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Crystal and Molecular Structure of Pentakis(2-imidazolidinone)copper(II) Perchlorate

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The crystal and molecular structure of $Cu(C_3H_6N_2O)_5(ClO_4)_2$ has been determined by single-crystal X-ray diffraction techniques. The compound crystallizes in space group $P\bar{1}$ with two molecules per unit cell with dimensions $a = 15.635$ (2) Å, $b = 9.343$ (1) Å, $c = 12.273$ (1) Å, $\alpha = 98.16$ (1)°, $\beta = 120.26$ (1)°, and $\gamma = 106.05$ (1)°. The structure was solved by the heavy-atom method and refined by block-diagonal least squares to a final R value of 0.07_1. The copper atoms are coordinated to the oxygens of the five ethyleneurea ligands with distorted 4 + 1 symmetry and with copper–oxygen distances of 1.952 (6), 1.954 (6), 1.935 (6), 1.940 (6), and 2.239 (6) Å, respectively. The molecules are packed in the cells as centrosymmetric hydrogen-bonded pairs. One of the perchlorate groups, although 2.994 (8) Å away, completes the distorted octahedron about the copper atom.

Introduction

The coordination chemistry of cyclic urea compounds has been of interest for many years since they show bonding similar to lactam systems found in biologically active molecules. Of particular interest is the metal ion coordination site on these molecules since bonding is possible to either the oxygen or the nitrogen or both. Additional spectral and magnetic studies have been undertaken on the urea complexes in an effort to understand the role they play as catalysts in the polymerization and cellulose cross-linking in cotton as a means of imparting resiliency.[1] This earlier research led to the preparation of two copper-cyclic urea complexes, $Cu(C_3H_6N_2O)_5(ClO_4)_2$ and $Cu(C_4H_8N_2O)Cl_2$, whose spectral and magnetic properties were very different. This study is the first step undertaken to understand and explain these differences.

Experimental Section

Crystals of the copper complex were furnished to us by A. Pierce of Southern Regional Laboratory, Department of Agriculture. A single blue crystal with dimensions 0.15 × 0.20 × 0.22 mm was mounted on a General Electric XRD-5 diffractometer with the (102) axis as the spindle axis. The lack of systematic extinctions or of rotational symmetry in the reciprocal lattice limited the space group possibilities to either $P1$ or $P\bar{1}$. Lattice constants for a primitive unit cell were determined by a least-squares fit of 28 carefully measured 2θ values of the Cu $K\alpha_1$ and Cu $K\alpha_2$ doublet for $2\theta > 70°$ under fine conditions (1° takeoff angle and 0.05° slit). The resultant lattice constants and their estimated standard deviations (esd's) are $a = 15.635$ (2) Å, $b = 9.343$ (1) Å, $c = 12.273$ (1) Å, $\alpha = 98.16$ (1)°, $\beta = 120.26$ (1)°, $\gamma = 106.05$ (1)°, and $V = 1400.2$ Å^3.

The calculated density of 1.64 g/cm^3 for two molecules per unit cell agrees well with the experimental density of 1.62 ± 0.02 g/cm^3 measured by flotation methods.

Intensity data were collected on a General Electric XRD-490 fully automated diffractometer by the stationary-crystal, stationary-counter method using balanced nickel and cobalt filters and copper $K\alpha$ radiation. A total of 4910 reflections were measured to $2\theta = 130°$. Of these reflections a total of 2905 (59%) were considered observed by the criterion $(I_{Ni} - 2\sigma(I_{Ni})) - (I_{Co} + 2\sigma(I_{Co})) > 150$ counts where the σ's were based entirely on counting statistics. After the standard Lorentz-polarization corrections, the intensities were corrected for $K\alpha_1$, $K\alpha_2$ splitting and for absorption. Absorption was corrected as a function of ϕ with a maximum difference of intensity of only 12% over the entire range of ϕ (linear absorption coefficient $\mu = 3.6$ cm^{-1} for Cu radiation).

Structure Determination

The coordinates of the two copper atoms were determined from a three-dimensional Patterson function and used in the phasing of a subsequent electron density map. This map showed the four chlorine atoms and from their positions relative to the copper atoms it was clear that they were related to each other by a center of symmetry. For this reason all subsequent refinements were limited to space group $P\bar{1}$. The copper and chlorine atoms were refined isotropically by block-diagonal least squares,[2] using 628 of the largest reflections, to $R, r = 0.318, 0.320$. Using these heavy atoms as the starting point, a series of Fourier maps and least-squares peak refinements was computed to obtain coordinates for the 41 unique nonhydrogen atoms. This trial structure was then refined isotropically, using all 2905 reflections, to $R, r = 0.137, 0.137$. A difference electron density map was calculated to locate the hydrogen atoms. Positive regions of electron density were found at the expected hydrogen positions but they did not show clear centers. Therefore, coordinates for the hydrogen atoms were calculated on the basis of expected geometry. The hydrogens were then included in subsequent structure factor calculations but not refined. Refinement was continued using anisotropic temperature factors for the nonhydrogen atoms and $1/\sigma^2$ weights until the shifts were less than one-tenth the estimated standard deviations of the respective parameters, resulting in final values of $R, r = 0.071, 0.067$.

Results and Discussion

Table I lists the final refined coordinates and anisotropic temperature factors for all of the nonhydrogen atoms together with their estimated standard deviation (esd). Table II lists the calculated positions of the hydrogen atoms included in the final cycles of refinement all having a fixed isotropic temperature factor of $B = 4.0$ Å^2. Figure 1 illustrates the coordination about the copper cation with bond distances and angles given. Table III lists the Cu-O distances and angles with their respective esd values.

The copper atom coordinates to the oxygens of the five ethyleneurea ligands with distorted 4 + 1 tetragonal-pyramidal geometry as shown in the ORTEP[3] stereodrawing, Figure 2. The copper rises slightly above the base plane (0.12 Å) in the direction of its fifth bond as has been reported for other five-coordinate copper complexes.[4,5] The distortion of the basal plane is due to a pair of hydrogen bonds between ring 2 and its centrosymmetric equivalent 2′ shown in the unit cell drawing, Figure 3. One of the bonds occurs between the complexing carbonyl oxygen of ring 2 and the hydrogen on the outer nitrogen of ring 2′. The other bond is the

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(2) Scattering factors for all nonhydrogen atoms are from D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965), and those for hydrogen are from R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965). R represents the conventional unweighted reliability factor. The expression for the weighted realibility factor (r) is $r = [\Sigma w|F_o| - |kF_c|^2/\Sigma w|F_o|^2]^{1/2}$.

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Table I. Fractional Coordinates and Anisotropic Thermal Parameters[a] (Standard Deviations × 10^4 in Parentheses)

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.2775 (1)	0.0915 (1)	0.4568 (1)	52 (1)	150 (2)	186 (2)	36 (1)	34 (1)	32 (1)
Cl(1)	0.7376 (2)	0.4254 (3)	0.2299 (2)	81 (2)	144 (4)	95 (3)	35 (3)	45 (2)	15 (3)
O(1-1)	0.8053 (8)	0.5599 (10)	0.2422 (9)	232 (13)	311 (21)	314 (19)	−6 (13)	177 (13)	32 (16)
O(2-1)	0.6900 (8)	0.3073 (10)	0.1163 (8)	325 (15)	306 (20)	212 (15)	−19 (14)	205 (13)	−94 (14)
O(3-1)	0.7774 (12)	0.3774 (14)	0.3283 (10)	583 (27)	600 (35)	242 (19)	438 (27)	131 (19)	235 (21)
O(4-1)	0.6634 (8)	0.4685 (12)	0.2318 (10)	223 (13)	589 (31)	357 (21)	192 (17)	187 (14)	94 (20)
Cl(2)	0.1745 (2)	0.2446 (3)	0.1076 (2)	87 (2)	249 (6)	86 (3)	61 (3)	38 (2)	62 (4)
O(1-2)	0.0702 (6)	0.2131 (12)	0.0177 (9)	90 (8)	675 (33)	252 (17)	75 (14)	11 (10)	229 (20)
O(2-2)	0.1920 (6)	0.1922 (9)	0.2151 (7)	166 (9)	404 (21)	133 (11)	112 (12)	86 (9)	149 (13)
O(3-2)	0.2100 (13)	0.1807 (19)	0.0505 (11)	648 (29)	1459 (65)	332 (22)	789 (39)	395 (23)	417 (32)
O(4-2)	0.2280 (9)	0.3983 (11)	0.1517 (12)	246 (14)	351 (25)	438 (25)	−1 (15)	30 (15)	262 (21)
O(-1)	0.1444 (4)	−0.0912 (6)	0.3156 (5)	42 (4)	128 (11)	126 (8)	24 (6)	21 (5)	39 (7)
C(1-1)	0.1140 (6)	−0.2321 (9)	0.3062 (8)	32 (6)	127 (16)	79 (11)	17 (8)	16 (7)	11 (10)
N(2-1)	0.1566 (5)	−0.2920 (8)	0.4020 (7)	63 (6)	122 (13)	92 (10)	24 (7)	13 (6)	4 (9)
C(3-1)	0.0977 (8)	−0.4612 (10)	0.3585 (10)	105 (10)	99 (17)	171 (17)	10 (11)	47 (11)	33 (14)
C(4-1)	0.0096 (8)	−0.5024 (10)	0.2112 (10)	96 (10)	87 (16)	154 (16)	−8 (12)	51 (10)	−9 (13)
N(5-1)	0.0296 (6)	−0.3500 (8)	0.1948 (7)	100 (7)	263 (17)	137 (11)	25 (9)	3 (7)	14 (11)
O(-2)	0.3686 (4)	0.0102 (6)	0.4258 (5)	38 (4)	170 (11)	51 (6)	37 (6)	15 (4)	7 (7)
C(1-2)	0.3506 (6)	−0.0703 (9)	0.3193 (7)	31 (6)	103 (14)	64 (10)	21 (7)	20 (6)	28 (9)
N(2-2)	0.2629 (5)	−0.1127 (9)	0.1955 (6)	53 (6)	251 (17)	57 (8)	71 (8)	16 (6)	5 (10)
C(3-2)	0.2674 (7)	−0.2052 (12)	0.0989 (8)	56 (8)	277 (23)	54 (11)	40 (11)	13 (8)	12 (13)
C(4-2)	0.3797 (7)	−0.2050 (11)	0.1792 (8)	75 (8)	200 (20)	85 (12)	53 (11)	40 (9)	22 (13)
N(5-2)	0.4186 (5)	−0.1226 (8)	0.3146 (6)	56 (6)	230 (16)	47 (8)	71 (8)	16 (6)	5 (9)
O(-3)	0.4092 (4)	0.2814 (6)	0.5779 (5)	55 (5)	86 (9)	119 (8)	27 (5)	38 (5)	38 (7)
C(1-3)	0.4261 (6)	0.4233 (10)	0.5854 (8)	36 (6)	191 (18)	87 (11)	34 (9)	43 (7)	36 (11)
N(2-3)	0.3641 (6)	0.4782 (8)	0.4945 (7)	71 (7)	136 (14)	122 (11)	33 (8)	35 (7)	49 (10)
C(3-3)	0.4094 (8)	0.6484 (11)	0.5415 (12)	108 (11)	180 (21)	297 (22)	82 (13)	127 (14)	155 (18)
C(4-3)	0.5167 (8)	0.6950 (10)	0.6703 (10)	121 (11)	123 (18)	169 (17)	15 (11)	91 (12)	31 (14)
N(5-3)	0.5136 (5)	0.5496 (8)	0.6895 (7)	66 (6)	106 (13)	117 (11)	6 (7)	30 (7)	27 (10)
O(-4)	0.1965 (4)	0.1998 (6)	0.4833 (5)	39 (4)	167 (11)	104 (8)	34 (6)	30 (5)	18 (8)
C(1-4)	0.0973 (6)	0.1642 (9)	0.4242 (8)	51 (7)	104 (15)	107 (12)	38 (8)	44 (8)	43 (11)
N(2-4)	0.0520 (5)	0.1927 (9)	0.4850 (7)	54 (6)	210 (16)	128 (11)	32 (8)	49 (7)	3 (11)
C(3-4)	−0.0619 (7)	0.1509 (11)	0.3928 (11)	63 (8)	190 (21)	231 (19)	51 (11)	83 (11)	70 (16)
C(4-4)	−0.0867 (7)	0.0602 (12)	0.2624 (10)	48 (8)	241 (22)	139 (15)	52 (11)	23 (9)	20 (15)
N(5-4)	0.0207 (5)	0.0953 (10)	0.2945 (7)	52 (6)	384 (23)	86 (10)	81 (10)	28 (7)	38 (12)
O(-5)	0.3111 (4)	−0.0043 (6)	0.6246 (5)	64 (5)	109 (10)	66 (7)	24 (6)	29 (5)	20 (7)
C(1-5)	0.3413 (6)	0.0681 (9)	0.7374 (8)	32 (6)	97 (14)	98 (11)	17 (7)	22 (7)	42 (10)
N(2-5)	0.3484 (6)	0.2114 (8)	0.7822 (7)	137 (9)	174 (15)	91 (10)	92 (10)	68 (8)	60 (10)
C(3-5)	0.3903 (7)	0.2633 (11)	0.9227 (9)	88 (9)	186 (20)	113 (14)	41 (11)	50 (10)	23 (13)
C(4-5)	0.3947 (7)	0.1188 (11)	0.9591 (9)	89 (9)	196 (20)	86 (12)	51 (11)	44 (9)	56 (13)
N(5-5)	0.3731 (7)	0.0165 (8)	0.8414 (7)	154 (10)	143 (15)	99 (11)	85 (10)	56 (9)	57 (10)

[a] Anistropic temperature factors of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

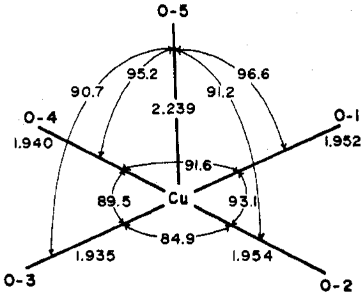

Figure 1. Coordination about the copper ion; distances and angles indicated.

reverse with the oxygen of 2′ bonded to the hydrogen on the nitrogen of ring 2. This interaction causes the molecules to pack in the cells as centrosymmetric hydrogen-bonded dimers.

Figure 3 also shows a close contact distance of 2.994 Å between the copper and a perchlorate oxygen, O(2-2). Although longer than the bond distances, this oxygen of the perchlorate group serves to complete the distorted octahedral symmetry about the copper which otherwise would have 4 + 1 coordination. The separation is less than the 3.35 Å one would predict for a nonbonding contact between a perchlorate oxygen and copper, but not as close as the 2.60 Å

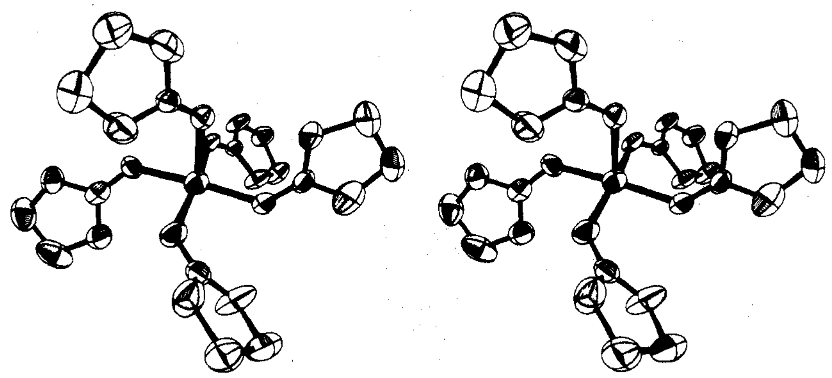

Figure 2. ORTEP stereodrawing of the cation.

Table II. Calculated Hydrogen Positions

Atom[a]	x	y	z
H(21)	0.224	−0.226	0.496
H(31)	0.065	−0.491	0.412
H(31′)	0.145	−0.523	0.373
H(41)	−0.066	−0.556	0.191
H(41′)	0.016	−0.580	0.152
H(51)	−0.018	−0.334	0.106
H(22)	0.199	−0.082	0.173
H(32)	0.255	−0.160	0.023
H(32′)	0.208	−0.319	0.051
H(42)	0.428	−0.149	0.150
H(42′)	0.378	−0.317	0.166
H(52)	0.492	−0.104	0.397
H(23)	0.294	0.408	0.404
H(33)	0.361	0.693	0.554
H(33′)	0.418	0.693	0.473
H(43)	0.526	0.773	0.747
H(43′)	0.580	0.750	0.664
H(53)	0.572	0.540	0.775
H(24)	0.093	0.238	0.588
H(34)	−0.079	0.249	0.387
H(34′)	−0.108	0.085	0.419
H(44)	−0.133	0.096	0.186
H(44′)	−0.130	−0.058	0.235
H(54)	0.037	0.072	0.223
H(25)	0.326	0.278	0.723
H(35)	0.341	0.300	0.939
H(35′)	0.464	0.353	0.978
H(45)	0.338	0.070	0.978
H(45′)	0.468	0.139	1.043
H(55)	0.382	−0.088	0.837

[a] Identifying number refers to atom to which the hydrogen is bonded.

Table III. Selected Interatomic Distances (Å) and Angles (deg) (Estimated Standard Deviations in Parentheses)

		Copper-Oxygen Parameters	
Cu-O(-1)	1.952 (6)	O(-5)-Cu-O(-4)	95.2 (3)
Cu-O(-2)	1.954 (6)	O(-3)	90.7 (2)
Cu-O(-3)	1.935 (6)	O(-2)	91.2 (2)
Cu-O(-4)	1.940 (6)	O(-1)	96.6 (2)
Cu-O(-5)	2.239 (6)	O(-4)-Cu-O(-3)	89.5 (3)
		O(-2)	171.5 (3)
		O(-1)	91.6 (3)
		O(-3)-Cu-O(-2)	84.9 (3)
		O(-1)	172.5 (3)
		O(-2)-Cu-O(-1)	93.1 (3)
		Perchlorate Groups	
Cl(1)-O(1-1)	1.33 (1)	O(4-1)-Cl(1)-O(3-1)	105.7 (1.0)
Cl(1)-O(2-1)	1.33 (1)	O(4-1)-Cl(1)-O(2-1)	109.9 (0.8)
Cl(1)-O(3-1)	1.26 (1)	O(4-1)-Cl(1)-O(1-1)	102.0 (0.7)
Cl(1)-O(4-1)	1.34 (1)	O(3-1)-Cl(1)-O(2-1)	109.6 (0.7)
		O(3-1)-Cl(1)-O(1-1)	114.8 (0.8)
		O(2-1)-Cl(1)-O(1-1)	114.3 (0.7)
Cl(2)-O(1-2)	1.34 (1)	O(4-2)-Cl(2)-O(3-2)	108.3 (1.0)
Cl(2)-O(2-2)	1.40 (1)	O(4-2)-Cl(2)-O(2-2)	109.7 (0.7)
Cl(2)-O(3-2)	1.27 (2)	O(4-2)-Cl(2)-O(1-2)	107.0 (0.8)
Cl(2)-O(4-2)	1.31 (1)	O(3-2)-Cl(2)-O(2-2)	108.7 (0.8)
		O(3-2)-Cl(2)-O(1-2)	109.6 (0.8)
		O(2-2)-Cl(2)-O(1-2)	113.4 (0.6)

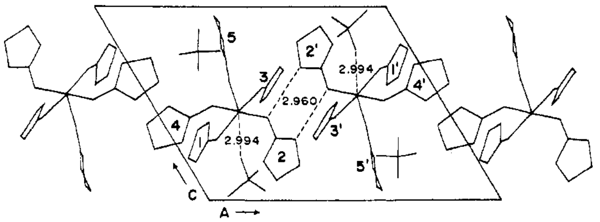

Figure 3. Unit cell contents projected down the b axis; close contacts less than 3.1 Å indicated.

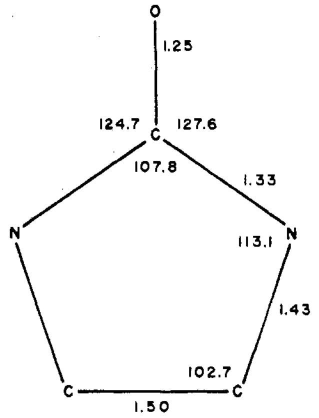

Figure 4. Schematic view of ethyleneurea moiety; average distances and angles indicated.

found when a perchlorate is directly bonded to a copper through one of its oxygens.[6] Perchlorates which have close contact distances to metal ions and show distortion from regular tetrahedral symmetry are said to exhibit a form of weak coordination, termed semicoordination.[7] The close contact distance and the approximate octahedral geometry are better indicators of semicoordination than the distortion of a perchlorate group. Deviations from tetrahedral symmetry in a perchlorate group are not uncommon in crystallographic studies[8] where some type of orientational disorder for this group is usually found. In this study, both of the perchlorate groups show a similar distortion (Table III), but only one of them is in a position close enough to coordinate with the copper.

Figure 4 is a drawing indicating the average distances and angles for the five ethyleneurea groups. All of the groups showed the same asymmetric bend of the carbonyl oxygen toward one of the nitrogens giving a significantly different average of 124.7 ± 0.7° for one side and 127.6 ± 0.6° for the other. This cannot be attributed to packing differences in the crystal state since each ethyleneurea group is in a totally different environment. The only distance that differed more than two standard deviations from the average is the 1.22 (1) Å carbonyl oxygen to carbon distance found on the ring number 5. This difference is statistically significant and can be rationalized on a chemical basis since it involves the unique ligand in the 4 + 1 coordination. One would anticipate a stronger carbonyl copper-oxygen bond (as the shorter distance implies) for that particular ligand in the 4 + 1 coordination which has a significantly longer, 2.239 (6) Å, and hence weaker copper-oxygen bond.

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Registry No. $Cu(C_3H_6N_2O)_5(ClO_4)_2$, 50600-83-4.

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

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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-74-1062.

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Molecules with an M_4X_4 Core. I. Crystal and Molecular Structure of Tetrameric Triphenylphosphinecopper(I) Chloride, a "Cubane-Like" Molecule, Including the Location and Refinement of All Hydrogen Atoms

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Tetrameric triphenylphosphinecopper(I) chloride, $[PPh_3CuCl]_4$, crystallizes in the centrosymmetric orthorhombic space group *Pbcn* [D_{2h}^{14}; No. 60] with $a = 17.468$ (2) Å, $b = 20.519$ (3) Å, and $c = 18.215$ (2) Å. The observed density of 1.45 (2) g cm^{-3} is consistent with the value of 1.471 g cm^{-3} calculated for $Z = 4$ and mol wt 1445. X-Ray diffraction data were collected with a Picker FACS-1 diffractometer and the structure was solved by means of Patterson, Fourier, and least-squares refinement techniques. All atoms, including hydrogens, have been located. The final discrepancy indices are $R_F = 8.7\%$ and $R_{wF} = 4.8\%$ for the 3067 independent reflections representing data complete to $2\theta = 40°$ [Mo Kα radiation] or $R_F = 3.8\%$ and $R_{wF} = 4.0\%$ for the 1818 reflections for which $I > 3\sigma(I)$. The molecule has precise (*i.e.*, crystallographically required) C_2 symmetry. The four copper and four chlorine atoms, taken alternately, define the eight corners of a slightly distorted cube within which the copper–chlorine bond lengths range from 2.363 (2) to 2.505 (2) Å. Intramolecular copper–copper distances are 3.118 (1), 3.118 (1), 3.337 (2), 3.417 (1), 3.417 (1), and 3.430 (1) Å, suggesting that there are no significant copper· · ·copper interactions. This result is at variance with the copper· · ·copper distance of 2.60 Å reported by Wells in 1936 for the analogous "cubane-like" molecule $[AsEt_3CuI]_4$ and suggests that this latter structural determination is of limited accuracy. Copper–phosphorus bond lengths in $[PPh_3CuCl]_4$ are 2.192 (2) and 2.193 (2) Å, other distances being P–C = 1.805 (7)–1.835 (7) Å (average 1.821 Å), C–C(phenyl) = 1.334 (12)–1.400 (15) Å (average 1.373 Å), and C–H = 0.79 (7)–1.04 (6) Å (average 0.90 Å).

Introduction

The copper(I) halides (CuX) form a diversity of products with monodentate tertiary phosphines and arsines (L), including stable isolable species of composition $[L_4Cu^+][X^-]$, L_3CuX, $[L_2CuX]_2$, $L_3Cu_2X_2$, and $[LCuX]_4$.[1] Perhaps surprisingly, an X-ray structural analysis has been performed on only one of the tetrameric species; Wells, in 1936, showed that triethylarsinecopper(I) iodide is tetrameric and that the Cu_4I_4 core of the molecule consists of "a tetrahedron of copper atoms, of side 2.60 Å, and an iodine atom rests on each face of the tetrahedron."[2] An equivalent (and more fashionable) description of the Cu_4I_4 core is "a cubane-like arrangement with alternating copper and iodine atoms."

Wells also showed that the species tri-*n*-butylcopper(I) iodide and triethylarsinesilver(I) iodide were tetrameric, but the crystallographic information on these species is qualitative only.[2]

Recent structural studies on copper cluster species have revealed copper–copper distances of 2.494 (6)–2.674 (5) Å in $[PPh_3CuH]_6$,[3] 2.663 (6)–2.829 (6) Å in $(PPh_3Ir)_2Cu_4(C{\equiv}CPh)_8$,[4] 2.69 Å in $[Cu(S_2CNEt_2)]_4$,[5] 2.701–3.057 Å in $[Cu(SOCNPr_2)]_6$,[6] 2.783–2.871 Å in $[Cu_8(S_2CC(CN)_2)_6{}^{4-}]$,[7] 2.48–2.70 Å in $[Cu(2\text{-}Me_2NC_6H_4)]_4(CuBr)_2$,[8] and 2.377 (3)–2.389 (3) Å in tetrameric (4-methyl-2-cupriobenzyl)dimethylamine.[9] While the partition of these copper–copper distances into "bonding" and "nonbonding" situations is a matter of some controversy, it is clear that the copper–copper distance of ~2.60 Å reported[2] for $[AsEt_3CuI]_4$ may well be incompatible with the view that the copper atoms in this species do not interact directly. The reported distance may thus be erroneous (or of lower accuracy than claimed) or, alternatively, the model for the bonding within $[LCuX]_4$ clusters may need to be carefully reexamined.

We have now completed a single-crystal X-ray diffraction study of the species $[PPh_3CuCl]_4$. As outlined below, the copper· · ·copper distances within this molecule range from 3.118 (1) to 3.430 (1) Å, suggesting that there is no significant direct metal· · ·metal interaction in these tetrameric species. A preliminary account of this work has appeared previously.[10]

Collection and Reduction of the X-Ray Diffraction Data

Crystals were obtained from CH_2Cl_2 solution as colorless needles, extended along the 001 direction. The crystal chosen for the analysis was essentially cylindrical in shape, with a length of 0.3 mm and a radius of 0.04 mm.

A preliminary photographic study [*hk*(0–2) Weissenberg photo-

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