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Crystal Structures of the Green and Yellow Thermochromic Modifications of Bis(*N*-methylphenethylammonium) Tetrachlorocuprate(II). Discrete Square-Planar and Flattened Tetrahedral $CuCl_4^{2-}$ Anions

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Received March 4, 1974

AIC401439

Investigation of the crystal structures of two thermochromic forms of bis(*N*-methylphenethylammonium)tetrachlorocuprate(II), $[C_6H_5CH_2CH_2NHCH_3H^+]_2[CuCl_4^{2-}]$, was prompted by marked differences in their solid-state electronic spectra, indicating rearrangement of the configuration of the $CuCl_4^{2-}$ anion in the course of the transition from green to yellow at 80°. At 25°, the green form displayed the maximum d-d transition at 16,100 cm^{-1}, whereas at approximately 90° the highest energy absorption was at 9100 cm^{-1}. Crystals of the green (low-temperature) modification are monoclinic, space group $P2_1/c$, with $a = 6.4952$ (3) Å, $b = 22.678$ (1) Å, $c = 8.5844$ (6) Å, $\beta = 116.08$ (1)°, $Z = 2$, $d_x = 1.397$ g cm^{-3}, and $d_m = 1.390$ g cm^{-3}. Crystals of the yellow (high-temperature) modification are monoclinic, space group $C2/c$, with $a = 24.93$ (3) Å, $b = 8.180$ (7) Å, $c = 12.586$ (8) Å, $\beta = 115.21$ (7)°, $Z = 4$, and $d_x = 1.367$ g cm^{-3}. Intensities were obtained from θ-2θ scans with a four-circle automatic diffractometer using graphite-monochromatized Mo Kα radiation. For the green modification, 1705 observed reflections refined to a conventional $R = 0.035$ using full-matrix least squares; 1114 observed reflections of the yellow modification refined to a conventional $R = 0.092$. In the green modification the copper atom is situated on a crystallographic center of symmetry with nearly square-planar coordination of the chlorine atoms: the Cu-Cl distances are 2.248 (1) and 2.281 (1) Å with angles of 89.9 and 90.1°. In the yellow form the copper atom is located on a twofold axis with the chlorine atoms coordinated to form an irregular, flattened tetrahedron; Cu-Cl distances are 2.227 (4) and 2.190 (4) Å with Cl-Cu-Cl angles of 101.3 (2), 98.4 (2), 123.0 (2), and 138.1 (2)°. The $CuCl_4^{2-}$ anion is hydrogen bonded to the *N*-methylphenethylammonium cations in both modifications, with stronger bonds being formed in the green modification. The cation is found to be disordered in crystals of the yellow form.

Introduction

The work reported here is an outgrowth of a comprehensive study of coordination compounds of hallucinogenic drugs (and other ligands that are both structurally related and physiologically active) with transitional metal ions essential to vital processes.[1] During efforts to prepare copper(II) complexes of *dl*-methamphetamine, *C-demethylation* and protonation occurred and the product isolated was $[(C_6H_5)CH_2CH_2NH(CH_3)H^+]_2[CuCl_4^{2-}]$, hereafter abbreviated $(nmpH)_2CuCl_4$. This salt is thermochromic: green at 25° and yellow at 80°. X-Ray powder diffraction patterns showed that the two forms are not isomorphous.

It was of interest to determine the structures of these two modifications because of current interest in the geometry and environment of the tetrachlorocuprate(II) anion. Thus far, this anion has been observed as discrete flattened tetrahedra and as essentially square-planar units linked in sheets or ribbons by axial Cu-Cl bonds resulting in tetragonally distorted octahedra. For the types M_2CuCl_4 and $MCuCl_4$ (where M is a uni- or divalent cation), a distorted tetrahedral anion of D_{2d} symmetry is expected when M is a large, bulky cation such as Cs^+,[2,3] $(CH_3)_4N^+$,[3] $C_6H_5CH_2N(CH_3)_3^+$,[4] $[(CH_3)_2NH_2]_3Cl^{2+}$,[5] or $(C_2H_5)_3NH^+$.[6] Effective sixfold coordination results with smaller cations such as NH_4^+,[7] $CH_3NH_3^+$,[7] $C_2H_5NH_3^+$,[7,8] $[(NH_3CH_2CH_2)_2NH_2]Cl^{2+}$,[9] or $NH_3CH_2CH_2NH_3^{2+}$.[10] The complex $[Pt(NH_3)_4][CuCl_4]$ is reported, on the basis of powder patterns, to be isomorphous with $[Cu(NH_3)_4][PtCl_4]$ which is square planar with respect to both Cu and Pt but which has Cu-Pt interactions of 3.22 Å in the axial sites.[11]

We report here the structure of a complex involving the first confirmed case of a discrete square-planar tetrachlorocuprate(II) anion. The synthesis, characterization, and spectral and other properties of the title compound will be described elsewhere in context with related copper(II) complexes.

Experimental Section

Electronic Spectra. The electronic absorption spectra, measured with a Cary 14, displayed d-d transition bands primarily in the near-infrared and visible regions (20,000-5000 cm^{-1}). Solid-state spectra were obtained using mineral oil mulls; for the low-temperature runs, a flat-window quartz dewar cooled by liquid nitrogen was used. Solution spectra were measured using 1-cm cells.

Crystallographic Data Collection. Green Modification. Long, dark green needles of $(nmpH)_2CuCl_4$ were obtained when a solution of the compound in acetone underwent solvent exchange with diethyl ether. Cleavage of a small section from the central portion of one needle (the needle axis was later designated the *a* axis) yielded a suitable crystal for measurement of both lattice dimensions and intensities. This crystal was a parallelepiped which measured 0.30 × 0.40 × 0.43 mm perpendicular to (021), (02$\bar{1}$), and (100), respectively. A preliminary study carried out on a Syntex $P2_1$ automatic diffractometer established that the crystals are monoclinic with space group $P2_1/c$ (No. 14) and yielded a set of approximate unit cell dimensions. A GE XRD-5 diffractometer was then used with a 2° takeoff angle and a 0.05° receiving slit to obtain the resolved Cu Kα_1 (λ 1.54050 Å) peak positions for 27 high-angle reflections (2θ = 99.9-147.2°) at 24°. Least-squares refinement of these reflections produced the following unit cell parameters: $a = 6.4952$ (3) Å, $b = 22.678$ (1) Å, $c = 8.5844$ (6) Å, $\beta = 116.08$ (1)°, and $V = 1135.7$ Å^3. With a formula weight of 477.8 and $Z = 2$, the calculated density is 1.397 g cm^{-3} which compares well with the value of 1.390 g cm^{-3} as measured by flotation in a mixture of benzene and carbon tetrachloride. Thus, each unit cell contains two tetrachlorocuprate(II)

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anions, with the Cu atoms located at crystallographic centers of symmetry, and four *N*-methylphenethylammonium cations.

Intensity data were collected on a Syntex $P2_1$ automatic diffractometer with Mo $K\alpha$ radiation monochromatized by a graphite crystal. The θ-2θ scan technique was employed with each scan ranging from 0.8° in 2θ below the $K\alpha_1$ peak to 1.2° beyond the $K\alpha_2$ peak and accumulating P counts. The scan rate, S, varied from 2.0 to 8.0° min^{-1} depending in a direct manner upon the intensity. Background counts, B_1 and B_2, were taken at both ends of the scan range, each for a time equal to half the scan time. A total of 2364 unique reflections of the type hkl and $hk\bar{l}$ were measured in the range $4° < 2\theta < 53°$. The intensities of four standard reflections were measured after every 46 reflections. Over the period of data collection, these intensities dropped an average of 5%, 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.

The net intensity, I (relative to a 1.0° min^{-1} scan rate), and its estimated standard deviation, $\sigma(I)$, were calculated as follows: $I = S[P - (B_1 + B_2)]$; $\sigma(I) = S(P + B_1 + B_2)^{1/2}$. Intensities which were less than $0.7\sigma(I)$ were set equal to that value. An absorption correction based on crystal shape was made with resulting transmission coefficients ranging from 0.56 to 0.68 ($\mu = 14.75$ cm^{-1}, Mo $K\alpha$). Conversion to structure amplitudes was completed with the application of Lorentz and polarization factors.

Yellow Modification. It had been demonstrated from earlier work with X-ray powder patterns that a sample of $(nmpH)_2CuCl_4$ could be cycled reversibly from the green form to the yellow form by alternately heating the sample to 80° and then cooling it back to 25°. Hence the first attempt to obtain a single crystal of the yellow form was simply to heat a single crystal of the green form to 80°. Unfortunately, an X-ray rotation photograph of the resulting yellow crystal (maintained at 80°) exhibited mostly powder rings with only a few isolated spots. Attempts to grow a crystal by evaporation from solutions held at 80° also failed.

The first single crystal of the yellow form was produced when a sample of the green modification, powdered and packed into the tip of a sealed 0.3-mm capillary of Lindemann glass, was heated to the melting point and then cooled slowly to 80°. The intensities of the reflections were rather low but a preliminary study on the Syntex $P2_1$ diffractometer showed the crystal to be monoclinic with two possible space groups: Cc (No. 9) or $C2/c$ (No. 15). Unsuccessful attempts were made to grow a crystal in the central region of a capillary away from the ill-shaped tip, consisting of a large ball of glass which would have caused significant absorption errors. The single crystal used for data collection was grown in the tip of a capillary by alternately heating the sample to the melting point and then cooling to 80° until a satisfactory crystal was produced. The crystal, which was cone shaped with a central height of approximately 0.3 mm and a maximum diameter of 0.28 mm, was mounted on the Syntex $P2_1$ diffractometer. Throughout the data collection and the measurement of the unit cell parameters, the temperature of the crystal was maintained at 80° by a warm stream of air. The following unit cell dimensions are mean values produced by the least-squares refinement of 15 low-angle reflections (Mo$K\alpha$, λ 0.71069 Å) utilizing the Syntex least-squares routine: $a = 24.93$ (3) Å, $b = 8.180$ (7) Å, $c = 12.586$ (8) Å, $\beta = 115.21$ (7)°. With $V = 2321.6$ $Å^3$ and $Z = 4$ the calculated density is 1.367 g cm^{-3} and, as expected, is somewhat less than the density of the green form. For space group $C2/c$ this implies that the Cu atoms must be located either at centers of symmetry or on twofold axes; for space group Cc all atoms would be in general positions.

Most of the aspects of the collection and correction of the intensity data for the yellow form were the same as for the green form. Some differences should be noted: (1) The maximum scan rate was decreased from 8.0 to 5.0° min^{-1}; (2) the scan range below the $K\alpha_1$ peak was increased from 0.8 to 1.2° in 2θ because of the somewhat broader nature of the peaks; (3) standard reflections were closely monitored and never allowed to vary by more than ±2% (the crystal had to be recentered several times) and showed no appreciable decline in intensity over the period of data collection; (4) because of the uncertainties in the absorption by the glass and in the shape of the crystal, an absorption correction was not made. A total of 1519 unique reflections of the type hkl and $hk\bar{l}$ were measured in the range $4° < 2\theta < 45°$.

Solution and Refinement of the Structures. The atomic scattering factors for Cu, Cl, C, and N were those of Cromer and Waber;[12] the scattering factor for Cu was corrected for $\Delta f'$.[13] For hydrogen, the scattering factor of Stewart, Davidson, and Simpson was used.[14]

The function minimized in the least-squares refinement was $\Sigma w \cdot (|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and w is the weight calculated as $1/\sigma^2(F_o)$ for those reflections where $I > 3\sigma(I)$ and assigned as zero for reflections where $I < 3\sigma(I)$. The value of $\sigma(F_o)$ is derived directly from $\sigma(I)$ taking into account the various corrections that were made. The discrepancy indices given below are (1) the conventional $R = (\Sigma||F_o| - |F_c||/|F_o|)$ and (2) the weighted $R_w = (\Sigma w(|F_o| - |F_c|)^2/wF_o^2)^{1/2}$. Only reflections for which $I > 3\sigma(I)$ were used in the least-squares refinement, and unless otherwise specified, the R values given represent only the discrepancies for these reflections. For the green modification, 1705 reflections were used; for the yellow, there were 1114 such reflections.

Green Modification. As pointed out earlier, the Cu atoms must be positioned at crystallographic centers of symmetry and thus the structure amplitudes were initially phased by placing the Cu atom at the origin. A three-dimensional Fourier map revealed the positions of the Cl atoms; a subsequent map showed the locations of the other nonhydrogen atoms. The positional and isotropic thermal parameters of these 13 atoms were refined to $R = 0.107$ and $R_w = 0.095$. Following one cycle of refinement with anisotropic temperature factors ($R = 0.057$ and $R_w = 0.065$) a difference map was calculated which revealed the positions of the H atoms; the H atoms were assigned an isotropic thermal parameter of 5.0 $Å^2$. Two cycles of refinement of the H positions placed them in reasonable locations. Further refinement of all positional parameters and anisotropic thermal parameters of the nonhydrogen atoms dropped the R values to $R = 0.035$ and $R_w = 0.030$ but caused the H(6)–C(7)–H(7) angle to increase to the unrealistic value of 127°. These two H atoms were then fixed at the semirefined positions found after the first two cycles of hydrogen atom refinement. Final refinement led to discrepancy values of $R = 0.035$ and $R_w = 0.029$. The largest shift in any parameter during the last cycle of refinement was 0.11σ. The conventional R for all 2364 reflections is 0.055.

The largest peak in the final difference map, 0.5 e/$Å^3$, is located at the origin, the Cu atom position; the largest negative peak, –0.5 e/$Å^3$, is also in the vicinity of the Cu atom. Smaller positive and negative peaks are located near the Cl atoms. The standard deviation of an observation of unit weight is 2.45. Extinction did not prove to be a problem.

A table of observed and calculated structure amplitudes is available.[15] Final positional and thermal parameters are given in Table I.

Yellow Modification. A Patterson map was used to locate the Cu atom, which was positioned on a crystallographic twofold axis (assuming space group $C2/c$), and the Cl atoms. After initial refinement of these atoms, including isotropic thermal parameters, a Fourier map clearly showed the positions of the N, C(4), and C(9) atoms. For the remainder of the C atoms, the map showed only broad and ill-defined peaks; in addition, the peak assigned to C(7) was only half the magnitude of the other C peaks. Refinement of the positions (all nonhydrogen atoms), including anisotropic thermal parameters for the Cu and Cl atoms and isotropic thermal parameters for the remaining C and N atoms, led to $R = 0.100$ and $R_w = 0.076$. A difference map at this point revealed major positive peaks close to C(1), C(5), C(6), and C(8) with the largest peak located in a position between C(1) and C(8) [later designated as C(7P)]. The cation was thus determined to be disordered with the following characteristics: atoms C(4), N, and C(9) at the two ends of the cation show the least evidence of disorder; atoms C(1), C(6), and C(8) in the central portion of the cation have the largest thermal motions indicative of small displacements (Fourier and difference maps yield broad unresolved peaks); atom C(7) shows the greatest disorder and is divided between two distinct positions, hereafter labeled as C(7) and C(7P). (A partial set of data collected using the first single crystal produced a Fourier map showing the same type of disorder.) Atom C(7P) was then added to the refinement; with the isotropic thermal parameters fixed at 8.0 $Å^2$, the occupation factors for C(7) and C(7P) refined to values of 0.415 and 0.585, respectively. These occupation factors were then fixed and refinement of all positional and thermal parameters continued; R reduced to 0.092 and R_w to 0.068. Having obtained the information of interest and having no way of effectively handling the disorder problem, the refinement of

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(15) See paragraph at end of paper regarding supplementary material.

Table I

Final Atomic Coordinates (with Estimated Standard Deviations in Parentheses) for the Green Modification of $(nmpH)_2CuCl_4$

Atom	*x*	*y*	*z*
Cu	0.0	0.0	0.0
Cl(1)	0.10722 (16)	0.06983 (5)	0.21243 (13)
Cl(2)	0.22332 (15)	0.04310 (4)	−0.10609 (11)
N	0.6517 (5)	0.07808 (13)	0.2721 (4)
C(1)	0.5890 (7)	0.24200 (16)	0.1690 (4)
C(2)	0.7914 (7)	0.27274 (19)	0.2351 (5)
C(3)	0.7942 (9)	0.33191 (24)	0.2697 (6)
C(4)	0.6012 (12)	0.36094 (21)	0.2382 (6)
C(5)	0.3987 (10)	0.33223 (27)	0.1712 (7)
C(6)	0.3899 (8)	0.27258 (21)	0.1367 (5)
C(7)	0.5857 (7)	0.17718 (17)	0.1383 (5)
C(8)	0.6529 (7)	0.14242 (17)	0.3023 (5)
C(9)	0.7088 (7)	0.04221 (18)	0.4295 (5)
H(1)	0.926 (6)	0.2503 (15)	0.259 (4)
H(2)	0.923 (6)	0.3467 (16)	0.319 (5)
H(3)	0.612 (6)	0.3999 (15)	0.258 (4)
H(4)	0.266 (6)	0.3468 (17)	0.139 (5)
H(5)	0.237 (6)	0.2494 (15)	0.088 (4)
H(6)[a]	0.438 (7)	0.1631 (17)	0.060 (5)
H(7)[a]	0.695 (7)	0.1669 (17)	0.100 (5)
H(8)	0.550 (6)	0.1485 (15)	0.337 (4)
H(9)	0.810 (6)	0.1530 (14)	0.390 (4)
H(10)	0.517 (6)	0.0683 (15)	0.191 (4)
H(11)	0.751 (6)	0.0670 (15)	0.233 (4)
H(12)	0.693 (6)	0.0027 (15)	0.404 (4)
H(13)	0.585 (6)	0.0488 (14)	0.467 (4)
H(14)	0.851 (6)	0.0551 (15)	0.528 (4)

Thermal Parameters[b] for the Green Modification

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	206 (2)	179 (1)	143 (1)	1 (1)	69 (1)	−2 (1)
Cl(1)	335 (4)	317 (3)	235 (2)	−41 (1)	173 (2)	−41 (1)
Cl(2)	336 (3)	192 (2)	179 (2)	−12 (1)	138 (2)	−5 (1)
N	266 (11)	201 (7)	161 (6)	−5 (2)	97 (7)	−9 (2)
C(1)	413 (16)	208 (10)	111 (7)	−10 (3)	90 (9)	0 (2)
C(2)	407 (17)	239 (12)	198 (9)	−6 (3)	119 (10)	4 (2)
C(3)	552 (24)	292 (15)	221 (11)	−49 (5)	139 (14)	−4 (3)
C(4)	852 (31)	230 (12)	190 (10)	−1 (6)	203 (16)	4 (3)
C(5)	564 (26)	377 (17)	221 (11)	52 (5)	150 (15)	9 (3)
C(6)	404 (19)	328 (14)	191 (9)	−6 (4)	91 (11)	−4 (3)
C(7)	540 (19)	230 (10)	162 (8)	−13 (3)	134 (10)	−6 (2)
C(8)	334 (15)	205 (9)	150 (8)	−10 (3)	105 (9)	−9 (2)
C(9)	435 (17)	223 (10)	183 (9)	7 (4)	142 (10)	4 (3)

[a] The positions of these atoms were only partially refined. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. All β's are $\times 10^4$ except β_{22} which is $\times 10^5$.

Table II

Final Atomic Coordinates (with Esd's in Parentheses) for the Yellow Modification of $(nmpH)_2CuCl_4$

Atom	*x*	*y*	*z*	*B*, Å^2
Cu	0.0	0.1523 (3)	0.25	
Cl(1)	0.0375 (2)	0.2480 (2)	0.4295 (3)	
Cl(2)	0.0779 (2)	0.0225 (6)	0.2470 (3)	
N	0.4180 (4)	0.6522 (14)	0.5014 (8)	7.5 (3)
C(1)	0.2577 (9)	0.5525 (26)	0.3720 (18)	13.4 (6)
C(2)	0.2318 (8)	0.4574 (21)	0.4263 (13)	10.5 (5)
C(3)	0.1693 (8)	0.4299 (20)	0.3712 (15)	10.4 (5)
C(4)	0.1352 (6)	0.5044 (20)	0.2692 (14)	9.2 (4)
C(5)	0.1581 (7)	0.6074 (20)	0.2146 (13)	10.3 (5)
C(6)	0.2213 (9)	0.6278 (25)	0.2641 (18)	14.5 (7)
C(7)	0.3299 (10)	0.5215 (29)	0.4038 (19)	7.1 (6)
C(7P)	0.3242 (15)	0.6590 (50)	0.4819 (29)	9.0 (10)
C(8)	0.3516 (8)	0.6600 (25)	0.4403 (15)	11.1 (5)
C(9)	0.4447 (6)	0.8020 (17)	0.5655 (11)	8.2 (4)

Anisotropic Thermal Parameters ($\times 10^4$) for Cu and Cl Atoms

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	33 (1)	289 (6)	107 (3)	0	28 (1)	0
Cl(1)	55 (2)	470 (13)	136 (5)	−39 (4)	42 (2)	−101 (6)
Cl(2)	49 (1)	484 (13)	187 (5)	65 (4)	61 (2)	81 (7)

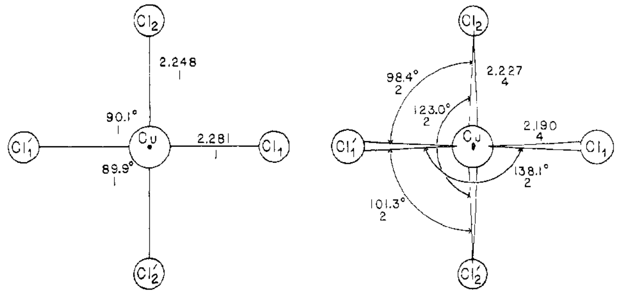

Figure 1. Bond distances and angles for the $CuCl_4^{2-}$ anion in the green (left) and yellow (right) modifications.

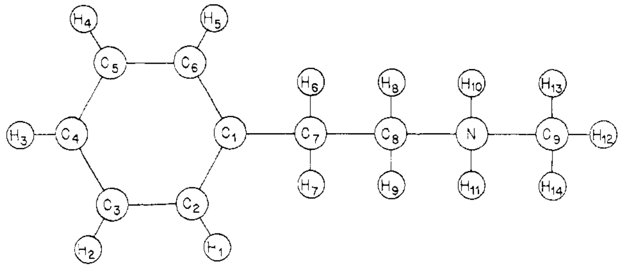

Figure 2. Atom-numbering scheme for the $nmpH^+$ cation.

the structure was considered complete. The conventional *R* for all 1519 reflections is 0.112. The final difference map was similar to the previous one with major peaks being found around the C atoms that are seriously disordered. The two largest peaks are located close to atoms C(1) and C(6) and are approximately 0.25 and 0.20% of the respective peaks on the Fourier map. The difference map shows only small positive and negative peaks in the area of the Cu and Cl atoms, indicating the proper refinement of these atoms.

The possibility that the disorder was only a manifestation of a refinement in an incorrect space group led to an attempt to refine the structure in space group *Cc*. Although the values of *R* and R_w decreased, many of the bond distances and angles produced as a result of this refinement were chemically unrealistic. This, coupled with the very large correlation coefficients (up to 0.82) between parameters of atoms formerly related by the twofold axis, led to the conclusion that the space group was indeed *C*2/*c*.

A table of observed and calculated structure amplitudes is available.[15] Final positional and thermal parameters are given in Table II.

Computer Programs. Programs used to solve and refine the two structures 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; DAEDS, distances, angles, and their estimated standard deviations, by D. R. Harris, modified by R. E. Davis; and ORTEP, by C. K. Johnson.

Discussion

Bond distances and angles for both modifications are shown in Figure 1 for the tetrachlorocuprate(II) anion and are tabulated in Table III for the *N*-methylphenethylammonium cation according to the atom-numbering scheme given in Figure 2. Hydrogen-bonding distances N-Cl and H-Cl are listed in Table IV and are illustrated in partial packing diagrams, Figures 3 and 4. The only other contact distance less than 3.5 Å between nonhydrogen atoms was the C(9)- - -C(1′) distance of 3.44 Å in the yellow form. Table V gives the results of least-squares mean plane calculations for the benzene ring in the two modifications.

Tetrachlorocuprate(II) Anion. Green Modification. Constricted to a planar configuration by crystallographic symmetry requirements, the $CuCl_4^{2-}$ anion is nearly square planar with the Cl(1)-Cu-Cl(2) angle being within one standard de-

Table III. Bond Distances (Å) and Angles (deg) for the nmpH Cation in the Green and Yellow Modifications of $(nmpH)_2CuCl_4$ (with Esd's in Parentheses)

Values for the Nonhydrogen Atoms

Atoms	Distances	
	Green	Yellow
C(1)-C(2)	1.372 (6)	1.37 (3)
C(2)-C(3)	1.373 (7)	1.43 (3)
C(3)-C(4)	1.334 (9)	1.35 (3)
C(4)-C(5)	1.349 (9)	1.36 (2)
C(5)-C(6)	1.381 (8)	1.44 (3)
C(1)-C(6)	1.384 (7)	1.41 (3)
C(1)-C(7)	1.492 (5)	1.69 (3)
C(1)-C(7P)		1.86 (4)
C(7)-C(8)	1.502 (6)	1.26 (3)
C(7P)-C(8)		1.02 (4)
C(8)-N	1.482 (5)	1.50 (2)
N-C(9)	1.478 (5)	1.46 (2)

Atoms	Angles	
	Green	Yellow
C(6)-C(1)-C(2)	118.0 (4)	119 (2)
C(1)-C(2)-C(3)	120.4 (4)	120 (2)
C(2)-C(3)-C(4)	121.1 (5)	121 (2)
C(3)-C(4)-C(5)	120.1 (5)	122 (2)
C(4)-C(5)-C(6)	120.4 (6)	118 (2)
C(5)-C(6)-C(1)	120.1 (5)	120 (2)
C(2)-C(1)-C(7)	120.7 (4)	119 (2)
C(2)-C(1)-C(7P)		111 (2)
C(6)-C(1)-C(7)	121.3 (4)	119 (2)
C(6)-C(1)-C(7P)		121 (2)
C(1)-C(7)-C(8)	113.3 (3)	102 (2)
C(1)-C(7P)-C(8)		102 (3)
C(7)-C(8)-N	112.1 (3)	111 (2)
C(7P)-C(8)-N		125 (3)
C(8)-N-C(9)	113.7 (3)	113 (1)
C(7)-C(8)-C(7P)		85 (3)
C(7)-C(1)-C(7P)		51 (2)

Values Involving Hydrogen Atoms (Green Form Only)

Atoms	Distances	Atoms	Distances
C(2)-H(1)	0.95 (4)	C(8)-H(8)	0.86 (4)
C(3)-H(2)	0.83 (4)	C(8)-H(9)	1.00 (4)
C(4)-H(3)	0.90 (4)	N-H(10)	0.88 (4)
C(5)-H(4)	0.85 (4)	N-H(11)	0.89 (4)
C(6)-H(5)	1.03 (4)	C(9)-H(12)	0.92 (4)
C(7)-H(6)	0.95 (4)	C(9)-H(13)	1.00 (4)
C(7)-H(7)	0.93 (4)	C(9)-H(14)	0.99 (4)

Atoms	Angles	Atoms	Angles
C(1)-C(2)-H(1)	116 (2)	C(7)-C(8)-H(9)	111 (2)
C(3)-C(2)-H(1)	124 (2)	N-C(8)-H(8)	106 (2)
C(2)-C(3)-H(2)	115 (3)	N-C(8)-H(9)	107 (2)
C(4)-C(3)-H(2)	124 (3)	H(8)-C(8)-H(9)	114 (3)
C(3)-C(4)-H(3)	117 (3)	C(8)-N-H(10)	108 (2)
C(5)-C(4)-H(3)	123 (3)	C(8)-N-H(11)	114 (2)
C(4)-C(5)-H(4)	128 (3)	C(9)-N-H(10)	110 (2)
C(6)-C(5)-H(4)	112 (3)	C(9)-N-H(11)	105 (2)
C(5)-C(6)-H(5)	122 (2)	H(10)-N-H(11)	106 (3)
C(1)-C(6)-H(5)	118 (2)	N-C(9)-H(12)	111 (2)
C(1)-C(7)-H(6)	113 (3)	N-C(9)-H(13)	107 (2)
C(1)-C(7)-H(7)	111 (3)	N-C(9)-H(14)	113 (2)
C(8)-C(7)-H(6)	106 (3)	H(12)-C(9)-H(13)	102 (3)
C(8)-C(7)-H(7)	104 (3)	H(12)-C(9)-H(14)	117 (3)
H(6)-C(7)-H(7)	111 (2)	H(13)-C(9)-H(14)	105 (3)
C(7)-C(8)-H(8)	107 (3)		

viation of 90° but with the Cu-Cl bond distances differing by 0.033 Å, a small but significant amount. The Cu-Cl bond lengths are undoubtedly affected by the different hydrogen-bonding environments of the two Cl atoms (Table IV). Because Cl(1) is more closely approached by H atoms than is Cl(2), it is not surprising that the Cu-Cl(1) bond length is longer.

Previous X-ray studies[7-10] of $CuCl_4^{2-}$ anions approaching square-planar coordination have yielded Cu-Cl distances ranging from 2.264 to 2.332 Å with the Cl-Cu-Cl angles all being within one standard deviation of 90°. The $CuCl_4^{2-}$ anion in each of these structures also has two Cl atoms from neighboring anions occupying octahedral sites with Cu-Cl distances varying from 2.79 to 3.10 Å. In the green form of $(nmpH)_2CuCl_4$ no such "octahedral" bonding occurs, giving rise to the unusual electronic spectrum discussed below and probably accounting for the unusually short Cu-Cl distance of 2.248 Å.

Table IV. Hydrogen-Bonding Distances (Å) in the Green and Yellow Forms

Atoms	Distance	Symmetry of Cl atom
	Green Form	
N-Cl(1)	3.349 (3)	x, y, z
N-Cl(2)	3.312 (3)	x, y, z
N-Cl(1)	3.223 (3)	$1 + x, y, z$
N-Cl(2)	3.356 (3)	$1 - x, -y, -z$
Av N-Cl	3.310	
H(10)-Cl(1)	2.75 (4)	x, y, z
H(10)-Cl(2)	2.49 (4)	x, y, z
H(11)-Cl(1)	2.40 (4)	$1 + x, y, z$
H(11)-Cl(2)	2.76 (4)	$1 - x, -y, -z$
	Yellow Form	
N-Cl(1)	3.55 (1)	$^1/_2 + x, ^1/_2 + y, z$
N-Cl(2)	3.35 (1)	$^1/_2 - x, ^1/_2 + y, ^1/_2 - z$
N-Cl(1)	3.45 (1)	$^1/_2 - x, ^1/_2 - y, 1 - z$
N-Cl(2)	3.44 (1)	$^1/_2 - x, ^1/_2 - y, 1 - z$
Av N-Cl	3.45	

Table V. Least-Squares Mean-Plane Calculations for the Benzene Ring in the Green and Yellow Forms of $(nmpH)_2CuCl_4$

Equation of Plane

Green form: $0.3173X + 0.2046Y - 0.9260Z - 0.9311 = 0$
Yellow form: $0.3564X - 0.7876Y - 0.5027Z + 4.1164 = 0$

Perpendicular Distances (Å) to the Plane (with Esd's)

Atoms	Green	Yellow	Atoms	Green	Yellow
C(1)[a]	−0.003 (4)	0.006 (21)	C(7)	−0.054 (4)	0.605 (24)
C(2)[a]	0.006 (4)	−0.026 (17)	C(7P)		−0.928 (39)
C(3)[a]	−0.003 (5)	0.016 (17)	H(1)	−0.02 (3)	
C(4)[a]	−0.003 (5)	0.012 (16)	H(2)	−0.08 (4)	
C(5)[a]	0.005 (5)	−0.031 (17)	H(3)	0.03 (4)	
C(6)[a]	−0.002 (4)	0.022 (21)	H(4)	0.07 (4)	
			H(5)	−0.02 (3)	

[a] Used in the plane calculations.

Tetrachlorocuprate(II) Anion. Yellow Modification. When the green form of $(nmpH)_2CuCl_4$ is heated to 80° and converted to the yellow form, a transformation takes place whereby the Cl atoms of the square-planar $CuCl_4^{2-}$ anion move out of the plane in a manner such as to produce a coordination geometry in the shape of a flattened tetrahedron. Although the crystallographic twofold axis constricts the anion to approximate D_{2d} symmetry, the resulting tetrahedron is somewhat irregular because the Cl(2) and Cl(2′) atoms have moved further out of the plane than Cl(1) and Cl(1′), giving rise to a Cl(2)-Cu-Cl(2′) angle of 123.0° as compared with 138.1° for the Cl(1)-Cu-Cl(1′) angle. Accompanying this change in coordination is a weakening of the hydrogen-bonding network (Table IV) and a corresponding shortening of Cu-Cl bonds (Figure 1). The average hydrogen-bonding N-Cl distance in the green form is 3.310 Å which increases to 3.45 Å in the yellow form. The longer Cu-Cl distance is once again associated with the Cl atom which is engaged in the strongest hydrogen bonding. The Cu-Cl bond distances are within the range 2.18-2.28 Å found for other $CuCl_4^{2-}$ anions with flattened tetrahedral coordination.[2-6] The Cl(1)-Cu-Cl(1′) angle of 138.1° is

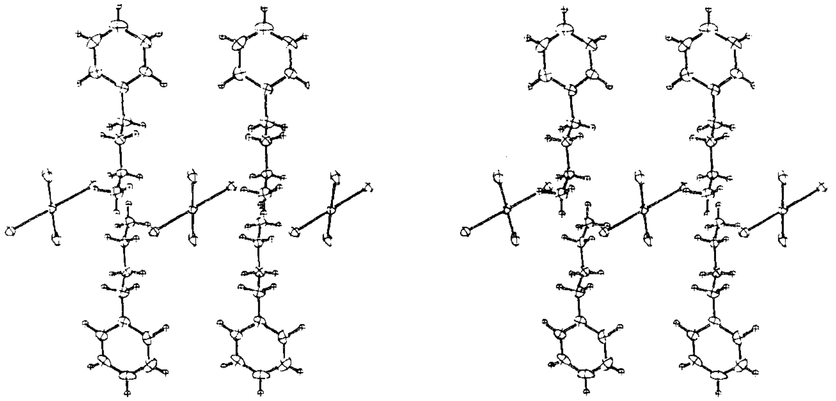

Figure 3. Partial packing diagram of the green modification of $(nmpH)_2CuCl_4$.

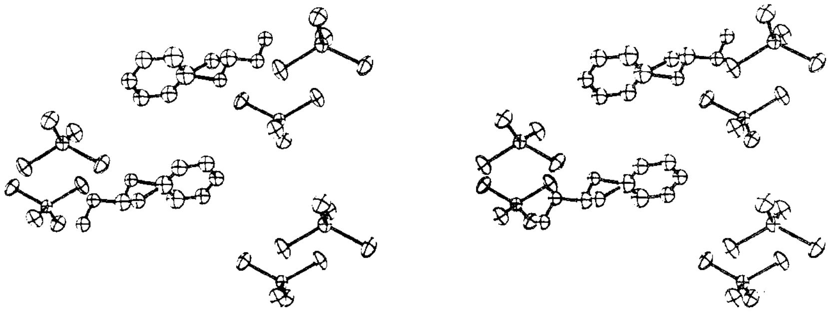

Figure 4. Partial packing diagram of the yellow modification of $(nmpH)_2CuCl_4$.

slightly larger (2°) than those previously reported, but all other angles are in agreement.

***N*-Methylphenethylammonium Cation. Both Modifications.** In the green form the nmpH cation refined to expected values for the bond distances and angles. The unreasonably short distances for C(3)-C(4) and C(4)-C(5), 1.334 and 1.349 Å, respectively, are a direct result of the large thermal motions of these atoms as is easily seen in Figure 3. Attempts to correct the bond distances for these motions have not been made. The benzene ring is planar to within 1.5σ (Table V) with C(7), the C atom of the side chain adjacent to the benzene ring, bent slightly out of the plane by 0.054 Å.

In the case of the yellow form, the isotropic thermal motions for many of the atoms in the nmpH cation are a direct result of the inability to account for the disorder that was found [particularly affected are C(1), C(6), and C(8)]. The disordered atoms have refined to average positions yielding deceptively fortuitous distances and angles within the benzene ring but totally unreasonable values for atoms C(7) and C(7P) which are bonded to the ring. Bond distances and angles around C(8) have also been seriously affected. The N atom appears to have refined well, indicating that it is held in place by hydrogen bonds. Thus, although no faith can be placed in any of the interatomic distances and angles, the hydrogen-bonding distances N-Cl are probably reliable. The disorder can be pictured (with some imagination) in Figure 4 which shows the two atoms C(7) and C(7P) both bonded to the ring and to atom C(8); the relative disorder of the other atoms in the cation can be seen to vary directly with the size of their respective ellipsoids. The benzene ring was found to be planar within 2σ but the disorder has caused C(7) to be 0.61 (2) Å above the plane whereas C(7P) is 0.93 (4) Å below the plane.

Electronic Spectra. Tetrachlorocuprate(II) anions[16,17] having tetragonally distorted octahedral geometry give an absorption maximum for the highest energy d-d transition of Cu(II) ($3d^9$) at approximately 13,000 cm^{-1} whereas the d-d transition for the flattened tetrahedral species occurs at approximately 9000 cm^{-1}. The $[Pt(NH_3)_4][CuCl_4]$ complex has an absorption maximum[16,17] at 14,300 cm^{-1}. It is probably square planar with respect to Cl atoms but has axial Cu-Pt interactions so that the d-orbital splitting is smaller than would be the case for truly square-planar coordination. The solid-state electronic spectrum of the $(nmpH)_2CuCl_4$ at 77°K showed three distinct peaks at 16,900, 14,300, and 12,500 cm^{-1}, which shifted to 16,100, 13,600, and 11,500 cm^{-1} at 25°. In the case of the yellow form at 90°, a single maximum with a broad tail extending to lower energies was observed at approximately 9100 cm^{-1}. A similar spectral curve was obtained for solutions of $(nmpH)_2CuCl_4$ in nitromethane at 25°, with the maximum shifted to 10,500 cm^{-1}. The spectra of the solid-state high-temperature modification (yellow) and of the solutions agree well with the spectra of $CuCl_4^{2-}$ with established tetrahedral symmetry, but the spectrum of the low-temperature modification shows maxima at higher energies than the spectrum of tetragonally distorted octahedral complexes and of $[Pt(NH_3)_4][CuCl_4]$. An increase in the overall splitting of the d-orbitals is expected in an octahedral environment as the ligands on the *z* axis are gradually withdrawn, with the limiting case being reached in the four-coordinate square-planar arrangement.[18] In the case of the green modification of $(nmpH)_2CuCl_4$ there are no interactions that are short enough to be interpreted as bonding interactions between the Cu atom and any other atom in a direction normal to the $CuCl_4^{2-}$ plane.

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Acknowledgment. This work was supported by the Robert A. Welch Foundation; the diffractometer was purchased with funds provided by the National Science Foundation (Grant GP-37028).

Registry No. $(\mathrm{nmpH})_2\mathrm{CuCl}_4$ (green), 51751-77-0; $(\mathrm{nmpH})_2\mathrm{CuCl}_4$ (yellow), 51751-78-1.

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 $4.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-2106.

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Dependence of Rates of Complex Formation on Ionic Strength and Chelation. Samarium Sulfate and Malonate

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Received July 5, 1973

AIC304950

An attempt has been made to correlate overall rate constants for metal complex formation reactions obtained by transient relaxation methods with the rate constants for the rate-determining step obtained by the ultrasound absorption technique. Sound absorption measurements on aqueous samarium sulfate solutions have been made as a function of the ionic strength of the medium. The supporting electrolyte was NaClO_4. No significant dependence of the rate constant for the rate-controlling step on ionic strength was observed. In the sound absorption spectra of aqueous samarium malonate solutions a new relaxation was observed at frequencies lower than that for samarium sulfate. This new relaxation has been attributed to a rate-determining ring-closure step. On a complete steady-state kinetic analysis of the multistep complex formation mechanism there was fair agreement between the calculated overall forward-rate constant and the value obtained experimentally by transient methods.

Introduction

The complexation of a metal ion by a ligand in solution can, in general terms, be described by the equation

$$\mathrm{M} + \mathrm{L} \rightleftarrows \mathrm{ML} \tag{1}$$

If the process is fast it is possible to study it by transient and by steady-state relaxation techniques. The former approach usually gives overall forward (k_f) and backward (k_b) rate constants while the latter yields stepwise rate constants (k_{ij}). The correlation between rate constants from the various methods can lead to a fuller interpretation of the overall stepwise mechanism which involves an uncertain number of steps. It is the purpose of this article to attempt such a correlation.

Excluding competing reactions such as hydrolysis etc., the generalized observed rate law for the formation of ML according to (1) is given by[3]

$$\mathrm{d}[\mathrm{ML}]/\mathrm{d}t = k_\mathrm{f}[\mathrm{M}][\mathrm{L}] - k_\mathrm{b}[\mathrm{L}] \tag{2}$$

The reaction involves a number of successive steps only one of which is rate controlling.[4] Three types of mechanisms have been described which are equally compatible with the rate law:[5] (1) dissociative, D; (2) associative, A; and (3) interchange, I. The mechanistic labels are descriptive of the fundamental differences in the structures of the activated complex. In terms of a multistep mechanism for complex formation the Diebler–Eigen (DE) concept[4] or some modification of it is still in favor. Two-step mechanisms are as prevalent as the original three-step (DE) mechanism in the current literature.

Much effort has been directed at the means for distinguishing a particular mechanism and in the majority of cases the evidence appears to favor a dissociative mechanism in which the rate-controlling step is cleavage of the metal–water bond to produce a metal ion of reduced coordination number in the transition state.[3] Working on this premise the overall effective forward rate constant can be related to k_{34}, the constant for the rate-controlling step in the (DE) description, by the equation[3] $k_\mathrm{f} = K_\mathrm{o}k_{34}$, where K_o is the outer ion-pair formation constant usually calculated from theory.[6,7] If the mechanism is truly dissociative, then k_{34} is equal to k_ex, the rate constant for solvent exchange. According to the steady-state kinetic analysis of the multistep process this elementary correlation between rate constants is only valid when the rate constants for the previous faster steps are much greater than the rate constants for the rate-determining step.[8] In cases where the rate of water exchange is rapid there is poor correlation between k_f measured and k_f calculated using $k_\mathrm{f} = K_\mathrm{o}k_{34}$. Some improvement is obtained if a steady-state kinetic analysis is done, replacing K_o by a function which consists only of rate constants for the faster steps.[8,9] The function which gives the best correspondence between observed rate constants is indicative of the number of steps in the mechanism.

An example of a system in which water exchange on the cation is rapid and for which a number of kinetic studies

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