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The Crystal and Molecular Structure of μ4-oxohexa-μ-chlorotetrakis(pyridine copper (II)), $Cu_4Cl_6O.4C_5H_5N$, a Polynuclear Copper Complex

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The crystal structure of the polynuclear complex, μ4-oxohexa-μ-chlorotetrakis(pyridinecopper(II)) has been solved and refined to an R value of 6.6% for 1435 observed reflections. The complex contains a central oxygen atom coordinated tetrahedrally to four copper atoms, the metal atoms being bridged in pairs by six chlorine atoms. Four pyridine molecules complete trigonal bipyramidal coordination about the four copper atoms. The central Cu_4Cl_6O unit is considerably distorted from its potential T_d symmetry and possible causes of this distortion are discussed. Average bond distances and angles are Cu-Cl 2.41 Å, Cu-O 1.90 Å, Cu-N 1.96 Å, Cl-Cu-Cl 119°, Cu-Cl-Cu 80°, O-Cu-Cl 85°.

Introduction

The crystal structure of diazoaminobenzenecopper(I)[1] contains discrete centrosymmetric dimeric molecules with an unusually small Cu-Cu separation. The preparation[2] of the potential ligand $C_6H_5-N=P(C_6H_5)_2-NH-C_6H_5$(DPB), which is analogous to diazoaminobenzene (DAB) but with $=P(C_6H_5)_2-$ replacing $=N-$, suggested that a complex (DPB Cu(I))$_2$ might also have an interesting Cu-Cu separation.

In an attempt to prepare[2] such a complex (by reaction of DPB with Cu$^+$ in pyridine solution) a few small (0.4 mm. length) golden-yellow air-stable crystals were obtained. Although there was no direct evidence that these crystals corresponded to the desired complex, we decided to carry out a structure determination by X-ray analysis. This showed that the crystals did not have the structure (DPB Cu(I))$_2$ but a quite unexpected one with 4 Cu atoms arranged in a tetrahedron. The final structure assigned to the complex is μ4-oxohexa-μ-chlorotetrakis(pyridinecopper(II)).

Experimental Section

Crystal data. Monoclinic, Space group P2$_1$|$_n$ (second setting), $a = 11.29 \pm 0.02$, $b = 21.40 \pm 0.04$, $c = 11.96 \pm 0.02$ Å, $\beta = 92.20 \pm 0.2°$, $U = 2887$ Å^3, $\mu(MoK_\alpha) = 35.9$ cm.$^{-1}$. The cell constants were measured from 30° precession photographs (Cu K$_\alpha$ radiation).

(1) I. D. Brown and J. D. Dunitz, *Acta Cryst.*, *14*, 480 (1961).
(2) H. Bock, H. Tom Dieck, H. Pyttlik and M. Schnöller, to be published.

The density of the crystals was not determined but was greater than 1.7 g/ml, the calculated value for 4 molecules of (DPB Cu(I))$_2$ in the unit cell being 1.97 g/ml.

Intensity Measurements. The intensities of reflections in the layers hKl (K, 0-19) were measured with a Hilger-Watts linear diffractometer (Mo K$_\alpha$ radiation, balanced filters) from a crystal with dimensions $0.35 \times 0.15 \times 0.10$ mm. Of the 3500 recorded reflections, about 1500 were observed to have F$>3\sigma$ (F) and only these values were used in the subsequent analysis. The intensities were placed on a common scale by reference to frequent measurements of a standard reflection and were corrected for LP factors. Absorption corrections were not calculated.

Structure Analysis. From the distribution of peaks in the Patterson function, it was apparent that the asymmetric unit must be more complicated than a simple dimer. From this point onwards the idea of a dimer was discarded and the structure solved solely from the X-ray data.

It was possible to derive atomic positions for four equally heavy atoms, the vectors between which accounted for the most prominent Patterson peaks, especially for a set of six, 3.1 Å from the origin. In addition, the positions of two atoms, with scattering power approximately half that of the previous four, could be deduced. Furthermore, it seemed that other «half-heavy» atoms must be present to account for the still unexplained peaks in the Patterson function.

The four heavy atoms were recognized as occupying the vertices of a fairly regular tetrahedron of side 3.1 Å, with the 2 «half-heavy» atoms neatly bridging two of the sides. From this point the analysis was continued by means of electron-density and difference maps.

Structure factors based on the six proposed positions, and on the provisional identification of the heavy atoms as Cu and of the «half-heavy» ones as P, gave an R value of 39%. The subsequent electron-density function confirmed the chosen positions and showed clearly the presence of four additional «half-heavy» atoms so situated as to bridge the remaining sides of the tetrahedron. The six «half-heavy» atoms thus occupied the vertices of an octahedron. Several electron-density maxima forming indistinct six-membered rings could

also be recognized, but no attempt was made to determine the corresponding atomic positions.

As the next step, the coordinates and isotropic temperature factors of the 10 atoms, whose positions were known, were refined by 2 cycles of full-matrix least-squares analysis (R value 21.6%). All temperature factors were satisfactory, B for the heavy atoms being 2.5 to 3.0 Å^2 and for «half-heavy» atoms 2.6 to 4.1 Å^2.

The electron-density map that was now calculated showed four roughly planar six-membered rings of «light atoms». Each of these rings was arranged so that a pair of opposite atoms (1,4) lay on the extension of the line from the centre to a vertex of the tetrahedron, the 4 distances, Cu-L$_1$, all being about 2 Å. The observed electron densities were, for the heavy atoms, 34, 34, 36, and 38 e/Å^3, for the «half-heavy» atoms, 15, 16, 16, 16, 16, and 18 e/Å^3, and for the ring atoms, 3 to 6 e/Å^3.

Surprisingly, there still remained one clearly defined peak (about 6 e/Å^3) at the exact centre of the tetrahedron. Since this peak could not be attributed to anisotropic vibration of the surrounding heavy atoms, we concluded that an atom was actually present at the centre of the tetrahedron.

The next steps in the structure analysis were two cycles of least-squares refinement, including in the calculations the 24 ring atoms with carbon scattering factors, and the central atom with nitrogen scattering factors. The R value fell to 11.5%, all shifts being reasonable. However, it was noticed that, in each ring, the atom closest to the heavy atom tetrahedron had a temperature factor markedly lower than other ring atoms (B's of 2 Å^2 compared with 5 Å^2).

Once the overall arrangement of atoms had been recognized, it seemed clear that the original, provisional identification of atom types had to be amended. It seemed more likely that the «half-heavy» atoms should be identified as *chlorine* and the light, central atom as *oxygen* to give a central unit Cu_4Cl_6O (analogous to basic beryllium acetate[3] or to Mg_4Br_6O.[4] The identification of the 6-membered rings as *pyridine* was established by the result of a mass spectrum* of a small crystal, thus accounting for the observed pattern of the temperature factors of the ring atoms.

The composition thus deduced, $Cu_4Cl_6O \cdot 4C_5H_5N$, was subsequently confirmed by the preparation[2] of the complex by a different method.

$$4\ CuCl_2 \cdot 2H_2O + 2NaOH \rightarrow (pyridine, 20°, 2\ days)$$

$$[Cu_4Cl_6O \cdot 4\ pyridine] + 2NaCl + 3H_2O$$
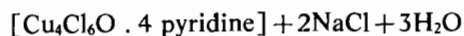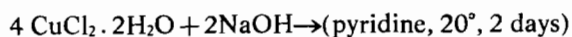
The solution in pyridine on standing changed colour from blue to green. After two days, it was evaporated under vacuum and the residue extracted with hot alcohol. The product separated out of the hot alcoholic solution as golden-yellow needles; (observed H 2.70%, C 30.21%, N 7.13%, Cl 27.2%; calculated for

$Cu_4Cl_6O \cdot 4C_5H_5N$, H 2.52%, C 30.05%, N 7.01%, Cl 26.7%). In the first preparation, the complex was presumably formed in small amounts by air oxidation of CuCl in pyridine solution.

Completion of Refinement. Correct scattering factors[5] were introduced, and the refinement was continued by least-squares analysis without any complications. Electron-density and difference maps confirmed that no further atoms (other than hdrogen) were present. The introduction of hydrogen atoms in calculated positions led to an insignificant change in R value from 8.0% to 7.9%. With anisotropic temperature factors for the 10 heavy atoms the final R value was 6.6%; R (Hamilton) 7.8%. The weighting scheme used in the final least squares cycle—$F_o \leqslant 84$, $w = (84)^{-1/2}\ F_o^{1/2}$, $F_o > 84$, $w = 84\ F^{-1}$—gave reasonably constant average values of the quantity $(\Sigma w^2 \Delta^2)/N$, where N is the number of observations in a given F_o range. Almost all the parameter shifts were less than half of the corresponding standard deviations. No attempt was made to estimate the anisotropy of the temperature factors for the C, N, and O atoms. Because of the relatively high standard deviations of the parameters of these atoms, σ (positional) 0.04 Å, σ (thermal) 0.6 Å^2, such a refinement would be of little value with respect to the computing time required.

Table I. Final positional parameters (fractional co-ordinates $\times 10^4$) for all atoms, and isotropic temperature factors (B's $\times 10$) for the light atoms (with corresponding standard deviations)

Atom	x	y	z	B
Cu(1)	3243 (3)	1107 (2)	2201 (3)	
Cu(2)	0706 (3)	1357 (2)	3003 (3)	
Cu(3)	1526 (3)	0000 (2)	2609 (3)	
Cu(4)	2614 (3)	0754 (2)	4615 (3)	
Cl(1)	−0358 (6)	0483 (4)	2212 (7)	
Cl(2)	1866 (6)	1993 (4)	1794 (7)	
Cl(3)	4306 (7)	1316 (4)	3925 (7)	
Cl(4)	0998 (7)	1441 (4)	4998 (7)	
Cl(5)	2410 (8)	−0352 (4)	4321 (6)	
Cl(6)	2804 (7)	0239 (4)	1041 (6)	
O	2021 (14)	0817 (8)	3104 (13)	27 (3)
N(1)	1038 (19)	−0818 (11)	1998 (18)	34 (5)
C(2)	1265 (25)	−1587 (15)	2488 (24)	40 (6)
C(3)	0970 (28)	−1936 (17)	2017 (28)	46 (7)
C(4)	0391 (28)	−1940 (16)	0971 (27)	44 (7)
C(5)	0131 (27)	−1391 (16)	0406 (26)	48 (7)
C(6)	0492 (26)	−0837 (15)	0960 (25)	42 (7)
N(7)	4567 (18)	1358 (10)	1315 (17)	29 (4)
C(8)	4457 (27)	1769 (15)	0479 (25)	41 (7)
C(9)	5372 (31)	1893 (18)	−0174 (30)	60 (8)
C(10)	6486 (30)	1571 (16)	0008 (28)	48 (8)
C(11)	6543 (32)	1121 (18)	0872 (30)	60 (8)
C(12)	5628 (28)	1046 (15)	1505 (27)	50 (7)
N(13)	3239 (20)	0668 (11)	6152 (19)	36 (5)
C(14)	2529 (29)	0588 (16)	6991 (29)	51 (8)
C(15)	2866 (28)	0557 (15)	8106 (26)	45 (7)
C(16)	4060 (28)	0584 (15)	8366 (27)	50 (7)
C(17)	4826 (30)	0605 (16)	7553 (29)	54 (8)
C(18)	4429 (29)	0671 (16)	6394 (27)	51 (8)
N(19)	−0727 (19)	1882 (11)	2924 (18)	34 (5)
C(20)	−0866 (26)	2332 (14)	2117 (24)	42 (6)
C(21)	−1959 (34)	2684 (19)	2010 (32)	71 (9)
C(22)	−2794 (34)	2528 (19)	2670 (36)	66 (10)
C(23)	−2663 (38)	2063 (21)	3512 (37)	80 (10)
C(24)	−1584 (33)	1739 (17)	3553 (30)	53 (8)

(*) We are grateful to Dr. Seibl for measuring the mass spectrum.

(3) L. Pauling and J. Sherman, *Proc. Natl. Acad. Sci. U.S.*, **20**, 340 (1934).

(4) G. Stucky and R. E. Rundle, *J. Amer. Chem. Soc.*, **86**, 4821 (1964).

(5) International Tables for X-ray Crystallography, Kynoch Press. Birmingham, vol. III (1962).

All calculations were carried out on the CDC 1604 A computer in the computing centre of the Swiss Fed. Inst. of Technology (ETH); the refinement programme used was a locally modified version of the Gantzel-Sparks-Trueblood full-matrix programme (A.C.A. 317); the drawings were prepared with the help of the ORTEP plotting programme (C.K. Johnson, Oak Ridge National Laboratory, USA).

Details of Structure. The final atomic co-ordinates are listed in Table I together with isotropic temperature factors for the light atoms. Anisotropic temperature factors for the four copper and six chlorine atoms are listed in Table II, together with the r.m.s. amplitudes of the principal axes of the corresponding thermal vibration ellipsoids. Calculated hydrogen positions are shown in Table III.

Table II. Anisotropic temperature factors (with standard deviations) for the 10 heavy atoms

$$T = \exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl) \times 10^{-4}]$$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu(1)	56(3)	15(1)	48(3)	− 8(3)	−11(5)	7(3)
Cu(2)	56(3)	16(1)	63(3)	8(3)	−19(5)	− 3(3)
Cu(3)	60(3)	15(1)	50(3)	− 10(3)	− 35(5)	2(3)
Cu(4)	71(3)	21(1)	39(3)	− 7(3)	− 36(5)	2(3)
Cl(1)	54(7)	21(2)	108(8)	− 4(6)	−44(11)	− 10(6)
Cl(2)	63(7)	17(2)	118(8)	− 8(6)	−43(12)	32(7)
Cl(3)	86(8)	36(3)	71(7)	− 55(8)	− 52(12)	20(7)
Cl(4)	94(8)	34(3)	66(7)	40(8)	− 37(12)	− 33(7)
Cl(5)	138(10)	21(2)	67(7)	− 3(7)	− 86(13)	18(6)
Cl(6)	104(8)	25(2)	41(6)	− 27(7)	− 9(11)	− 12(6)

Root-mean-square amplitudes of the principal axes of the thermal ellipsoids, $Å \times 10^{-3}$

Cu(1)	173	176	214
Cu(2)	172	195	229
Cu(3)	152	183	232
Cu(4)	146	214	238
Cl(1)	168	223	294
Cl(2)	174	189	316
Cl(3)	169	220	340
Cl(4)	191	208	323
Cl(5)	166	227	331
Cl(6)	165	216	282

Table III. Positional parameters (fractional co-ordinates $\times 10^3$) for the hydrogen atoms, calculated assuming C_{2v} symmetry at the carbon atom and C-H 1.0 Å. (H2 is bonded to C2, H3 to C3 and so on.)

Atom	x	y	z
H(2)	172	− 139	332
H(3)	119	− 238	246
H(4)	013	− 239	058
H(5)	− 033	− 139	− 043
H(6)	032	− 039	052
H(8)	361	201	032
H(9)	526	224	− 085
H(10)	725	167	− 050
H(11)	735	083	102
H(12)	572	072	222
H(14)	157	054	677
H(15)	221	051	875
H(16)	439	059	925
H(17)	578	057	777
H(18)	507	072	573
H(20)	− 015	243	155
H(21)	− 208	307	140
H(22)	− 365	277	257
H(23)	− 336	196	409
H(24)	− 146	135	414

A listing of the 1435 observed and calculated structure factors is given in Table IV.

The labelling system used is given in Figure 1, which shows a perspective view of the molecule. The direction of viewing is in the $a*b$ plane, along a line rotated 10° from $a*$ towards b. This direction, rather than one exactly along $a*$, was chosen in order to clarify the orientation of the ring N(13)-C(18).

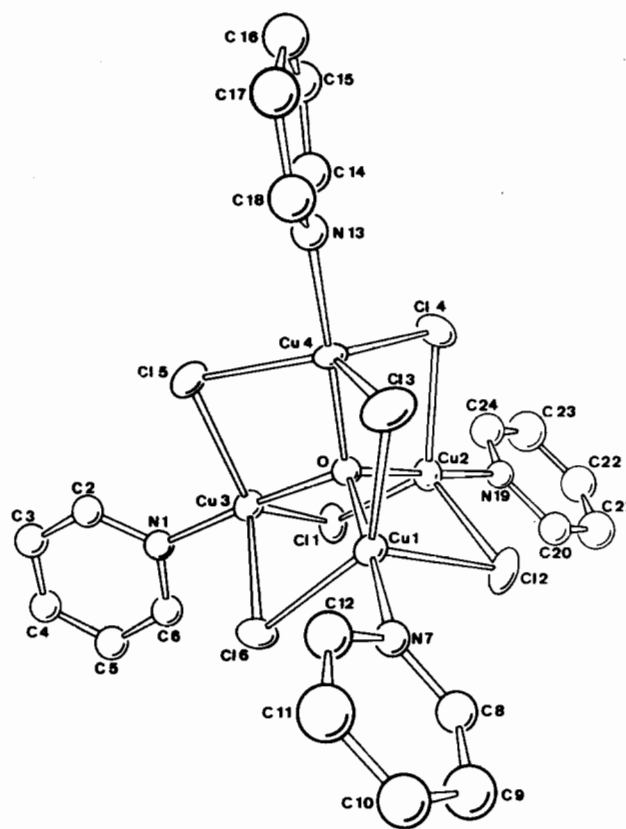Figures 2 and 3 illustrate the packing of the molecules within the crystal.

Figure 1. Perspective drawing of the molecule showing the numbering system. The «shapes» of the atoms represent the corresponding thermal ellipsoids.
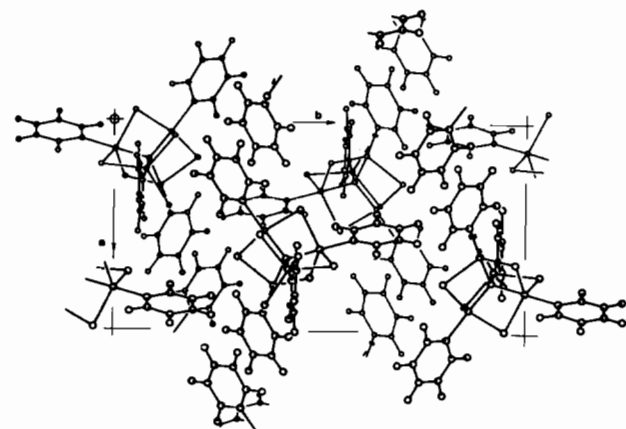

Figure 2. The contents of one unit cell projected on the $a\,b$ plane to illustrate the packing.

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Table IV. List of observed and calculated structure factors for μ-oxohexa-μ-chlorotetrakis(pyridinecopper(II)). The col contain the values of h, 10F_obs, and 10F_calc
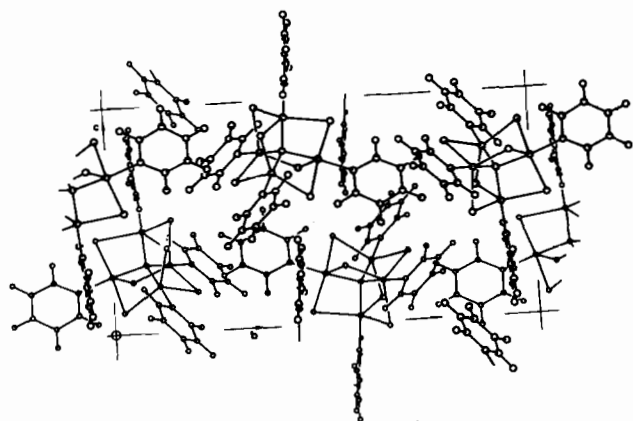
Figure 3. The contents of one unit cell projected on the $b\ c$ plane to illustrate the packing.

Interatomic Distances and Angles. Bond distances and angles, with their standard deviations, are listed, along with certain intramolecular non-bonded distances, in Table V. Relevant inter- and intra-molecular contact distances, as calculated from the proposed model, are summarized in Table VI. Some distances involving hydrogen atoms are too short. This simply reflects the uncertainties in the calculated positions of the hydrogen atoms listed in Table III (based on the assumptions C-H (1.0 Å) in the plane of C-C-C and bisecting the angle C-C-C). These assumptions must obviously break down if they lead to an unreasonable model in which serious overcrowding of the hydrogen atoms with other atoms occurs. Nevertheless, the model is useful in that it indicates the regions where distortions (due to overcrowding) from a more regular geometry would be expected to occur.

Discussion

This complex contains the structural unit, Cu_4Cl_6O in which a central oxygen atom is co-ordinated tetrahedrally to four metal atoms, bridged in pairs by six chlorine atoms. Somewhat similar arrangements have been recognized in basic beryllium acetate[3] and closely related compounds,[6,7] where the metal atoms may be regarded as 4-co-ordinated. In contrast, however, in the present compound, by virtue of the co-ordinated pyridine molecules, the metal atoms are 5 co-ordinated.

While the present paper was being prepared, a preliminary communication[8] appeared describing the compound $Cu_4Cl_6O \cdot 4(OPPh_3)$, which has an analogous structure to that described here, with $OPPh_3$ replacing NC_5H_5. The dimensions reported[8] are similar to those listed here. Unlike the NC_5H_5 complex though, the $OPPh_3$ complex has crystallographic T_d symmetry.

The structure of a Grignard reagent oxidation product $Mg_4Br_6O \cdot 4O(C_2H_5)_2$[4] is also of the same general type $(M^{2+})_4(X^-)_6O^{2-} \cdot 4L$. From experiments on the X-ray scattering from acetone solutions of potassium

(6) H. Koyama and Y. Saito, *Bull. Soc. Chem. Japan*, 27, 112 (1954).
(7) A. B. Blake, *Chem. Comm.*, 16, 569 (1966).
(8) J. A. Bertrand and J. A. Kelley, *J. Amer. Chem. Soc.*, 88, 4746 (1966).

Table V. Interatomic distances (Å) and angles (°) (with estimated standard deviations)

Cu(1)-Cl(2)	2.486 (9)	Cl(2)-Cu(1)-Cl(3)	108.0 (3)
-Cl(3)	2.373	Cl(2)-Cu(1)-Cl(6)	112.1
-Cl(6)	2.355	Cl(3)-Cu(1)-Cl(6)	137.9
Cu(2)-Cl(1)	2.392 (9)	Cl(1)-Cu(2)-Cl(2)	118.7 (3)
-Cl(2)	2.420	Cl(1)-Cu(2)-Cl(4)	119.5
-Cl(4)	2.397	Cl(2)-Cu(2)-Cl(4)	120.0
Cu(3)-Cl(1)	2.390 (9)	Cl(1)-Cu(3)-Cl(5)	130.1 (3)
-Cl(5)	2.355	Cl(1)-Cu(3)-Cl(6)	107.9
-Cl(6)	2.477	Cl(5)-Cu(3)-Cl(6)	119.1
Cu(4)-Cl(3)	2.439 (9)	Cl(3)-Cu(4)-Cl(4)	112.2 (3)
-Cl(4)	2.406	Cl(3)-Cu(4)-Cl(5)	120.5
-Cl(5)	2.403	Cl(4)-Cu(4)-Cl(5)	124.2
O -Cu(1)	1.90 (2)	Cu(1)-O-Cu(2)	111 (1)
-Cu(2)	1.88	Cu(1)-O-Cu(3)	109
-Cu(3)	1.92	Cu(1)-O-Cu(4)	110
-Cu(4)	1.90	Cu(2)-O-Cu(3)	109
		Cu(2)-O-Cu(4)	110
		Cu(3)-O-Cu(4)	108
N(7) -Cu(1)	1.95 (2)	N(7) -Cu(1)-O	176 (1)
N(19)-Cu(2)	1.97	N(19)-Cu(2)-O	177
N(1) -Cu(3)	1.97	N(1) -Cu(3)-O	176
N(13)-Cu(4)	1.94	N(13)-Cu(4)-O	179
Cu(2)-Cl(1)-Cu(3)	80.5 (3)	Cu(1)-Cl(2)-Cu(2)	78.8 (3)
Cu(1)-Cl(3)-Cu(4)	80.2	Cu(2)-Cl(4)-Cu(4)	80.3
Cu(3)-Cl(5)-Cu(4)	81.0	Cu(1)-Cl(6)-Cu(3)	80.2
O-Cu(1)-Cl(2)	83.9 (6)	O-Cu(2)-Cl(1)	85.6 (6)
O-Cu(1)-Cl(3)	85.3	O-Cu(2)-Cl(2)	86.2
O-Cu(1)-Cl(6)	86.6	O-Cu(2)-Cl(4)	85.1
O-Cu(3)-Cl(1)	84.8	O-Cu(4)-Cl(3)	83.5
O-Cu(3)-Cl(5)	85.4	O-Cu(4)-Cl(4)	84.4
O-Cu(3)-Cl(6)	82.7	O-Cu(4)-Cl(5)	84.5
N(7)-Cu(1)-Cl(2)	99.9 (7)	N(19)-Cu(2)-Cl(1)	91.9 (7)
N(7)-Cu(1)-Cl(3)	93.0	N(19)-Cu(2)-Cl(2)	96.8
N(7)-Cu(1)-Cl(6)	92.4	N(19)-Cu(2)-Cl(4)	94.3
N(1)-Cu(3)-Cl(1)	94.7	N(13)-Cu(4)-Cl(3)	96.5
N(1)-Cu(3)-Cl(5)	97.8	N(13)-Cu(4)-Cl(4)	96.9
N(1)-Cu(3)-Cl(6)	93.8	N(13)-Cu(4)-Cl(5)	94.2
N(1) -C(2)	1.37 (4)	C(6) -N(1) -C(2)	115 (3)
C(2) -C(3)	1.34	N(1) -C(2) -C(3)	124
C(3) -C(4)	1.38	C(2) -C(3) -C(4)	119
C(4) -C(5)	1.38	C(3) -C(4) -C(5)	121
C(5) -C(6)	1.41	C(4) -C(5) -C(6)	116
C(6) -N(1)	1.36	C(5) -C(6) -N(1)	124
N(7) -C(8)	1.33	C(12)-N(7) -C(8)	119
C(8) -C(9)	1.35	N(7) -C(8) -C(9)	121
C(9) -C(10)	1.44	C(8) -C(9) -(10)	120
C(10)-C(11)	1.41	C(9) -C(10)-C(11)	116
C(11)-C(12)	1.32	C(10)-C(11)-C(12)	120
C(12)-N(7)	1.38	C(11)-C(12)-N(7)	123
N(13-(C(14)	1.33 (4)	C(18)-N(13)-C(14)	118 (3)
C(14)-C(15)	1.37	N(13)-C(14)-C(15)	126
C(15)-C(16)	1.37	C(14)-C(15)-C(16)	116
C(16)-C(17)	1.34	C(15)-C(16)-C(17)	120
C(17)-C(18)	1.44	C(16)-C(17)-C(18)	121
C(18)-N(13)	1.36	C(17)-C(18)-N(13)	117
N(19)-C(20)	1.37	C(24)-N(19)-C(20)	121
C(20)-C(21)	1.45	N(19)-C(20)-C(21)	120
C(21)-C(22)	1.30	C(20)-C(21)-C(22)	117
C(22)-C(23)	1.42	C(21)-C(22)-C(23)	124
C(23)-C(24)	1.40	C(22)-C(23)-C(24)	116
C(24)-N(19)	1.29	C(23)-C(24)-N(19)	123
Cu(1)...Cu(2)	3.11	Cu(2)...Cu(3)	3.09
Cu(1)...Cu(3)	3.11	Cu(2)...Cu(4)	3.10
Cu(1)...Cu(4)	3.10	Cu(3)...Cu(4)	3.09
O...Cl(1)	2.92	O...Cl(2)	2.96
O...Cl(3)	2.91	O...Cl(4)	2.92
O...Cl(5)	2.92	O...Cl(6)	2.94
Average values			
Cu-Cl	2.408	Cl-Cu-Cl	119.2
Cu-O	1.90	Cu-Cl-Cu	80.2
Cu-N	1.96	O-Cu-Cl	84.8
N-C	1.35	N-Cu-Cl	95.2
C-C	1.38		

Table VI. Certain non-bonded interatomic distances, Å

Cl(1)...H(6)	(i)	2.9		Cl(1)...H(14)	(v)	2.9
Cl(2)...H(20)	(i)	2.5		Cl(2)...H(5)	(ii)	2.7
Cl(2)...H(3)	(iv)	2.7		Cl(2)...H(8)	(i)	2.7
Cl(3)...H(18)	(i)	2.6		Cl(3)...H(4)	(iv)	2.9
Cl(3)...H(12)	(i)	2.9		Cl(3)...H(23)	(vi)	3.0
Cl(4)...H(21)	(iii)	2.9		Cl(4)...H(14)	(i)	2.9
Cl(4)...H(24)	(i)	2.9				
Cl(5)...H(2)	(i)	2.6		Cl(5)...H(18)	(vii)	3.0
Cl(6)...H(17)	(vii)	2.7		Cl(6)...H(15)	(viii)	2.8
Cl(6)...H(16)	(viii)	3.0				
N(19)...H(9)	(ix)	2.6				
H(6)...H(6)	(ii)	2.2				

The Roman numeral after the second atom gives the position of that atom in terms of the listed co-ordinates:

(i)	:	x, y, z
(ii)	:	$-x, -y, -z$
(iii)	:	$1/2+x, 1/2-y, 1/2+z$
(iv)	:	$1/2-x, 1/2+y, 1/2-z$
(v)	:	$-x, -y, 1-z$
(vi)	:	$1+x, y, z$
(vii)	:	$1-x, -y, 1-z$
(viii)	:	$x, y, z-1$
(ix)	:	$x-1/2, 1/2-y, 1/2+z$

iodide and silver iodide, the existence of the ion $[Ag_4I_6]^{2-}$ has been postulated[9] with a structure similar to that of the Cu_4Cl_6 unit described here.

Although the central Cu_4Cl_6O unit has potential T_d ($\overline{4}3$ m) symmetry, the highest possible symmetry for the molecule as a whole is reduced to D_{2d} ($\overline{4}2$ m) by the presence of the pyridine rings. In the crystal, the four pyridine ligands attached to each central Cu_4Cl_6O unit are not even approximately equivalent, but nevertheless one might expect the central unit itself to be relatively insensitive to the orientations of the pyridine ligands and hence to approximate closely to T_d symmetry. This is not the case. Although the tetrahedron formed by the 4 Cu atoms with the O atom at its centre, is regular within experimental error (Cu-O, 1.88-1.92 Å; Cu-O-Cu, 108-111°; Cu...Cu, 3.09-3.11 Å) and although the 4 N atoms are also equivalent within experimental error (Cu-N, 1.94-1.97 Å; O-Cu-N, 176-179°; O...N, 3.84-3.88 Å), the octahedron of Cl atoms deviates quite markedly from regularity. The 6 O...Cl distances are nearly equal (2.92-2.96 Å) but the 12 formally equivalent Cl...Cl distances vary from 3.93 Å to 4.41 Å with a corresponding variation in the Cl-O-Cl angles from 84° to 98°. These distortions from regularity are associated with variations in the Cu-Cl distances (2.36-2.49 Å) and especially in the Cl-Cu-Cl angles (108°-138°), but not in the Cu-Cl-Cu angles (79°-81°).

The co-ordination of the four Cu atoms is shown in Figure 4, which represents the four appearances of the molecule when viewed down each of the four potential three-fold axes (N-Cu-O) in turn, the Cu-O vector going vertically downwards from the plane of the paper. The upper and lower sets of three chlorine atoms are drawn in each case, together with an indication of the approximate plane of the pyridine ring. The ideal trigonal bipyramidal co-ordination, with the Cu atom displaced

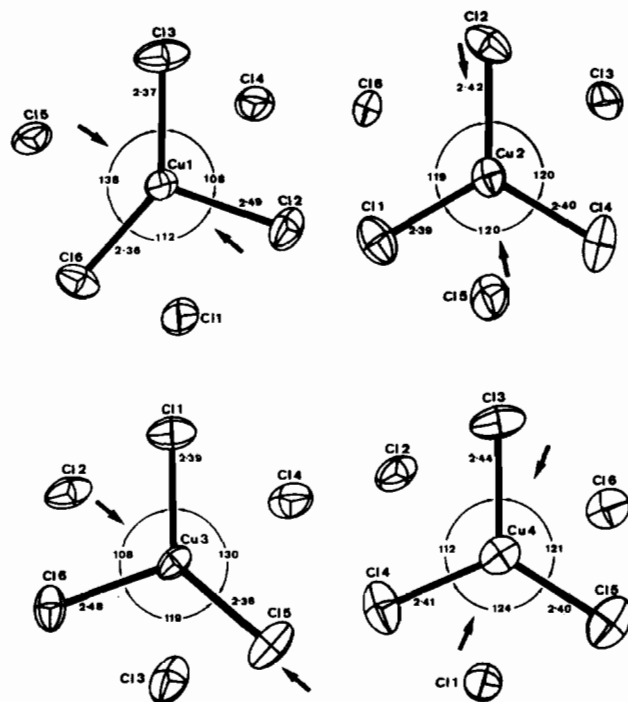(9) G. Dallinga and E. L. Mackor, *Rec. Trav. Chim. Pays-Bas*, 75. 796 (1956).

Figure 4. The environments of the four independent copper atoms viewed down the approximate three-fold axes, with relevant distances (Å) and angles (°). The heavy arrows indicate the approximate plane of the pyridine ring attached to each copper.

out of the plane of the three nearest Cl atoms by about 0.2 Å in the direction of the N atom, is approached only in the case of Cu(2) (Cu-Cl, 2.40, 2.42, 2.39 Å; Cl-Cu-Cl, 120°, 120°, 119°). For the other three Cu atoms, and especially for Cu(1) (Cu-Cl, 2.36, 2.37, 2.49 Å; Cl-Cu-Cl, 138°, 112°, 108°) the deviation from trigonal symmetry is very marked and quite outside the experimental uncertainties.

Two possible questions that now arise are (i) what is the cause of the distortion from a more regular arrangement? and (ii) why is the distortion ordered throughout the crystal? One answer might in fact suffice for both questions.

In order to provide a quantitative measure of the distortion, an «ideal» octahedron of six chlorine atoms was derived. The Cu_4O unit is experimentally regular, so the «ideal» position of each chlorine atom was assumed to lie on the external bisector of the Cu-O-Cu angle, to be within the plane defined by the atoms Cu-O-Cu, and to be at a distance of 2.93 Å from the oxygen. The atomic co-ordinates calculated with these assumptions are given in Table VII.

For the «ideal» octahedron of six chlorine atoms, the twelve formally equivalent Cl...Cl distances all lie between 4.1 and 4.2 Å, and the Cl-O-Cl angles range from 89° to 91.5°, thus confirming its regularity. The displacements of the observed positions from such ideal positions are 0.1, 0.1, 0.35, 0.15, 0.35 and 0.35 Å, respectively, for the six chlorine atoms; that is to say Cl(1), Cl(2), and Cl(4) are the closest to «ideality» whereas Cl(3), Cl(5), and Cl(6) show the greatest distortions.

Table VII. Calculated positional parameters (fractional coordinates $\times 10^4$) for the «ideal» octahedron of chlorine atoms assuming C_{2v} symmetry at the central oxygen atom (with respect to the Cu-O-Cu group and the Cl atom) and a Cl-O distance of 2.93 Å

Atom	x	y	z
Cl(1)	− 0404	0516	2291
Cl(2)	1884	1963	1762
Cl(3)	4430	1167	3889
Cl(4)	1043	1509	4960
Cl(5)	2165	− 0318	4472
Cl(6)	3010	0169	1206

Within an individual molecule, the most serious cause of strain and distortion would appear to be associated with overcrowding between the chlorine atoms and the α-hydrogen atoms of the pyridines. In a molecule of maximum possible symmetry with normal bond distances and angles, the shortest non-bonded H....Cl distances would be about 2.4 Å with the pyridine ring co-planar with Cl-Cu-N. When the pyridine ring is tilted 30° to the Cl-Cu-N plane, that is, at right angles to another Cl-Cu-N plane, the H....Cl distance increases to about 2.65 Å. (For estimated Cl....H distances in the actual molecule see Table VI). These distances are considerably shorter than the van der Waals distance between chlorine and hydrogen $(1.8 + 1.2$, about 3 Å) and one might well imagine that the steric strain could be relieved by distortion of the Cl octahedron and of the pyridine ligands. The latter effect may well occur but it is virtually unobservable because of the large uncertainties in the light-atom positions.

It might be tentatively expected that, because of steric strain and, possibly, other factors operating within a single molecule, there might be a relationship between the angles Cl-Cu-Cl and the orientations of the pyridine rings, for example, a closing of the Cl-Cu-Cl sector when the pyridine ring does *not* lie in that sector. No such relationship, however, is found. Likewise, there is no correlation between the Cu-Cl bond lengths and the orientation of the pyridine rings (see Figure 4 and Table VIII). Thus there appears, in fact, to be no relationship whatsoever between the distortion of the chlorine octahedron and the *intra*-molecular interatomic contacts.

Table VIII. Certain torsion angles about the Cu-N bonds (°)

C(8) -N(7) -Cu(1)-Cl(2)	− 20
C(8) -N(7) -Cu(1)-Cl(3)	− 128
C(12)-N(7) -Cu(1)-Cl(6)	− 80
C(12)-N(7) -Cu(1)-Cl(3)	58
C(20)-N(19)-Cu(2)-Cl(1)	− 105
C(20)-N(19)-Cu(2)-Cl(2)	15
C(24)-N(19)-Cu(2)-Cl(4)	− 53
C(24)-N(19)-Cu(2)-Cl(2)	− 174
C(2) -N(1) -Cu(3)-Cl(1)	− 135
C(2) -N(1) -Cu(3)-Cl(5)	− 3
C(6) -N(1) -Cu(3)-Cl(6)	− 58
C(6) -N(1) -Cu(3)-Cl(5)	− 178
C(14)-N(13)-Cu(4)-Cl(3)	156
C(14)-N(13)-Cu(4)-Cl(4)	43
C(18)-N(13)-Cu(4)-Cl(5)	96
C(18)-N(13)-Cu(4)-Cl(4)	− 139

Positive values indicate a right-handed sense of screw.

We might now try to correlate the distortion of the octahedron with the intermolecular packing. The distortions of individual chlorine octahedra from regularity occur in an ordered fashion. Some kind of interaction must exist between individual molecules, whereby information regarding the nature of the distortion in a given molecule is transmitted to its neighbours. Otherwise, in a crystal composed of loosely coupled molecules, we would expect the distortions from regularity in any one molecule to be largely independent of the distortions in others, leading to a disordered structure in which the averaged Cl octahedron was apparently regular but with very large temperature factors.

The main intermolecular contacts are between the peripheral pyridine ligands of different molecules and between pyridines on one molecule and chlorine atoms on others (see Figures 2 and 3). Several intermolecular Cl...H contacts are not longer than the shorter intramolecular Cl...H distances and one might seek in these the origin of the distortion and of the ordering.

Inter- and intramolecular distances, already calculated for the observed structure, were recalculated with the six «ideal» chlorine positions replacing the six observed positions, and examined for changes in Cl...H contact distances. The only appreciable changes in the shorter contact distances were for Cl(3) and Cl(6) (Cl(3)...H(18), ideal 2.5 Å, observed 2.6 Å; Cl(3)...H(12) ideal 2.7 Å, observed 2.9 Å; Cl(6)...H(17), ideal 2.4 Å, observed 2.7 Å), and of these only Cl(6)...H(17) is an intermolecular contact. The Cl(5)...H distances (involving the third «displaced» chlorine atom) are no shorter in the idealized structure than in the observed. In all these considerations we are severely handicapped by our ignorance of the actual positions of the hydrogen atoms.

In conclusion, we are unable to explain the distortion from ideal T_d symmetry of the Cu_4Cl_6O unit in terms of specific interactions. Nevertheless it seems likely that intramolecular interactions are less important than intermolecular. Certainly the latter must be responsible for the ordering of the distortions from molecule to molecule.*

Bond distances. The bond lengths in $Cu_4Cl_6O \cdot 4$-pyridine can be compared with those found in $CuCl_2 \cdot 2$-pyridine.[10] The latter compound is built from chains of distorted octahedra, each Cu having $(4 + 2)$ coordination and each chlorine acting as a bridging ligand ($CuCl_2 \cdot 2py$, Cu-Cl 2.28/3.05 Å, Cu-N 2.02 Å, Cu-Cl-Cu 92°). A distance of about 2.3 Å from Cu to bridging -Cl- is also found in several other complexes with similar chain structures (e.g. $CuCl_2 \cdot 2H_2O$ and $CuCl_2$).[11] The

(10) J. D. Dunitz, *Acta Cryst.*, 10, 307 (1957).
(11) A. F. Wells, *Structural Inorg. Chem.*, Oxford Univ. Press, 872 (1962).

longer distance (2.41 Å average) found in the present complex could be a consequence of the change in co-ordination number, or of the special structural arrangement in $Cu_4Cl_6O.4py.$, or of both. A shorter Cu-Cl distance, while increasing the Cu-Cl-Cu angle, would decrease an already short non-bonded Cl . . . O distance. The anion $CuCl_5^{3-}$, with trigonal bipyramidal co-ordinated copper[12] but without bridging chlorine, has a Cu-Cl equatorial distance of 2.35 Å and a Cu-Cl apical distance of 2.32 Å, thus suggesting that the still longer Cu-Cl bond in the present complex is a consequence not only of the change in co-ordination number but also of the special structural arrangement.

Magnetic and Spectral properties. The complex molecule contains 4 formally d^9 atoms, 3.1 Å apart, at the corners of a tetrahedron, and the magnetic moment is of interest in that it may indicate possible interaction between the copper atoms. The measured value of 1.86 B.M.[13] is to be compared with the calculated spin-only moment of 1.73 B.M., with the usually observed values for distorted octahedral co-ordination of around 2.0 B.M., and with the predicted[14] and observed[8] value for symmetrical trigonal bipyramidal co-ordination of 2.2 B.M. Further investigation of the magnetic properties are being made.[13]

The compound appears to exist not only in the solid state, the absorption spectrum of $Cu_4Cl_6O.4py.$ in acetone solution[13] showing a peak at 8650 mμ and a shoulder at 7800 mμ. The spectrum reported for $Cu_4Cl_6O.4OPPh_3$ is similar, with a peak at 9100 mμ.[8]

The compound $Cu_4Cl_6O.4py.$ can be considered as one of a series in which atoms with formally unpaired electrons are bridged by oxygen; such a series would comprise linear, e.g. $[(RuCl_5)_2O]^{4-}$,[15] triangular e.g. $Cr_3(acetate)_6O.Cl.5H_2O$,[16] and tetrahedral complexes, e.g. $Cu_4Cl_6O.4py.$ and $Co_4(pivalate)_6O.$[7]

(12) M. Mori, Y. Saito and T. Watanabe, *Bull. Chem. Soc. Japan,* 34, 245 (1961).
(13) P. Baccini, private communication.
(14) E. A. Boudreaux, *Trans. Farad. Soc.,* 59, 1055 (1963).
(15) A. McL. Mathieson, D. P. Mellor and N. C. Stephenson, *Acta Cryst.,* 5, 185 (1952).
(16) B. N. Figgis and G. B. Robertson, *Nature,* 205, 694 (1965).