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Crystal Structure of *N*-Methylphenethylammonium Trichlorocuprate(II). Distorted Trigonal-Bipyramidal Coordination

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Investigation of the crystal structure of *N*-methylphenethylammonium trichlorocuprate(II), $[(C_6H_5)CH_2CH_2NH(CH_3)H^+]$-$(CuCl_3^-)$, was prompted by the observation of a solid-state electronic spectrum different from those previously reported for trichlorocuprate(II) salts of known Cu–Cl geometry. At 77°K, d–d transition bands were at 11,100, 9170, and 7520 cm^{-1}, with a weak but distinct shoulder at 19,600 cm^{-1} on a more intense charge-transfer band. Crystals of the red-brown compound are monoclinic, space group $P2_1/c$, with $a = 6.193$ (1), $b = 8.365$ (1), $c = 25.435$ (2) Å; $\beta = 104.71$ (1)°; $Z = 4$; $d_x = 1.595$, $d_m = 1.593$ g cm^{-3}. Intensities for 2927 independent reflections were measured with θ–2θ scans using a Syntex $P2_1$ diffractometer with monochromatized Mo Kα radiation. A total of 1824 reflections with $I > 3\sigma(I)$ were used to refine all positional parameters, anisotropic thermal parameters of the nonhydrogen atoms, and isotropic thermal parameters of the hydrogen atoms; at convergence, the conventional R was 0.046. The $CuCl_3^-$ anions exist as infinite chains in the direction of the a axis with two of the chlorines serving as bridging atoms. The coordination about the Cu atom is that of a distorted trigonal-bipyramid with equatorial Cu–Cl distances of 2.528 (1), 2.372 (1), and 2.257 (1) Å and with axial distances of 2.283 (1) and 2.306 (1) Å. The equatorial angles Cl–Cu–Cl are 101.6 (1), 124.4 (1), and 133.9 (1)° with the axial–equatorial angles all within the range 84.9–93.1°. Hydrogen bonding occurs from the $-NH_2-$ group of the *N*-methylphenethylammonium cation primarily to the terminal chlorine atom, with N–Cl distances of 3.158 (5) and 3.192 (5) Å and H–Cl distances of 2.11 (6) and 2.40 (6) Å.

Introduction

Investigation[1] of the thermochromic compound bis(*N*-methylphenethylammonium) tetrachlorocuprate(II), $(nmpH)_2CuCl_4$, revealed the first instance of discrete square-planar tetrachlorocuprate(II) anions in the green phase (25°); a transition at 80° yielded the yellow phase in which the copper atom showed the more familiar distorted tetrahedral coordination. Thus it was of interest to examine another chlorocuprate(II) derived from *N*-methylphenethylamine hydrochloride: the complex $[(C_6H_5)CH_2CH_2NH(CH_3)H^+]$-$(CuCl_3^-)$, hereafter abbreviated $(nmpH)CuCl_3$.

Trichlorocuprate(II) salts have been shown to exhibit a variety of coordination numbers and configurations of Cl^- ions about the Cu^{2+} ion. With supporting cations of K^+ or NH_4^+, essentially planar $Cu_2Cl_6^{2-}$ dimers are found interconnected by two long Cu–Cl bonds (2.9 Å compared with 2.3 Å for the four equatorial bonds) perpendicular to the dimeric plane, thus producing tetragonally distorted octahedral coordination about the Cu atom.[2] In $[(CH_3)_2NH_2]$-$CuCl_3$, the sixth octahedral position is vacant, giving rise to a distorted square-pyramidal arrangement.[3] There are no bonds between dimeric units in $[(C_6H_5)_4As]CuCl_3$; further, the dimers are distorted from planarity in a fashion such that each Cu atom has a highly flattened tetrahedral array of Cl atoms about it.[4] There is a tetragonally distorted octahedral configuration in $CsCuCl_3$, but instead of dimeric units there are infinite chains of $CuCl_3^-$ monomers with all Cl atoms bridging.[5]

We report here an unusual polymeric trichlorocuprate(II) structure with one terminal and four bridging Cl atoms about each Cu atom producing a distorted trigonal-bipyramidal configuration. 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. Solid-state electronic absorption spectra, measured with a Cary 14, were obtained using mineral oil mulls. For the low-temperature runs, a flat-window quartz dewar cooled with liquid nitrogen was used.

Infrared Spectra. The infrared region 4000–700 cm^{-1} was examined with a Beckman IR-7 instrument using mineral oil and Fluorolube mulls between sodium chloride disks. Mineral oil mulls between sheets of polyethylene were used for the far-infrared region 700–95 cm^{-1} employing a Beckman IR-11 instrument.

Crystallographic Data Collection. The red-brown crystal selected for the measurement of lattice parameters and intensity data had dimensions of 0.17 × 0.17 × 0.36 mm perpendicular to (012), $(01\bar{2})$ and $(10\bar{2})$, respectively. Mounted on a Syntex $P2_1$ diffractometer, a preliminary study showed the crystal to be monoclinic with space group $P2_1/c$ (No. 14) and produced a set of approximate unit cell parameters. These parameters were later refined by least squares using the Bragg angles of Cu Kα_1 peaks of 30 high-angle reflections ($2\theta > 101°$) measured on a GE XRD-5 diffractometer (λ(Cu Kα_1) 1.54050 Å) with a 2° takeoff angle and a 0.05° receiving slit: at 24°, $a = 6.193$ (1), $b = 8.365$ (1), $c = 25.435$ (2) Å; $\beta = 104.71$ (1)°; $V = 1274.3$ Å^3. With a formula weight of 306.03, the calculated density of 1.595 g cm^{-3} for 4 molecules per unit cell is in excellent agreement with the measured density (by flotation in a mixture of $CHCl_3$ and $CHBr_3$) of 1.593 g cm^{-3}.

Intensity data were collected on a Syntex $P2_1$ computer-controlled diffractometer with Mo Kα radiation monochromatized by a graphite crystal. The θ–2θ scan technique was employed with each scan ranging from 1.0° in 2θ below the Kα_1 peak to 1.0° beyond the Kα_2 peak accumulating P counts. The scan rate, S, varied from 2.0 to 5.0° min^{-1} depending 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 2927 unique reflections of the type hkl and $hk\bar{l}$ were measured in the range $4° < 2\theta < 55°$. No change in the intensities of four standard reflections, measured after every 96 reflections, was noted. Coincidence losses were corrected by calculation based on the counting system's dead time.

The net intensity, I (relative to a scan rate of 1.0° min^{-1}), and its estimated standard deviation, $\sigma(I)$, were calculated as follows: $I = S[P - (B_1 + B_2)]$; $\sigma(I) = S(P + B_1 + B_2)^{1/2}$. An absorption correction based on crystal shape was made with resulting transmission coefficients ranging from 0.63 to 0.73 ($\mu = 23.59$ cm^{-1}, Mo Kα). Conversion to structure amplitudes was completed with the application of Lorentz and polarization factors.

Solution and Refinement of the Structure. The structure was solved by the heavy-atom method. The positional and isotropic thermal parameters of the 14 nonhydrogen atoms were refined by full-matrix least squares to a conventional $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ of 0.110 and a weighted $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$ of 0.080 for the 1824 reflections for which $I > 3\sigma(I)$ (these were the

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

[2] R. D. Willett, C. Dwiggins, Jr., R. F. Kruh, and R. E. Rundle, *J. Chem. Phys.*, 38, 2429 (1963).

[3] R. D. Willett, *J. Chem. Phys.*, 44, 39 (1966).

[4] R. D. Willett and C. Chow, *Acta Crystallogr., Sect. B*, 30, 207 (1974).

[5] A. W. Schlueter, R. A. Jacobson, and R. E. Rundle, *Inorg. Chem.*, 5, 277 (1966).

Table I. Final Positional and Thermal Parameters for *N*-Methylphenethylammonium Trichlorocuprate(II)[a]

(a) Positional Parameters of the Nonhydrogen Atoms

Atom	x	y	z
Cu	0.22006 (10)	−0.06610 (8)	−0.02445 (3)
Cl(1)	0.5271 (2)	−0.0558 (2)	0.06264 (5)
Cl(2)	0.0272 (2)	0.1761 (2)	−0.01956 (5)
Cl(3)	0.1660 (2)	−0.2711 (2)	−0.08402 (6)
N	0.3419 (8)	0.3491 (6)	0.0942 (2)
C(1)	0.6327 (9)	0.2078 (6)	0.2349 (2)
C(2)	0.6118 (10)	0.2880 (7)	0.2808 (2)
C(3)	0.7891 (15)	0.2909 (9)	0.3269 (3)
C(4)	0.9866 (13)	0.2134 (10)	0.3275 (3)
C(5)	0.0089 (12)	0.1331 (10)	0.2821 (3)
C(6)	0.8322 (12)	0.1319 (9)	0.2363 (3)
C(7)	0.4502 (11)	0.2106 (8)	0.1837 (2)
C(8)	0.4453 (11)	0.3679 (7)	0.1537 (2)
C(9)	0.3344 (15)	0.5017 (10)	0.0638 (3)

(b) Positional and Thermal (Isotropic) Parameters (Å^2) of the Hydrogen Atoms

Atom	x	y	z	U
H(1)	0.458 (7)	0.348 (6)	0.279 (2)	0.07 (2)
H(2)	0.784 (12)	0.366 (9)	0.354 (3)	0.17 (4)
H(3)	0.118 (11)	0.226 (9)	0.362 (3)	0.16 (3)
H(4)	0.163 (10)	0.074 (8)	0.280 (2)	0.14 (3)
H(5)	0.851 (9)	0.070 (7)	0.208 (2)	0.10 (2)
H(6)	0.309 (8)	0.190 (6)	0.194 (2)	0.07 (2)
H(7)	0.483 (8)	0.114 (7)	0.161 (2)	0.09 (2)
H(8)	0.375 (8)	0.455 (7)	0.175 (2)	0.10 (2)
H(9)	0.599 (9)	0.411 (7)	0.160 (2)	0.09 (2)
H(10)	0.178 (10)	0.298 (7)	0.090 (2)	0.13 (3)
H(11)	0.447 (10)	0.254 (8)	0.084 (2)	0.13 (3)
H(12)	0.285 (9)	0.476 (7)	0.022 (2)	0.10 (2)
H(13)	0.504 (11)	0.550 (9)	0.076 (3)	0.17 (3)
H(14)	0.254 (12)	0.570 (9)	0.082 (3)	0.18 (4)

(c) Anisotropic Thermal Parameters of the Nonhydrogen Atoms

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	0.0331 (3)	0.0413 (4)	0.0366 (4)	−0.0000 (3)	0.0135 (3)	−0.0021 (4)
Cl(1)	0.0449 (7)	0.0861 (11)	0.0506 (8)	−0.0055 (8)	0.0115 (6)	0.0080 (9)
Cl(2)	0.0537 (8)	0.0494 (9)	0.0594 (8)	0.0036 (7)	0.0217 (7)	0.0054 (7)
Cl(3)	0.0592 (9)	0.1045 (14)	0.1002 (12)	−0.0229 (9)	0.0415 (9)	−0.0521 (11)
N	0.047 (3)	0.060 (3)	0.051 (3)	0.001 (2)	0.007 (2)	0.003 (3)
C(1)	0.060 (3)	0.047 (4)	0.047 (3)	−0.001 (3)	0.010 (3)	0.001 (3)
C(2)	0.077 (5)	0.060 (4)	0.055 (4)	0.012 (4)	0.013 (3)	0.002 (3)
C(3)	0.129 (7)	0.061 (5)	0.055 (5)	0.002 (5)	0.006 (4)	−0.001 (4)
C(4)	0.080 (5)	0.103 (7)	0.083 (6)	−0.007 (5)	−0.014 (5)	0.025 (5)
C(5)	0.070 (5)	0.130 (8)	0.085 (6)	0.023 (5)	0.014 (5)	0.022 (5)
C(6)	0.079 (5)	0.085 (5)	0.070 (5)	0.019 (4)	0.027 (4)	0.005 (4)
C(7)	0.067 (4)	0.060 (5)	0.061 (4)	−0.011 (4)	0.010 (3)	0.006 (4)
C(8)	0.065 (4)	0.056 (4)	0.046 (4)	−0.001 (2)	0.008 (3)	−0.007 (3)
C(9)	0.100 (6)	0.074 (5)	0.065 (5)	0.003 (4)	0.005 (4)	0.025 (4)

[a] Esd's in parentheses. [b] Thermal parameters of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^*)]$.

only reflections used in the least-squares refinement). The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where w is the weight calculated as $1/\sigma^2(F_o)$. One cycle of refinement with anisotropic thermal parameters reduced R and R_w to 0.057 and 0.048, respectively. A difference map clearly revealed the positions of the hydrogen atoms. Final cycles of refinement on all positional parameters, the anisotropic thermal parameters of the nonhydrogen atoms, and the isotropic thermal parameters of the hydrogen atoms converged with $R = 0.046$ and $R_w = 0.030$. For all 2927 reflections, the conventional R was found to be 0.078.

The final positional and thermal parameters are listed in Table I. The largest shift in any parameter during the last cycle of the least-squares refinement was 0.25σ. The standard deviation of an observation of unit weight is 2.47; extinction did not prove to be a problem. The largest peak in the final difference map was located near the copper atom and had a magnitude of 0.3 e Å^{-3}. The atomic scattering factors used for the nonhydrogen atoms were those of Cromer and Waber;[6] the scattering factors for Cu and Cl were corrected for $\Delta f'$ and $\Delta f''$ as given by Cromer.[7] For the hydrogen atoms, the scattering factors of Stewart, Davidson, and Simpson were used.[8] A table of observed and calculated structure amplitudes is available.[9]

Computer Programs. Programs used to solve and refine the two structures include 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 are shown in Figure 1 for the trichlorocuprate(II) anion and are tabulated in Table II for the *N*-methylphenethylammonium cation according to the atom-numbering scheme given in Figure 2. Possible hydrogen-bonding interactions are listed in Table III and are illustrated in Figure 3, a partial packing diagram. No other un-

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(6) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(7) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(8) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

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

Table II. Bond Distances (Å) and Angles (deg) for the nmpH Cation[a]

Bond Distances for the Nonhydrogen Atom			
C(1)-C(2)	1.381 (8)	C(1)-C(6)	1.382 (9)
C(2)-C(3)	1.390 (10)	C(1)-C(7)	1.493 (8)
C(3)-C(4)	1.381 (12)	C(7)-C(8)	1.517 (9)
C(4)-C(5)	1.375 (12)	C(8)-N	1.494 (7)
C(5)-C(6)	1.380 (11)	N-C(9)	1.488 (9)
Bond Angles for the Nonhydrogen Atom			
C(6)-C(1)-C(2)	118.5 (5)	C(2)-C(1)-C(7)	121.2 (5)
C(1)-C(2)-C(3)	119.9 (6)	C(6)-C(1)-C(7)	120.3 (5)
C(2)-C(3)-C(4)	120.6 (7)	C(1)-C(7)-C(8)	111.5 (5)
C(3)-C(4)-C(5)	119.9 (7)	C(7)-C(8)-N	111.5 (5)
C(4)-C(5)-C(6)	119.0 (7)	C(8)-N-C(9)	112.6 (5)
C(5)-C(6)-C(1)	122.1 (7)		
Bond Distances Involving Hydrogen Atom			
C(2)-H(1)	1.07 (5)	C(8)-H(8)	1.07 (6)
C(3)-H(2)	0.95 (7)	C(8)-H(9)	0.99 (5)
C(4)-H(3)	1.05 (7)	N-H(10)	1.08 (6)
C(5)-H(4)	1.09 (7)	N-H(11)	1.10 (6)
C(6)-H(5)	0.91 (6)	C(9)-H(12)	1.05 (6)
C(7)-H(6)	0.99 (5)	C(9)-H(13)	1.09 (7)
C(7)-H(7)	1.04 (5)	C(9)-H(14)	0.96 (8)
Bond Angles Involving Hydrogen Atoms			
C(1)-C(2)-H(1)	118 (3)	C(7)-C(8)-H(9)	110 (3)
C(3)-C(2)-H(1)	123 (3)	N-C(8)-H(8)	118 (3)
C(2)-C(3)-H(2)	118 (5)	N-C(8)-H(9)	110 (3)
C(4)-C(3)-H(2)	120 (5)	H(8)-C(8)-H(9)	100 (4)
C(3)-C(4)-H(3)	117 (4)	C(8)-N-H(10)	107 (3)
C(5)-C(4)-H(3)	123 (4)	C(8)-N-H(11)	101 (3)
C(4)-C(5)-H(4)	123 (3)	C(9)-N-H(10)	113 (3)
C(6)-C(5)-H(4)	118 (3)	C(9)-N-H(11)	116 (3)
C(5)-C(6)-H(5)	116 (4)	H(10)-N-H(11)	107 (5)
C(1)-C(6)-H(5)	122 (4)	N-C(9)-H(12)	108 (3)
C(1)-C(7)-H(6)	107 (3)	N-C(9)-H(13)	106 (4)
C(1)-C(7)-H(7)	105 (3)	N-C(9)-H(14)	102 (5)
C(8)-C(7)-H(6)	112 (3)	H(12)-C(9)-H(13)	112 (5)
C(8)-C(7)-H(7)	112 (3)	H(12)-C(9)-H(14)	124 (6)
H(6)-C(7)-H(7)	108 (4)	H(13)-C(9)-H(14)	103 (6)
C(7)-C(8)-H(8)	107 (3)		

[a] Esd's in parentheses.

Table III. Hydrogen-Bonding Interactions for $(nmpH)CuCl_3$

Atoms	Distances, Å	Atoms	Angle, deg
N-Cl(3)′	3.158 (5)		
N-Cl(3)″	3.192 (5)		
N-Cl(2)	3.377 (5)		
N-Cl(1)	3.729 (5)		
H(10)-Cl(3)′	2.11 (6)	N-H(10)- - -Cl(3)′	163 (5)
H(11)-Cl(3)″	2.40 (6)	N-H(11)- - -Cl(3)″	127 (4)
H(11)-Cl(1)	2.72 (6)	N-H(11)- - -Cl(1)	152 (4)
H(10)-Cl(2)	2.90 (6)	N-H(10)- - -Cl(2)	107 (4)

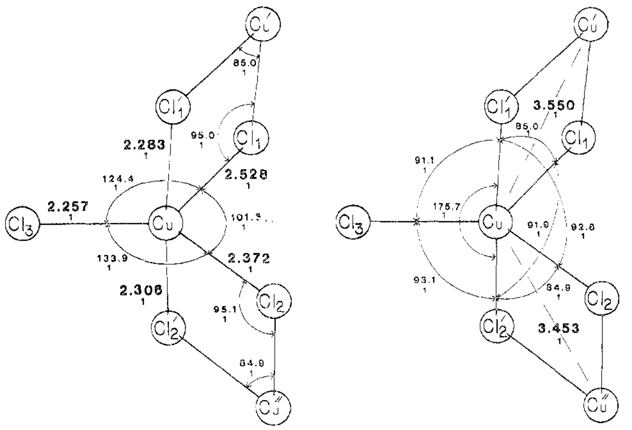

Figure 1. Bond distances and angles for the $CuCl_3^-$ anion.

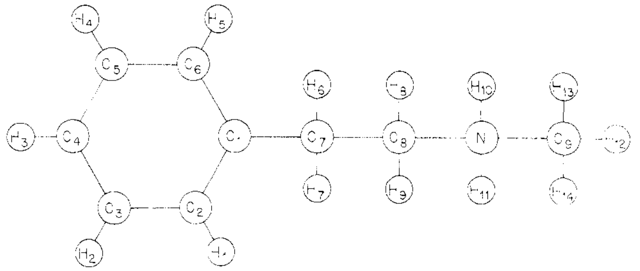

Figure 2. Atom-numbering scheme for the $nmpH^+$ cation.

Table IV. Least-Squares Mean-Plane Calculations

(a) For the Equatorial Atoms of the Copper Coordination Sphere
Equation: $0.7379X + 0.4610Y - 0.4929Z - 1.1414 = 0$

Atoms used in plane calculn	Distances,[a] Å	Other atoms	Distances,[a] Å
Cu	0.0223 (6)	Cl(1)′	2.293 (1)
Cl(1)	−0.006 (1)	Cl(2)′	−2.275 (1)
Cl(2)	−0.007 (1)		
Cl(3)	−0.009 (2)		

(b) For the Benzene Ring
Equation: $0.4447X + 0.8336Y - 0.3277Z - 0.6241 = 0$

Atoms used in plane calculn	Distance,[a] Å	Other atoms	Distance,[a] Å
C(1)	−0.002 (5)	C(7)	0.076 (7)
C(2)	−0.001 (6)	H(1)	0.02 (5)
C(3)	0.002 (8)	H(2)	0.21 (7)
C(4)	−0.001 (9)	H(3)	0.06 (7)
C(5)	−0.002 (8)	H(4)	0.03 (7)
C(6)	0.003 (7)	H(5)	−0.07 (6)

[a] Perpendicular distances to the plane with esd's in parentheses.

usual interionic contacts were noted. Table IV shows the results of two mean-plane calculations, one for the equatorial atoms of the copper coordination sphere and the other for the benzene ring of the cation.

Trichlorocuprate(II) Anion. The trichlorocuprate(II) anion is involved in the formation of an unusual infinite chain with a general formula of $[Cu(Cl_{bridging})_2(Cl_{terminal})]_n$ such that each copper atom is coordinated to five Cl atoms to form a distorted trigonal bipyramid. The bridging Cl atoms and the Cu atoms to which they are bound are located about centers of symmetry in the direction of the *a* axis. This structure represents a new type of trichlorocuprate(II) polymer differing from either the $Cu_2Cl_6^{2-}$ dimers or the $(CuCl_3^-)_n$ infinite chains where all Cl atoms are bridging.

The shortest Cu-Cl bond, 2.257 (1) Å, is that to the terminal chlorine atom Cl(3), and this is in agreement with other trichlorocuprate(II) structures that contain both terminal and bridging chlorine atoms.[2,3] However, the fact that the shortest bond is situated in the equatorial plane of the bipyramidal coordination sphere differs from the case of the $CuCl_5^{3-}$ anion, the only other structural example of trigonal-bipyramidal chlorocuprate(II) coordination, where the equatorial bonds are significantly longer than the axial bonds: 2.39 *vs.* 2.30 Å.[10,11] It is interesting to note, however, that the other two equatorial bonds are the longest of the five by a considerable margin, thus confirming the trend found for the $CuCl_5^{3-}$ anion.

The Cl-Cu-Cl angles differ significantly from the angles expected for a regular trigonal bipyramid; the structure contains equatorial-equatorial angles which vary from 101.6 (1)

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(10) K. N. Raymond, D. W. Meek, and J. A. Ibers, *Inorg. Chem.*, **7**, 1111 (1968).

(11) I. Bernal, N. Elliott, R. A. Lalancette and T. Brennan in "Progress in Coordination Chemistry," Proceedings of the Eleventh International Conference on Coordination Chemistry, Haifa and Jerusalem, Sept 1968, Elsevier, 1968, p 518.

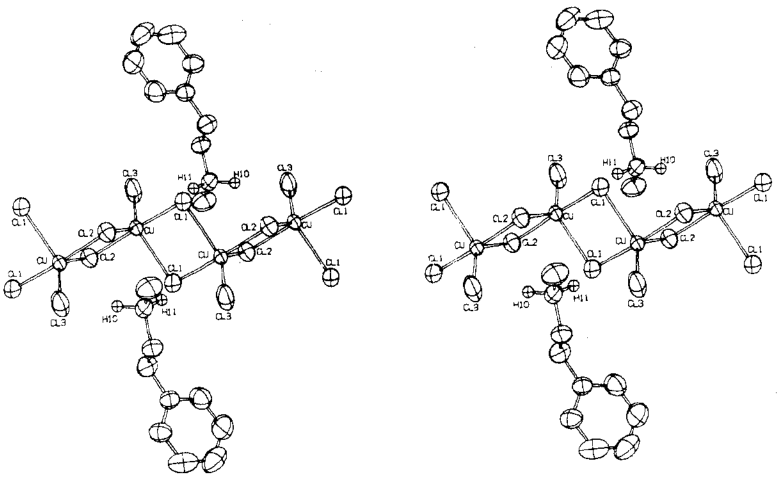

Figure 3. Partial packing diagram of (nmpH)$CuCl_3$. The view is parallel to the *b* axis; the *a* axis is horizontal.

to 133.9 (1)° and axial-equatorial from 84.9 (1) to 93.1 (1)°. In addition, a mean-plane calculation (Table IV) for the four equatorial atoms shows that the copper atom is slightly out of the plane of the three chlorine atoms by approximately 0.023 Å.

The two chlorine bridges are seen to be unsymmetric, with each forming an equatorial bond which is significantly longer than the axial bond: for Cl(1), 2.528 (1) *vs.* 2.283 (1) Å; for Cl(2), 2.372 (1) *vs.* 2.306 (1) Å. Differences in the bridging bond lengths are reflected in two Cu-Cu distances of 3.453 (1) and 3.550 (1) Å. The Cu-Cl-Cu angles, 95.0 (1) and 95.1 (1)°, and the Cl-Cu-Cl angles, 85.0 (1) and 84.9 (1)°, for the bridging chlorines are virtually identical.

At 25°, the electronic absorption spectrum showed d-d transition bands at 10,600 and 7690 cm^{-1}; these were shifted and further resolved at 77°K to 11,100, 9170, and 7520 cm^{-1}. In addition, at the lower temperature there was a weak but distinct shoulder at 19,600 cm^{-1} on a more intense charge-transfer band. For the previously reported Cu-Cl coordination geometries found in trichlorocuprates(II) discussed above, the following maximum energy d-d transition bands at 77°K are observed: tetragonally distorted octahedral, 12,900 cm^{-1};[12] highly flattened tetrahedral, 12,200 cm^{-1};[4] and distorted square pyramidal, 12,000 cm^{-1}.[13] By comparison, pentachlorocuprate(II) ions with rigorous trigonal-bipyramidal symmetry, as exemplified[10] by $[Cr(NH_3)_6]CuCl_5$, display their maximum-energy d-d band[14] at 10,800 cm^{-1}. The relative energies of these bands are consistent with the d-orbital splittings of a simple point charge model of the ligands about the central metal ion. It is therefore not surprising that (nmpH)$CuCl_3$, with a geometry intermediate between trigonal bipyramidal and square pyramidal, but closer to the former, displays a maximum d-d band at 11,100 cm^{-1}. The shoulder at 19,600 cm^{-1} is probably a polarized charge-transfer band, thus accounting for its weak absorbance; these have been noted in $Cu_2Cl_6^{2-}$ dimers[12] and in polymeric $CsCuCl_3$.[15,16]

Interpretation of the far-infrared spectrum was hampered by a large number of cation vibrations in the region of interest. Careful examination of the curve shapes, however, revealed bands at approximately 290 and 275 cm^{-1}, which could be safely assigned as terminal and bridging Cu-Cl stretching frequencies, respectively.

***N*-Methylphenethylammonium Cation.** All distances and angles for the cation are those expected and agree well with those found for the same cation in the green form of $(nmpH)_2CuCl_4$,[1] except where errors in the latter structure were produced as a result of large thermal motions. A mean-plane calculation (Table IV) shows that the benzene ring is planar to within one standard deviation, with the atom bonded to the ring, C(7), and slightly out of the plane by 0.076 (7) Å.

Hydrogen Bonding. The interionic N-H- - -Cl hydrogen-bonding scheme can be most aptly described as follows. The nitrogen atom of the nmpH cation sits approximately midway between the terminal Cl(3) atoms with distances of 3.158 (5) and 3.192 (5) Å. The hydrogen atoms, however, approach the chlorine atoms in quite different fashions: H(10) forms a very strong bond with a H(10)- - -Cl(3) distance of 2.11 (6) Å and a nearly linear N-H(10)- - -Cl(3) angle of 163 (6)°, while H(11) is unsymmetrically bifurcated with distances of 2.40 (6) and 2.72 (6) Å for the H(11)- - -Cl(3) and H(11)- - -Cl(1) bonds, respectively. Atom H(10) also approaches atom Cl(2), but the distance, 2.90 (6) Å, is almost equal to the van der Waals distance of 3.0 Å, and the N-H-(10)- - -Cl(2) angle is far from linear, 107 (4)°.

In the parent amine hydrochloride, absorptions associated with ν(N-H) are found at 2790 (very strong) and 2465 (strong) cm^{-1}, in agreement with secondary amine hydrochlorides.[17] In (nmpH)$CuCl_3$, one of these bands is shifted to 3160 (strong) cm^{-1}, implying a strong N-H bond as electron density is removed from the N-H- - -Cl interaction and into the Cu-Cl bond. Another strong band occurs, however, at 2375 cm^{-1}, possibly associated with the strong N-H(10)- - -Cl(3) interaction which brings about a weakening of the N-H(10) bond.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition

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Structure and Bonding in 4,4′-Dinitro-*trans*-stilbenebis(triphenylphosphine)platinum, $Pt[(C_6H_4NO_2)CHCH(C_6H_4NO_2)][P(C_6H_5)_3]_2$

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The crystal and molecular structure of a disubstituted olefin complex of platinum, $Pt[(C_6H_4NO_2)CHCH(C_6H_4NO_2)]$-$[P(C_6H_5)_3]_2$, has been determined from three-dimensional X-ray diffraction data. The complex crystallizes in space group $P\bar{1}$ of the triclinic system, with two molecules in a unit cell of dimensions $a = 12.955$ (3), $b = 15.012$ (3), $c = 11.169$ (3) Å; $\alpha = 96.65$ (1), $\beta = 97.93$ (1), $\gamma = 93.00$ (1)°. No symmetry is crystallographically imposed upon the molecules. The structural parameters were refined by least-squares techniques, the R factor on F converging to 6.6% for the 2785 independent reflections measured using a four-circle diffractometer for which $2\theta \leqslant 35°$. Coordination around platinum is approximately planar, the most significant distortion being the displacement of one olefinic carbon atom by 0.22 (1) Å from the plane defined by the other four atoms; the dihedral angle between the PtP_2 and PtC_2 planes is 8.7 (7)°. The olefinic carbon–carbon separation is 1.416 (15) Å and these carbon atoms are approximately equidistant from platinum, the Pt–C distances being 2.093 (14) and 2.165 (12) Å. The Pt–P bond lengths are 2.261 (4) and 2.298 (4) Å, which differ significantly, the longer being trans to the shorter Pt–C separation. Both 4-nitrophenyl substituents are almost exactly perpendicular to the PtC_2 plane, the dihedral angles being 86.6 (6) and 87.5 (4)°. This perpendicular orientation maximizes electron withdrawal by π-symmetry orbitals of the substituents. So that hydrogen–hydrogen contacts within the olefin do not become impossibly short in this perpendicular orientation, it is necessary for the olefin substituents to be bent away from platinum to different extents, the observed angles being 33 (2) and 5 (2)°; electronic effects stemming from this difference may be the cause of the asymmetry in the bond lengths to platinum.

Introduction

Many olefin–platinum complexes of the general formula $Pt[L][P(C_6H_5)_3]_2$, where L is the olefin, have been prepared[1,2] and X-ray diffraction studies have delineated the overall structural characteristics of this class of compounds.[3-8] The olefinic carbon atoms are approximately equidistant from platinum and the olefinic carbon–carbon separation increases upon coordination to platinum, reported values ranging from 1.42 to 1.62 Å. However, some of the diffraction experiments were of relatively low precision and crystallographic disorder was a problem in other cases: consequently, few of these carbon–carbon separations differ significantly from each other. In order to elucidate the relationships between the electronic effects of the substituents upon the olefin and the changes in olefin geometry that occur upon coordination, we intend to determine the structures of a number of complexes formed by olefins with extreme properties.

The olefins that bind most strongly to platinum have substituents that are electron withdrawing in a π fashion and 4,4′-dinitro-*trans*-stilbene, I, is one of the most strongly bound olefins of all.[1] A study of the complex formed by I has the particular advantage that the olefin must adopt a sterically unfavorable conformation for optimum use to be made of the electron-withdrawing ability of the substituents. The plane of each 4-nitrophenyl ring must be perpendicular to the plane defined by the platinum and two olefinic carbon atoms for maximum overlap of the π-symmetry orbitals. Such an orientation causes the ortho hydrogen atoms of each substituent ring to be at a minimum separation from the hydrogen atoms on the olefinic carbon atoms. Thus the operation of the electron-withdrawing mechanism will be made manifest by the otherwise unfavored orientation of the substituents. Furthermore, the derived olefinic C–C separation will provide a bench-mark value for comparisons with other results, particularly since, as it will be seen, a precise value is obtained.

Experimental Section

Preparation of the Crystals. The literature method[1] was modified slightly in order to obtain crystals of sufficient size (rather than to maximize product yield). The reaction was performed under nitrogen using Schlenk apparatus. $PtCl_2[P(C_6H_5)_3]_2$, 0.20 g dissolved in 7 ml of ethanol, was heated to 60° in the reaction flask, and hydrazine hydrate, 0.3 ml, was added to give a clear, colorless solution. 4,4′-Dinitro-*trans*-stilbene, 0.10 g dissolved in 30 ml of ethanol, was heated to 60° and added slowly to the reaction mixture. The clear orange-red solution was permitted to cool to room temperature very slowly, whereupon thin, platelike crystals of the product, $Pt[(C_6H_4NO_2)CHCH(C_6H_4NO_2)][P(C_6H_5)_3]_2$, formed.

Collection and Reduction of X-Ray Diffraction Data. Optical examination and preliminary X-ray photography revealed no symmetry and the crystal was assigned to the triclinic system. Successful refinement of the structure confirmed the initial assumption of $P\bar{1}$ for the space group. The cell constants, obtained by least-squares refinement using the setting angles of 12 reflections centered on a Picker four-circle automatic diffractometer with Mo $K\alpha_1$ X-radiation

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