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2-Picoline N-Oxide Complexes of Copper(II) Chloride. The Crystal Structure of $Cu_3Cl_6(C_6H_7NO)_2 \cdot 2H_2O$

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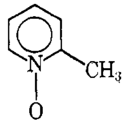
The crystal structure of polybis(μ-(2-picoline N-oxide)-chlorocopper(II)di-μ-chloro-)diaquocopper(II), $Cu_3Cl_6(C_6H_7NO)_2 \cdot 2H_2O$, has been determined by single-crystal X-ray diffraction techniques. The multiple-film equiinclination Weissenberg technique was used to collect 1893 nonzero reflections whose intensities were visually estimated. The crystals are triclinic, $P\bar{1}$, with unit cell dimensions $a = 9.732$ (7) Å, $b = 7.380$ (5) Å, $c = 9.596$ (7) Å, $\alpha = 104°\ 26\ (5)'$, $\beta = 119°\ 21\ (5)'$, and $\gamma = 68°\ 15\ (5)'$. There is one formula weight per unit cell and the observed and calculated densities are 1.94 and 1.96 g/cm^3, respectively. The structure was refined by least-squares methods to a conventional R factor of 10.3%. The complex consists of $Cu_2Cl_4(C_6H_7NO)_2$ dimers bridged by $CuCl_2 \cdot 2H_2O$ groups through long (2.955 and 2.654 Å) Cu–Cl bonds to form infinite chains. The chains are postulated to be held together by hydrogen bonding. The copper ions are found in distorted octahedral and pentacoordinated square-pyramidal environments. The unit cell dimensions and space group of $CuCl_2(C_6H_7NO)(CH_3OH)$ also are reported.

Introduction

The reaction of $CuCl_2$ with derivatives of pyridine N-oxide to form complexes with a 1:1 metal-to-ligand ratio has been studied extensively.[1-4] It was found that a 1:1 ethanol solution of $CuCl_2$ and 2-picoline N-oxide, C_6H_7NO, does not yield the expected 1:1 complex, but rather a complex having the empirical formula $Cu_3Cl_6(C_6H_7NO)_2 \cdot 2H_2O$.[1,5] The magnetic properties[1] and the infrared spectra of this complex have been studied. It was suggested[5] that the complex is similar to those studied by Willett and Rundle[6] which were discrete molecules and could be formulated as $(CuCl_2)_x$-L_2 where $x = 2$ and 3 for L = acetonitrile and $x = 5$ for L = n-propyl alcohol. We have completed a three-dimensional X-ray diffraction analysis of $Cu_3Cl_6(C_6H_7NO)_2 \cdot 2H_2O$, and we wish to report the results of this study. The structure has a number of interesting features.

Experimental Section

The 2-picoline N-oxide (I), Reilly Tar & Chemical, was purified by vacuum distillation. Equimolar quantities of ligand and $CuCl_2$ dissolved in ethanol were mixed, and a green powder precipitated immediately. Green needle-shaped crystals were obtained upon recrystallization from an ethanol solution. Good single crystals of optimum dimensions could not be found, as the crystals were of irregular cross section. A crystal of approximate dimensions 0.09 × 0.22 × 0.40 mm was selected.



I

Unit cell dimensions were determined from precession, c axis rotation, and zero-level Weissenberg photographs calibrated with NaCl powder lines, $a = 5.6402$ Å. The unit cell dimensions at room temperature are $a = 9.732$ (7) Å, $b = 7.380$ (5) Å, $c = 9.596$ (7) Å, $\alpha = 104°\ 26\ (5')$, $\beta = 119°\ 21\ (5')$, and $\gamma = 68°\ 15\ (5)'$. The errors in cell edges are average deviations obtained from the measurement of a number of reflections. The errors in angles are average deviations obtained from a series of independent measurements of the same angle. The calculated density for one formula weight per unit cell is 1.96 g/cm^3, which agrees with the experimental value of 1.94 g/cm^3 determined by the flotation method using a mixture of carbon tetrachloride and bromoform. Three-dimensional intensity data were collected at room temperature around the c axis for levels 0 through 10 using the multiple-film (three films) equiinclination Weissenberg technique.

Zirconium-filtered molybdenum radiation (λ (Mo Kα) 0.71069 Å) was used. The intensities of 1893 nonzero reflections were estimated visually by comparison with a calibration strip. Lorentz-polarization corrections were made, and the data were corrected for absorption using Bond's values[7] for a cylinder with $\mu = 36.6$ cm^{-1} and $\mu R = 0.36$. The space group is either P1 or $P\bar{1}$.

Recrystallization of $Cu_3Cl_6(C_6H_7NO)_2 \cdot 2H_2O$ from methanol yielded green cube-shaped crystals which decomposed at 207–208°. *Anal.* Calcd for $CuCl_2(C_6H_7NO)(CH_3OH)$: Cu, 23.05; C, 30.05; H, 4.02; N, 5.08. Found: Cu, 23.08; C, 29.80; H, 3.94; N, 4.95. The complex is unstable at room temperature and loses weight slowly. A sample was warmed over a period of several weeks at approximately 55° until a constant weight was obtained. The loss in weight corresponded to the weight of methanol present initially.

The crystals of $CuCl_2(C_6H_7NO)(CH_3OH)$ are monoclinic and belong to space group $P2_1/c$. The unit cell dimensions are $a = 11.81$, $b = 10.47$, $c = 9.02$ Å, and $\beta = 103°\ 49'$. The calculated density for four molecules per unit cell is 1.69 g/cm^3 compared with an experimental value of 1.71 g/cm^3.

Structure Determination

The following computer program were used: (1) W. H. Watson and R. J. Williams, "Data Reduction Program" (IBM 1620); (2) D. Hall and R. Shiono, "General Three-Dimensional Fourier Synthesis Program" (IBM 1620, 8.4.006); (3) D. Hall and R. Shiono, "Alphabetic Plotting Program for Output of Fourier Synthesis Program" (IBM 1620, 8.4.007); (4) R. Shiono, "Structure Factor Calculations in X-Ray Crys-

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[1] M. R. Kidd, R. S. Sager, and W. H. Watson, *Inorg. Chem.*, **6**, 946 (1967).

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[3] W. E. Hatfield, Y. Muto, H. B. Jonassen, and J. S. Paschal, *Inorg. Chem.*, **4**, 97 (1965).

[4] W. E. Hatfield and J. C. Morrison, *ibid.*, **5**, 1391 (1966).

[5] R. Whyman and W. E. Hatfield, *ibid.*, **6**, 1859 (1967).

[6] R. D. Willett and R. E. Rundle, *J. Chem. Phys.*, **40**, 838 (1964).

[7] "International Tables for X-Ray Crystallography," Vol. II, The Kynoch Press, Birmingham, England, 1959, p 295.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $Cu_3Cl_6(C_6H_7NO)_2 \cdot 2H_2O$

h	k	F_o	F_c
l = 0			
2	0	55	49
4	0	40	40
5	0	39	33
6	0	24	24
7	0	26	25
8	0	30	31
9	0	23	24
10	0	12	11
-1	1	59	59
-2	1	9	8
-3	1	13	14
3	1	62	57
4	1	43	41
-4	1	50	51
-5	1	60	72
5	1	53	56
6	1	16	16
-6	1	47	50
-7	1	47	48
-8	1	25	26
-9	1	21	22
0	2	76	77
-1	2	80	82
2	2	42	37
-2	2	54	50
3	2	17	16
-4	2	21	21
-5	2	25	25
5	2	8	9
-6	2	46	49
-7	2	15	13
7	2	10	10
-8	2	15	17
-9	2	14	14
-10	2	14	16
10	2	11	11
1	3	23	24
-1	3	33	27
-2	3	34	28
2	3	15	16
-3	3	26	26
-4	3	6	7
4	3	7	4
5	3	20	16
-5	3	34	32
6	3	21	21
-6	3	22	21
7	3	15	14
-7	3	14	13
-8	3	9	5
8	3	13	12
9	3	24	26
10	3	12	14
0	4	15	12
1	4	36	35
2	4	51	55
-2	4	10	7
-3	4	17	15
3	4	20	20
-4	4	20	19
4	4	9	7
5	4	9	7
9	4	13	15
0	5	10	12
1	5	15	14
-2	5	10	11
-3	5	26	24
4	5	9	9
-4	5	23	27
-5	5	11	10
6	5	21	21
11	5	14	18
-1	6	21	19
1	6	18	17
-2	6	27	27
-3	6	11	12
4	6	13	15
5	6	27	27
6	6	34	39
7	6	35	40
8	6	11	11
11	6	13	15
0	7	33	35
-1	7	29	28
1	7	25	23
-2	7	27	21
2	7	24	23
3	7	23	22
4	7	14	15
5	7	21	20
6	7	23	20
7	7	22	21
0	8	12	10
-1	8	13	12
1	8	17	18
-2	8	16	19
2	8	17	17
3	8	16	17
-3	8	15	17
4	8	22	23
-4	8	11	12
5	8	31	35
6	8	29	30
7	8	13	14
0	9	16	16
1	9	15	16
-1	9	17	19
-3	9	14	13
l = 1			
1	0	23	18
2	0	55	50
3	0	15	12
-3	0	29	27
-4	0	18	18
4	0	27	27
-5	0	35	40
5	0	47	48
6	0	29	27
-6	0	35	37
-7	0	27	26
8	0	10	9
9	0	12	14
10	0	17	17
-10	0	12	12
1	-1	10	10
1	1	25	26
2	1	32	32
2	-1	40	38
-3	-1	34	34
3	-1	18	16
3	1	74	73
-4	-1	5	5
4	1	79	89
-5	-1	17	18
5	1	47	56
5	-1	40	35
-6	-1	23	22
6	1	26	23
6	-1	9	7
7	-1	27	24
8	-1	18	15
9	1	26	24
10	1	24	22
11	1	18	17
12	1	14	14
0	2	45	48
1	2	32	39
-1	-2	26	16
1	-2	40	33
-1	2	56	78
2	2	13	12
2	-2	34	33
-2	2	48	46
-2	-2	11	10
3	2	33	45
3	-2	51	47
-3	2	65	70
4	-2	15	13
-4	-2	16	15
-4	2	53	60
4	2	47	108
-5	-2	37	36
-5	2	48	51
5	2	87	87
6	2	41	44
7	2	24	27
8	2	25	27
8	-2	11	12
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-1	3	83	97
2	3	27	26
2	-3	18	15
-2	3	83	79
3	-3	9	10
3	3	50	49
-3	3	45	50
-4	3	28	30
4	3	54	54
-4	3	38	30
4	-3	10	9
5	3	28	26
-5	3	15	15
5	-3	10	8
-6	-3	34	32
6	3	9	8
-7	-3	49	51
7	3	10	7
-7	3	20	18
7	-3	12	14
8	-3	21	25
8	3	22	22
-8	3	21	22
-8	-3	41	37
9	3	23	23
-9	3	28	25
9	-3	12	10
0	-4	62	60
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1	-4	50	38
-1	4	51	48
2	-4	13	11
-2	4	48	47
-2	-4	79	76
3	-4	15	12
-3	4	31	26
-3	-4	65	64
3	4	34	39
4	-4	12	12
4	4	43	52
5	4	23	22
-5	4	35	33
-6	-4	16	15
6	-4	14	13
-7	-4	55	61
-8	-4	37	38
0	-5	25	23
1	5	19	16
1	-5	21	19
-1	-5	44	41
-1	5	35	30
2	-5	23	23
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-2	-5	60	60
3	-5	19	15
-3	-5	65	59
-3	5	8	13
4	-5	26	23
-4	-5	43	40
5	5	20	19
5	-5	29	28
-5	-5	39	36
6	5	21	23
6	-5	28	26
-6	-5	46	45
-7	-5	40	37
7	-5	18	16
-8	-5	36	34
0	6	22	21
0	-6	38	36
1	6	26	27
-1	-6	55	61
1	-6	39	36
2	-6	30	28
-2	-6	35	35
3	-6	28	29
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4	-6	16	14
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-6	-6	30	31
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0	7	24	19
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2	-7	10	10
-2	-7	36	40
3	-7	11	11
4	-7	11	13
5	-7	15	14
-6	-7	12	13
6	-7	18	19
7	-7	15	14
-2	-8	10	7
-4	-8	12	14
-3	-9	14	10
-3	-10	15	15
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-5	0	23	23
6	0	22	21
7	0	24	23
-8	0	24	24
8	0	14	16
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0	1	83	55
1	1	26	20
1	-1	54	47
2	1	25	21
-2	1	35	38
2	-1	28	28
-2	-1	86	77
3	-1	12	12
3	1	45	49
-3	-1	101	110
-3	1	8	6
-4	1	12	13
4	-1	12	10
-4	-1	68	75
4	1	9	7
5	1	21	18
-5	1	18	16
5	-1	8	8
6	1	27	24
-6	1	40	34
6	-1	16	12
-7	-1	23	26
-7	1	29	20
7	-1	26	14
7	1	17	16
-8	-1	34	36
-8	1	10	10
-9	-1	30	34
9	1	12	14
-9	1	13	14
-10	1	10	11
-10	-1	26	30
-11	-1	20	20
0	-2	20	14
0	2	42	36
1	2	14	10
1	-2	43	38
-1	2	62	67
-2	2	59	66
2	-2	30	29
-2	-2	63	87
2	2	12	8
3	2	21	19
-3	2	16	17
3	-2	45	47
-3	-2	135	138
4	-2	41	39
-4	-2	78	102
4	2	16	9
-4	2	8	7
-5	-2	66	55
5	-2	45	56
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6	2	7	9
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7	-2	19	20
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-7	-2	28	34
7	2	15	16
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0	-3	46	41
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4	-3	36	37
-5	-3	8	6
5	3	8	9
5	-3	19	18
-6	-3	17	16
6	-3	18	16
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5	5	33	33
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6	5	13	16
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7	5	19	25
8	5	25	32
9	5	14	14
0	6	33	31
0	-6	9	8
1	6	35	33
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1	-6	16	16
2	6	40	37
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3	6	33	30
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2	-8	11	12
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4	-8	12	8
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-11	-8	12	4
-3	-9	9	10
-4	-9	12	14
-5	-9	16	15
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-8	-9	12	15
-9	-9	12	11
0	-10	15	15
-8	-10	15	14
-9	-10	14	18
l = 3			
1	0	128	138
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3	0	44	44
-4	0	48	57
4	0	15	12
-5	0	44	54
5	0	31	29
-6	0	31	32
6	0	13	12
-7	0	44	45
7	0	13	12
-8	0	31	32
-9	0	16	12
9	0	19	18
10	0	14	13
-10	0	7	8
-11	0	13	12
-12	0	13	11
0	1	37	36
-1	1	53	56
1	1	72	78
1	-1	57	60
2	1	50	47
2	-1	70	73
-3	1	55	64
3	1	19	18
3	-1	22	22
-4	-1	56	63
-4	1	79	98
4	1	26	17
4	-1	22	26
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-5	1	60	60
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5	-1	18	19
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-6	1	45	40
6	1	24	25
6	-1	42	42
-7	-1	10	9
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7	-1	36	38
-8	1	21	21
8	-1	23	25
-9	1	11	11
9	-1	17	17
10	-1	12	12
-11	-1	12	9
-11	1	14	14
-12	-1	10	7
-12	1	17	16
-13	1	12	11
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0	-2	10	7
-1	-2	30	26
-1	2	30	33
1	2	39	40
1	-2	71	78
-2	-2	24	22
-2	2	5	3
2	-2	77	83
-3	-2	19	12
-3	2	19	18
3	2	11	12
3	-2	41	44
-4	2	39	37
4	2	15	15
-5	-2	18	16
-5	2	31	31
5	-2	13	14
-6	-2	26	24
-6	2	28	26
6	-2	27	27
-7	-2	19	19
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-8	2	19	18
8	-2	11	10
-9	-2	17	16
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9	-2	11	12
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0	-3	8	5
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1	-3	19	18
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2	3	30	29
2	-3	23	20
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4	-3	16	17
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-10	-4	13	13
0	-5	20	19
-1	-5	11	11
-1	5	8	8
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-1	-7	10	11
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-4	7	11	10
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-10	-8	11	7
-5	-9	7	10
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2	-7	12	[illegible]
-3	-7	15	[illegible]
-8	-7	9	[illegible]
-9	-7	8	[illegible]
-10	-7	10	[illegible]
-3	-8	[illegible]	[illegible]
-7	-8	[illegible]	[illegible]
-3	-8	[illegible]	[illegible]
-9	-8	[illegible]	[illegible]

tallography (IBM 1620); (5) Y. Okaya, "Full-Matrix Least-Squares Refinement" (modified for IBM 360/50); (6) Y. Okaya, "Standard Deviation Program from Least-Squares Matrix" (IBM 360/50); (7) Y. Okaya, "Bonds and Angles Program" (IBM 360/50); (8) H. G. Norment, "Least-Squares Line and Plane Fitter" (IBM 1620).

Patterson projections along the *a* and *b* axes were used to determine the relative positions of three copper ions and four bridging chloride ions. Fourier projections

TABLE II

ATOMIC PARAMETERS WITH STANDARD DEVIATIONS[a]

Atom	X	Y	Z	B, Å^2	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu_1	0.5000	0.5000	0.5000	1.99 (5)	0.86 (3)	1.14 (4)	0.59 (2)	−0.39 (5)	0.32 (4)	0.35 (5)
Cu_2	0.5181 (2)	0.6216 (2)	0.1718 (2)	1.60 (4)	0.68 (2)	0.95 (3)	0.53 (2)	−0.41 (2)	0.22 (3)	0.21 (3)
Cl_1	0.3431 (3)	0.4744 (4)	0.2314 (3)	2.27 (7)	0.93 (4)	1.50 (6)	0.67 (3)	−1.03 (8)	0.24 (5)	0.39 (7)
Cl_2	0.7272 (4)	0.5739 (5)	0.4150 (3)	2.54 (7)	0.86 (4)	1.81 (7)	0.67 (3)	−0.59 (8)	0.07 (5)	0.40 (7)
Cl_3	0.3940 (4)	0.9394 (4)	0.2145 (3)	2.19 (7)	1.04 (4)	0.96 (5)	0.80 (4)	−0.51 (7)	0.53 (6)	0.11 (6)
$O(H_2)$	0.407 (1)	0.790 (1)	0.503 (1)	2.2 (2)	1.02 (13)	1.30 (18)	0.65 (11)	−0.29 (23)	0.58 (17)	0.25 (21)
O	0.6217 (9)	0.380 (1)	0.0634 (8)	1.8 (2)	0.66 (10)	1.16 (16)	0.36 (8)	−0.02 (20)	0.02 (13)	0.14 (17)
N	0.741 (1)	0.225 (1)	0.147 (1)	1.9 (2)	0.74 (13)	0.88 (17)	0.80 (13)	−0.36 (24)	0.49 (19)	0.20 (22)
C_2	0.901 (1)	0.204 (2)	0.187 (2)	2.6 (3)	0.82 (16)	2.18 (31)	0.85 (16)	−0.88 (35)	0.25 (23)	1.17 (35)
C_3	0.015 (2)	0.034 (3)	0.269 (2)	3.6 (4)	0.62 (17)	2.75 (42)	1.78 (27)	0.38 (43)	0.27 (31)	2.50 (56)
C_4	0.972 (2)	−0.093 (2)	0.305 (2)	3.5 (4)	1.30 (23)	1.88 (37)	1.72 (26)	0.39 (46)	1.00 (38)	1.81 (51)
C_5	0.806 (2)	−0.063 (2)	0.257 (2)	3.6 (4)	1.65 (24)	1.76 (30)	1.23 (21)	−0.50 (42)	1.27 (35)	0.95 (30)
C_6	0.691 (1)	0.096 (2)	0.180 (2)	2.4 (3)	1.17 (18)	1.40 (25)	0.79 (16)	−0.49 (33)	0.97 (26)	0.40 (30)
C_7	0.941 (2)	0.348 (3)	0.144 (3)	4.5 (4)	1.03 (19)	2.14 (38)	2.64 (37)	−0.86 (43)	0.92 (40)	1.42 (59)

[a] Standard deviations of last significant figures are given in parentheses. [b] Anisotropic temperature factors × 10^2. The anisotropic temperature factors have the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

along all three axes located the other two chloride ions. It had been assumed that the molecule was acentric, but it was evident that the positions of the three copper ions were collinear, and three of the chloride ions were related to the other three by a center of symmetry. $P\bar{1}$ was chosen as the correct space group. Successful refinement of the structure appears to justify this choice.

A three-dimensional Fourier map was calculated in which the signs were determined from structure factor calculations using the positions of the copper and chloride ions. The value of R was 0.35, where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. The positions of all other atoms in the structure were assigned tentatively from this Fourier. Structure factor calculations including all atoms lowered the R value to only 0.33. A second three-dimensional Fourier map was calculated, and a better set of atomic positions was obtained. These positions yielded an R value of 0.23.

Plots of ln (F_o/F_c) *vs.* $(\sin^2 \theta)/\lambda^2$ were used to scale the levels together since the least-squares program does not vary the individual scale factors for the levels. Positional and isotropic thermal parameters were refined by six least-squares cycles on the IBM 360 Model 50. The contributions of the hydrogen atoms have been ignored. The quantity $\Sigma[w(|F_o| - |F_c|)^2]$ was minimized. A modified Hughes[8] weighting scheme used was $w = 1.00$ for $F_o < 4F_{\min}$ and $w = (4F_{\min}/F_o)^2$ for $F_o > 4F_{\min}$. Atomic scattering factors were taken from the tables of Cromer and Waber.[9] Those for Cu^{2+} and Cl^- were corrected for both the real and the imaginary parts of anomalous dispersion using Cromer's values.[10] After the six cycles, the parametric shifts were all much less than the corresponding estimated standard deviations, but the R factor had only dropped to 14.7%.

An examination of the crystal used for intensity measurements shows that a cylinder is not an adequate approximation for the absorption corrections. Calculations of the maximum and minimum absorption indicated the maximum error in any structure factor due to this approximation could be as much as 11%, so we decided to make an absorption correction to our data which would take into account the irregular shape of the crystal. The absorption program used for this correction, based on Burnham's GNABS, uses the equations of the crystal faces and does not depend on the crystal class.

Three more isotropic least-squares cycles were computed with the corrected data. The R factor remained at 14.7%. Two further least-squares cycles were used to refine positional and anisotropic thermal parameters. After the last refinement cycle, the largest shift was less than half the estimated standard deviation for that parameter. The final value of R was 10.3%. The least-squares program does not give a weighted R value. Examination of strong reflections of low sin θ indicated that none was significantly affected by extinction, so extinction corrections were not made.

Observed and calculated structure factors are listed in Table I, and Table II gives the final positional and thermal parameters and deviations. The estimated standard deviations are obtained from the normal equations matrix of the last least-squares cycle. Table III lists bond lengths, bond angles, and other short nonbonding distances with their estimated standard deviations. A final three-dimensional difference Fourier was calculated. Peaks of magnitude 0.4–1.0 e$^-$/Å^3 were found at several, but not all, of the expected hydrogen positions. No peaks higher than 1.2 e$^-$/Å were found in the difference Fourier.

Discussion of the Structure

The structure of $Cu_3Cl_6(C_6H_7NO)_2 \cdot 2H_2O$ is shown in Figure 1. The complex consists of infinite chains along the c direction containing both five- and six-coordinated copper ions, bridged by both chloride and oxygen atoms. The chains are possibly held together by hydrogen bonding in the b direction between copper-coordinated water molecules and chloride atoms. Each chain is separated from adjacent chains in the a direction by ordinary van der Waals distances; a water oxy-

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(8) E. W. Hughes, *J. Am. Chem. Soc.*, **63**, 1737 (1941).
(9) D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).
(10) D. T. Cromer, *ibid.*, **18**, 17 (1965).

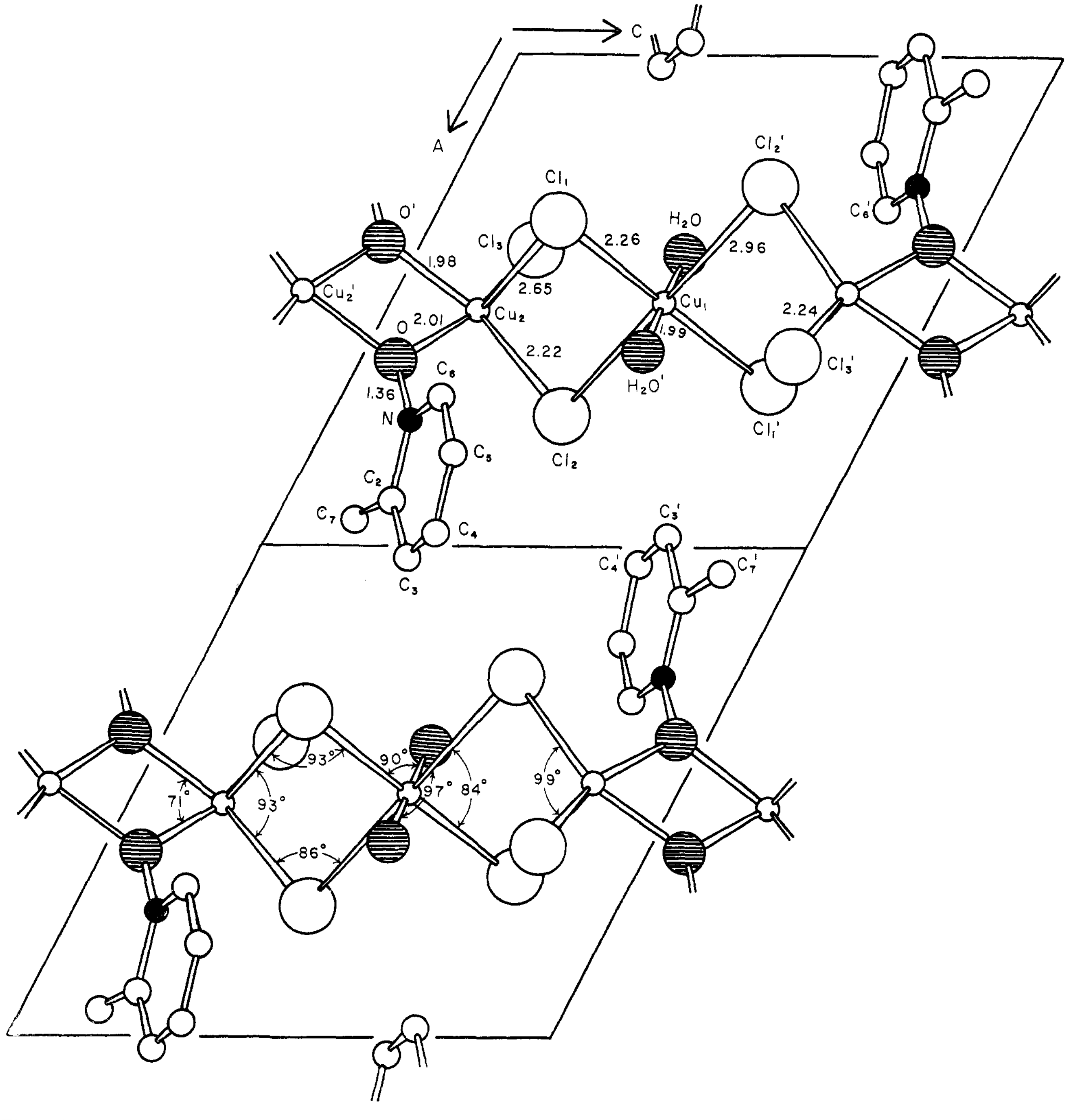

Figure 1.—A projection of $Cu_3Cl_6(C_6H_7NO)_2 \bullet 2H_2O$ showing the contents of two unit cells. The *b* axis is going into the plane of the paper.

gen is 3.37 Å from a C_3 belonging to an adjacent chain and two C_4's on different chains are separated by 3.50 Å.

The six-coordinated copper ions lie at centers of symmetry and are bridged to two adjacent copper ions by pairs of chloride ions. Two water molecules complete the distorted octahedral configuration. Each five-coordinated copper ion is bridged to another five-coordinated copper ion by oxygen atoms from two 2-picoline N-oxide ligands and to an octahedrally coordinated copper ion by two chloride ions. A nonbridging chloride ion occupies the fifth coordination site completing the square-pyramidal structure.

The independent bond distances around the octahedral copper ion are Cu–Cl = 2.264 and 2.955 Å and Cu–OH_2 = 1.99 Å. In the copper–chlorine plane the Cl–Cu–Cl angle is 84.4°, and the Cu–O bond makes an angle of 82.6° with this plane. The structure of $CuCl_2 \cdot 2H_2O$[11,12] affords a comparison with this portion of the molecule. The copper ion in $CuCl_2 \cdot 2H_2O$ lies in a distorted octahedral environment with Cu–Cl bonds of 2.28 and 2.91 Å and a Cu–O bond of 1.93 Å.

It is interesting to speculate on the location of the hydrogen atoms of the water molecule. Figure 2 is a

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(11) D. Harker, *Z. Krist.*, **93**, 136 (1936).

(12) S. W. Peterson and H. A. Levy, *J. Chem. Phys.*, **26**, 220 (1957).

TABLE III

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (DEG)[a]

Cu_1–Cu_2	3.581 (2)	Cl_1–Cl_2	3.543 (5)	Cl_1–Cu_2–O′	95.7 (3)
Cu_2–Cu_2′	3.255 (3)	Cl_1–OH_2	3.011 (9)	Cl_3–Cu_2–O	157.2 (3)
Cu_1–Cl_1	2.264 (3)	Cl_1′–OH_2	3.020 (9)	Cl_3–Cu_2–O′	92.9 (3)
Cu_1–Cl_2	2.955 (3)	Cl_2–C_7	3.80 (2)	Cl_3–H_2O–Cl_1	73.6 (3)
Cu_1–OH_2	1.99 (1)	Cl_3′–C_3′	3.76 (2)	Cl_1–Cu_1–OH_2	90.1 (3)
Cu_2–Cl_1	2.654 (4)	H_2O′–C_3	3.37 (2)	Cu_2–Cl_2–Cu_1	86.3 (1)
Cu_2–Cl_2	2.221 (4)	C_4–C_4′	3.50 (3)	Cl_1–Cu_1–Cl_2	84.4 (1)
Cu_2–Cl_3	2.244 (4)	Cl_2–C_7′	3.92 (2)	Cl_2–Cu_1–OH_2	97.4 (3)
Cu_2–O	2.01 (1)	C_3–C_4′	3.95 (3)	N–O–O′	165.7 (9)
Cu_2–O′	1.98 (1)	Cl_1′–Cl_2	3.894 (5)	Cu_2′–O–N	127.1 (8)
N–O	1.36 (2)	Cl_2–Cl_3	3.389 (6)	Cu_2–O–N	121.6 (8)
N–C_2	1.36 (2)	Cl_1–Cl_3	3.697 (5)	O–N–C_2	118 (1)
N–C_6	1.37 (2)	Cu_2′–O–Cu_2	109.3 (5)	O–N–C_6	117 (1)
C_2–C_3	1.42 (3)	O–Cu_2–O′	70.7 (4)	C_2–N–C_6	124 (1)
C_2–C_7	1.46 (3)	Cu_2–Cl_1–Cu_1	93.1 (1)	N–C_2–C_7	120 (2)
C_3–C_4	1.33 (3)	Cu_2′–Cu_2–Cu_1	130.3 (1)	C_3–C_2–C_7	126 (2)
C_4–C_5	1.40 (2)	Cl_1–Cu_2–Cl_2	92.8 (1)	N–C_2–C_3	114 (2)
C_5–C_6	1.35 (3)	Cl_2–Cu_2–Cl_3	98.7 (2)	C_2–C_3–C_4	124 (2)
Cl_3′–C_6′	3.66 (2)	Cl_2–Cu_2–O	95.4 (3)	C_3–C_4–C_5	119 (2)
O–O′	2.32 (2)	Cl_2–Cu_2–O′	164.6 (3)	C_4–C_5–C_6	120 (2)
Cl_3–OH_2	3.155 (9)	Cl_1–Cu_2–Cl_3	97.7 (2)	C_5–C_6–N	119 (2)
		Cl_1–Cu_2–O	99.3 (3)	Cl_3–H_2O–Cu_1	110.2 (5)

[a] Standard deviations of last significant figures are given in parentheses.

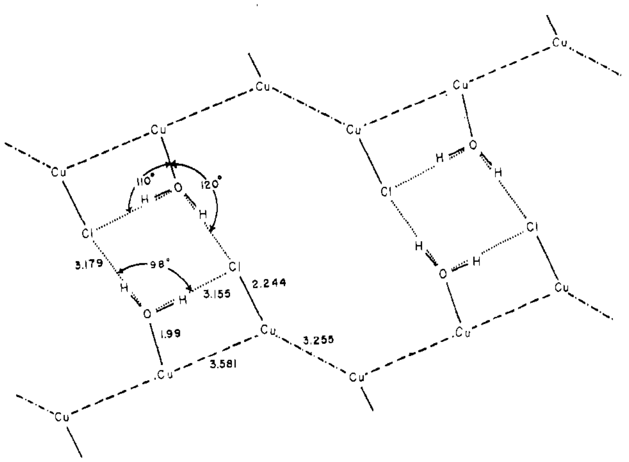

Figure 2.—Possible location of the water molecule hydrogen atoms in $Cu_3Cl_6(C_6H_7NO)_2 \cdot 2H_2O$. The projection is along the *a* axis.

sketch showing the relative locations of copper ions, proposed water molecules, and appropriate chloride ions (Cl_3). The distance from the water oxygen atom to a nonbridging chloride ion on the same chain is 3.155 Å while the distance to a nonbridging chloride ion on an adjacent chain is 3.179 Å. The Cl–O–Cl angle is 98.2°. This angle and the unusually short chlorine–water distances lead one to believe that the chains are linked together by hydrogen bonds. The distances are again similar to those of $CuCl_2 \cdot 2H_2O$ (3.18 Å for Cl–O),[12] which has been shown by neutron diffraction to have its water hydrogens slightly off the lines between the oxygen and chlorine atoms. These distances are close to the expected Cl–O distance of 3.1 Å for a hydrogen bond between a water molecule and a chloride ion.[13]

The similarity to $CuCl_2 \cdot 2H_2O$ cannot be extended further. In $CuCl_2 \cdot 2H_2O$ the Cu–O bond bisects the Cl–O–Cl angle and the water molecule is in the same plane as the linear Cl–Cu–Cl unit. This enables the oxygen to form an sp^2 hybrid σ bond with the metal and also a metal–oxygen π bond utilizing the p_z orbital on the oxygen. This planarity is not found in $Cu_3Cl_6(C_6H_7NO)_2 \cdot 2H_2O$. The Cu–$H_2O$ bond makes an angle of 130.4° with the bisector of the Cl–O–Cl angle. The Cl_3 atoms are 1.08 and 2.05 Å out of the plane formed by Cu_1, H_2O, Cl_1, and Cl_1′. It appears that if the water hydrogens are pointing toward the chloride ions, some rehybridization of the oxygen orbitals must take place in order for the orbitals to be in a favorable position to bond to the copper.

An alternative possibility is that the water is hydrogen bonded only to the Cl_3 on the adjacent chain. This would enable the Cu–O bond to bisect the H–O–H angle, and the line formed by Cl_1–Cu_1–Cl_1′ would be almost coplanar with the water molecule. The Cl_3 on the same chain could still be close to the water molecule even if it is not hydrogen bonded; the Cl_1–Cu_2–Cl_3 and Cl_2–Cu_2–Cl_3 angles of 98 and 99° show that the Cl_3 position in the square-pyramidal configuration is not distorted by any hydrogen bonding. Until a neutron diffraction structure determination is carried out, it remains to be seen where the hydrogens are located and if the chains are really linked by hydrogen bonding.

The symmetry about the five-coordinated copper ions is that of a square pyramid with the two bridging oxygens, one bridging chloride ion, and the nonbridging chloride ion forming the base of the pyramid and a bridging chloride ion at the apex. The angles formed by these ligands with the copper ion are shown in Figure 3. The Cu–Cl distances of 2.221 and 2.244 Å and the Cu–O distances of 2.01 and 1.98 Å which form the base are normal, but the distance from the copper ion to the chloride ion occupying the apex position is 2.654 Å. A plane, in which the weights of the atoms were based on their atomic number, was least-squares fitted to the two chloride and two oxygen atoms of the base. The copper ion is 0.23 Å out of the plane in the direction of the apex. The bond from the copper ion to the apex chloride ion makes an angle of 87.6° with the basal plane.

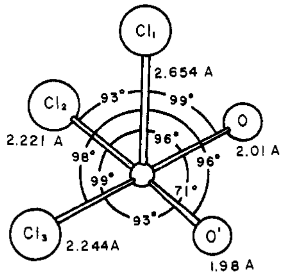

Figure 3.—Coordination about the pentacoordinated copper ion (Cu_2).

The oxygen-bridged portion of the molecule is similar to the structure of di-μ-(pyridine N-oxide)-bis(dichlorocopper(II)).[14,15] The two copper ions and the two oxygen atoms define a plane since they lie about a center of symmetry. The Cu–O–Cu angle is 109° and the O–Cu–O angle is 71°, compared with 108 and 72° for the

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(14) R. S. Sager, R. J. Williams, and W. H. Watson, *Inorg. Chem.*, **6**, 951 (1967).

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corresponding angles in the pyridine N-oxide complex. The two oxygen atoms are within 2.32 Å of each other, somewhat shorter than the O–O distance of 2.37 Å in the pyridine N-oxide complex. Since chloride ions are much larger than oxygen atoms, chlorine–chlorine and chlorine–oxygen repulsions should cause a significant decrease in the O–Cu–O angle in a pseudo-planar structure. The Cu–O distances of 2.01 and 1.98 Å in $Cu_3Cl_6(C_6H_7NO)_2 \cdot 2H_2O$ are similar to the values of 2.04 and 1.98 Å found in the pyridine N-oxide complex and 1.97 and 1.93 Å found in the yellow form of dichlorobis-(2,6-lutidine N-oxide)copper(II).[16]

The N–O bond distance is 1.36 Å and the bond lies 1.9° out of the plane of the 2-picoline ring. The long N–O distance is consistent with loss of double-bond character owing to complex formation. In the pyridine N-oxide complex, the N–O bond lies 8.4° from the plane defined by the copper and oxygen atoms, whereas in the 2-picoline N-oxide complex the N–O bond makes an angle of 13.5° with the copper–oxygen plane. The angle of the 2-picoline ring relative to the copper–oxygen plane is 88.8° while the pyridine ring made an angle of 70.0° relative to the copper–oxygen plane. The 2-picoline ring is planar, and a least-squares fit with the atoms weighted relative to their atomic number showed the largest deviation from the plane to be 0.010 Å. This is smaller than the estimated standard deviations of the ring carbon atoms. The average C–N bond length is 1.37 Å and the average C–C distance is 1.38 Å. The bond distances around the ring are too inaccurate for individual distances to be discussed. If one considers the carbon–carbon bonds to be chemically equivalent, it appears that the estimated standard deviations in some cases are optimistic by a factor of about 2.

The observed magnetic susceptibility data can be interpreted in terms of the structure. The structure can be thought of as consisting of alternating $Cu_2Cl_4(C_6H_7NO)_2$ units and $CuCl_2 \cdot 2H_2O$ units joined by long (2.955 and 2.654 Å) Cu–Cl bonds. The copper ions in the $Cu_2Cl_4(C_6H_7NO)_2$ units interact antiferromagnetically through the bridging oxygens. The copper ions of the $CuCl_2 \cdot 2H_2O$ units do not interact through the chloride bridges with the five-coordinated copper ions and therefore show normal magnetic behavior. Thus the entire complex has an experimental magnetic moment slightly greater than that expected for an isolated copper ion.[1,5] The moment varies only slightly as the temperature is lowered from room temperature to 77°K. Since $CuCl_2 \cdot 2H_2O$ undergoes an antiferromagnetic transition at 4.3°K, it should be interesting to investigate the magnetic susceptibility of $Cu_3Cl_6(C_6H_7NO)_2 \cdot 2H_2O$ below liquid nitrogen temperatures.

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[16] R. S. Sager and W. H. Watson, submitted for publication.

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Synthesis and Magnetic Resonance Studies of Some Paramagnetic Transition Metal Aminotroponiminates

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The synthesis and proton magnetic resonance spectra of a number of aminotroponimine chelates of the first-row transition metals—V, Cr, Mn, Fe, and Co—are reported. The majority of these complexes are paramagnetic and show large Fermi contact shifts in their nmr spectra. The interpretation of these shifts in terms of metal-to-ligand and ligand-to-metal charge transfer is considered.

Introduction

The observation and interpretation of the very large chemical shifts associated with protons on the ligands of paramagnetic transition metal complexes has proved to be a fruitful source of information regarding the electronic nature of metal–ligand bonding. In cases where the large chemical shifts can be ascribed to Fermi contact interaction between unpaired electron spin and nuclear spin of the proton, the results can be interpreted in terms of electron spin density distributions. This is a concept made familiar by electron spin resonance studies of aromatic radicals. The important point for the present purpose is that the spin density distribution corresponding to a given molecular orbital can be easily calculated, at least to a qualitatively reliable approximation, and comparison of such calculations with experimental results hopefully will allow identification of the spin-containing ligand molecular orbital. Using this information, deductions can then be made regarding metal–ligand orbital interactions and bonding.