two large (greater than 109.47°) angles is the simplest;[18] (2) the Cl–Cu–Cl dihedral angle has been used and values have been tabulated for a number of tetrachlorocuprates(II);[13] (3) a distortion parameter based on the distances between opposite edges of the tetrahedron has also been employed.[17] We have chosen the first method, with the average large angle defined as Θ, because it is the most easily calculated and can be interpreted and visualized in a straightforward manner. However, results similar to those discussed here can be obtained no matter which distortion quantity is used.

As mentioned in the Introduction, there have been two recent attempts to correlate empirically the maximum d–d transition for several $CuCl_4^{2-}$ salts with the amount of distortion from T_d symmetry as determined from X-ray crystal structure

Table IV. Comparison of the Maximum d–d Transitions for Several Chlorocuprate(II) Complexes Containing the $CuCl_4$ Chromophore[a]

Compd	Max d–d transition, cm^{-1}	Θ, deg	Av Cu–Cl dist, Å
Cs_2CuCl_4	9,050 (17, 23, 24)	129.2 (12)	2.230
$[C_6H_5CH_2N(CH_3)_3]_2CuCl_4$	9,250 (17, 25)	132.5 (8)	2.256
$[(C_2H_5)_3NH]_2CuCl_4$	9,390 (17)	134.8 (13)	2.241
$[(CH_3)_2NH_2]_3Cl\cdot CuCl_4$	9,520 (*b*)	135.8 (11)	2.230
(*d*-mampH)$_2$CuCl$_4$	10,200 (*b*)	138.3 (*b*)	2.238
$[(C_6H_5)_4P]_2Cu_2Cl_6$	11,250 (26, *b*)	143.5 (27)	2.248
$[(C_6H_5)_4As]_2Cu_2Cl_6$	11,500 (26, 28)	144.9 (29)	2.263
$[(C_6H_5)CH_2CH_2NH_2CH_3]_2CuCl_4$	16,100 (1)	180.0 (1)	2.265

[a] The distortion of the chromophore from tetrahedral symmetry is denoted by θ, the average of the two Cl–Cu–Cl angles which are greater than 109.47°. An average value for the d–d transition is given wherever more than one spectral reference is listed. References are given in parentheses. [b] This work.

studies: Lamotte-Brasseur[17] and Willett et al.[18] Both are somewhat limited in scope and have failed to use the revised structural results for Cs_2CuCl_4.[12] The first investigation further suffers from the difficulty of interpreting the distortion parameter, calculated by method 3, in terms of the geometry of the chlorine atoms about the copper atom. The second work avoids this difficulty by employing method 1 but uses the absorption spectrum of $[Pt(NH_3)_4]CuCl_4$ as the limiting case of four-coordinate square-planar geometry when in fact there are axial Cu–Cl interactions of 3.22 Å which perturb the electronic spectrum.[22]

The criteria for the selection of suitable compounds to be included in the present study of spectrum vs. distortion are as follows. (1) Only recent structures, with no disordering problems, are included. (2) No restriction is placed on the type of chlorocuprate(II) anions considered; i.e., compounds other than tetrachlorocuprates(II) are reviewed. For example, salts containing the $Cu_2Cl_6^{2-}$ anion, which consists of two $CuCl_4$ chromophores, are included in this study. (3) Structures in which the Cu atom is not truly four-coordinate are excluded. This eliminates structures wherein the Cu atom has long axial (Cu–Cl or Cu–metal atom) interactions producing five- and six-coordinate Cu atoms. (4) Both spectral and structural data should have been obtained at 25°. The spectrum generally improves in quality as one lowers the temperature, but a comparison of a structure determined with data collected at 25° with a spectrum obtained at 77°K, for example, assumes no change in the distortion of the $CuCl_4$ chromophore, an assumption which has yet to be experimentally validated.

Table IV shows the results of our survey, listing the value of Θ and the maximum d–d transition for eight compounds that fell within the framework of the above criteria. Also listed are the average Cu–Cl distances for each compound which are found to vary from the overall average of 2.246 Å by less than 0.02 Å. Included in the table are the results for the only discrete square-planar $CuCl_4^{2-}$ complex yet reported.[1] On the other hand, the values for $[(CH_3)_3NH]_3Cu_2Cl_7$, which contains $CuCl_4^{2-}$ anions of approximately C_{3v} symmetry (nearly tetrahedral), are not included;[6] the spectrum of this compound cannot be interpreted in a straightforward manner because of the additional absorption bands due to the presence of $[CuCl_3^-]_n$ infinite chains with the Cu atom in a tetragonally distorted octahedral environment.

The value of θ for (*d*-mampH)$_2$CuCl$_4$ is the average value for the two $CuCl_4^{2-}$ moieties, which individually have values of 139.2 and 137.3° for anions 1 and 2, respectively. This average value, 138.3°, is the largest of the D_{2d} $CuCl_4^{2-}$ compounds in Table IV and readily explains the high energy associated with the maximum d–d transition.

A graph of the maximum d–d transition vs. θ is presented in Figure 3 where a least-squares straight line has been drawn for lack of enough points to define the curve properly. The equation for this line is as follows: maximum d–d transition (cm^{-1}) = 1.445 × Θ − 9784. The straight-line approximation predicts that a $CuCl_4^{2-}$ complex with regular tetrahedral coordination should have a maximum d–d transition in the neighborhood of 6030 cm^{-1}; this certainly appears reasonable.[23]

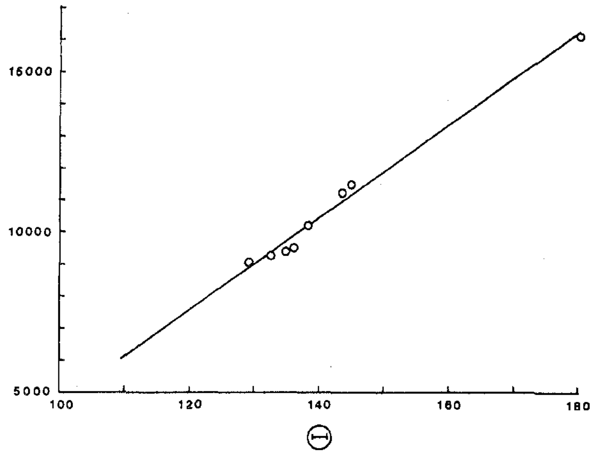

Figure 3. Graphical representation of the maximum d–d transition (cm^{-1}) vs. distortion (degrees) data listed in Table IV.

There are two generalizations which can be noted regarding the possibility of "filling the gaps" in Figure 3 at least where the $CuCl_4^{2-}$ salts are concerned. First, the cation which is present must be rather large in order to prevent the $CuCl_4^{2-}$ ions from interacting with each other to produce distorted square-pyramidal or octahedral coordination.[1] Second, deformation of the tetrahedron generally increases with any feature of the structure which reduces the chlorine–chlorine repulsion;[18] such features presently include bridging of the Cl atom to a second Cu atom (as in anions of the type $Cu_2Cl_6^{2-}$) and/or the formation of strong Cl–H hydrogen bonds.

With this in mind, a review of the spectral properties of a number of $CuCl_4^{2-}$ salts has revealed four interesting compounds with crystal structures yet to be determined: the nicotinium, the bis(tetraphenylphosphonium), the bis(quinolinium), and the bis(diethylammonium) salts. The first three compounds were reported by Lamotte-Brasseur[17] to have maximum d–d transitions at 7750, 7970, and 8160 cm^{-1}, respectively, which have predicted distortions (Θ values) of 121–124° calculated with the least-squares equation given above. The distortion from T_d symmetry is thus predicted to be much less in these compounds than that found for the tetrachlorocuprates(II) listed in Table IV. The spectrum of the fourth compound was reported by Willett et al.;[18] at 9.2°K, the spectrum shows three bands at 15,300, 12,900, and 9900 cm^{-1} with an intensity pattern similar to that displayed by the square-planar modification of bis(*N*-methylphenethylammonium) tetrachlorocuprate(II) at 77°K (16,900, 14,300, and 12,500 cm^{-1}).[1] Assuming that the Cu atom is truly four-coordinate with a maximum d–d transition of 15,300 cm^{-1} and assuming that Figure 3 is a reasonable representation of the maximum d–d transition vs. distortion as long as both are measured at the same temperature, it is predicted that the bis(diethylammonium) salt at 9.2°K should have a distortion value of 175°, i.e., nearly square planar. This value is larger than that proposed by Willett et al. (162 ± 5°), who derived their value using the 12,900-cm^{-1} absorption as the maximum-energy d–d transition and utilizing an absorption vs. distortion graph, which, as noted earlier, uses the maximum d–d absorption for $[Pt(NH_3)_4]CuCl_4$ as the limiting case of four-coordinate square-planar geometry. The X-ray crystal structures of the four compounds mentioned above are presently under consideration.

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Registry No. $[C_6H_5CH_2CH(CH_3)NH_2CH_3]_2CuCl_4$, 55030-07-4.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC50007J.

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A Structural Trans Effect at Nickel(II). Crystal and Molecular Structure of Bromo[bis(2-((2-pyridylmethyl)amino)ethyl) disulfide]nickel(II) Perchlorate

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The crystal and molecular structure of bromo[bis(2-((2-pyridylmethyl)amino)ethyl) disulfide]nickel(II) perchlorate, $[Ni(C_{16}H_{22}N_4S_2)Br]ClO_4$, has been determined by single-crystal X-ray diffraction techniques using counter methods and has been refined by full-matrix least-squares procedures to a final conventional R index of 0.046. The deep blue-violet crystals form as rectangular prisms in the orthorhombic space group *Pbca* with a = 23.838 (6), b = 14.686 (4), and c = 12.823 (2) Å, with eight molecules per unit cell. The nickel(II) ion is coordinated octahedrally by two amine nitrogen atoms, two pyridyl nitrogen atoms, one bromide ion, and one sulfur atom of the disulfide group. It is isostructural with the previously reported chloro compound. The two amine nitrogen atoms, equivalent in the ligand, show different nickel–nitrogen approach distances depending upon whether the trans group is the bromide ion (2.162 (5) Å) or a pyridyl nitrogen atom (2.114 (5) Å). The nickel(II)–sulfur distance, 2.456 (2) Å, is comparable with the sum of the corresponding Pauling covalent radii, 2.43 Å, indicating a strong interaction. Neither the sulfur–sulfur bond, 2.040 (3) Å, nor the CSSC torsion angle, 85°, has been modified by coordination to Ni(II). The precision of this work is approximately 3 times that reported for the corresponding chloro compound and great enough to indicate clearly a structural trans effect.

Introduction

The trans effect has been discussed, both kinetically and structurally, for an increasing number of transition metals, beginning with square-planar Pt(II)[1] and octahedral Co(III).[1-4] More recently, as new physical methods for studying rapid-exchange processes have been introduced and as crystallographic results have become more precise, trans effects and general labilizing effects have been noted for other ions, such as Ru(II)[5] and Co(II).[6]

Octahedral Ni(II) has been the object of kinetic and thermodynamic study[7,8] and its ligand substitution behavior has been comprehensively reviewed.[9-12] In no case has a specific structural or kinetic trans effect been discussed, although general labilizing effects consistent with the trans-directing sequence are reported.

Previous work in this laboratory on the crystal structure of chloro[bis(2-((2-pyridylmethyl)amino)ethyl) disulfide]nickel(II) perchlorate,[13] $[Ni(PMS)Cl]ClO_4$, and that of chloro[α,α'-(dithiobis(*o*-phenylenenitrilo))di-2-picoline]nickel(II) perchlorate,[14] $[Ni(DTPP)Cl]ClO_4$, indicated a structural trans effect, but in a marginally significant manner. The nitrogen atom trans to the chloride ion was found to be further from Ni(II) than was a second nitrogen atom equivalent to the first in the uncoordinated ligand. In the first complex,[13] $[Ni(PMS)Cl]ClO_4$, the difference in amino nitrogen bond lengths to Ni(II) was 0.086 (21) Å; in the second case,[14] [Ni(DT-