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The Preparation and Properties of μ_4-Oxo-hexa-μ-chloro-tetrakis[(2-methylpyridine)copper(II)] Hydrate, $Cu_4OCl_6(2\text{-mepy})_4 \cdot xH_2O$, and Di-$\mu$-methoxo-bis[chloro(2-methylpyridine)copper(II)], $[CuCl(OCH_3)(2\text{-mepy})]_2$, and X-Ray Structure Analysis of $Cu_4OCl_6(2\text{-mepy})_4 \cdot xH_2O$

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The preparation of $Cu_4OCl_6(2\text{-mepy})_4 \cdot xH_2O$ and $[CuCl(OCH_3)(2\text{-mepy})]_2$ by the reaction of copper(II) chloride with 2-methylpyridine in methanol and the conversion of the first compound into the second in solution have been studied. The infrared and electronic spectra and the magnetic moments of both compounds and the molecular structure of $Cu_4OCl_6(2\text{-mepy})_4$ have been determined. $Cu_4OCl_6(2\text{-mepy})_4 \cdot xH_2O$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 12.73 \pm 0.02$, $b = 12.07 \pm 0.02$, $c = 21.54 \pm 0.03$ Å, $\beta = 90.7 \pm 0.2°$; $Z = 4$. Positions of all atoms except hydrogen in the $Cu_4OCl_6(2\text{-mepy})_4$ molecule were determined and the structure was refined to an R factor of 0.082 for 1824 reflections measured from multiple-film Weissenberg photographs. The Cu_4OCl_6 cluster is more distorted than in other known structures of this type, possibly due to steric interference by the methyl groups of the 2-methylpyridine ligands. The water of crystallization indicated by chemical analysis and the infrared spectrum was not revealed by the X-ray analysis and must therefore be assumed to be in a disordered state. It has been shown that the oxygen atom in the cluster is derived from water.

The deep blue compound dichlorobis(2-methylpyridine)copper(II), $Cu(2\text{-mepy})_2Cl_2$, is well known[1] and its structure has been determined.[2] McWhinnie[1b] reported that, when copper(II) chloride dihydrate reacts with 2-methylpyridine in methanol or ethanol, a mixture of $Cu(2\text{-mepy})_2Cl_2$ and a green solid was formed and he formulated the latter as $Cu(2\text{-mepy})Cl_2$. We have now studied this compound and determined its structure.

Experimental Section

Analytical reagent grade methanol was used in all preparations. Magnetic measurements were carried out by the Gouy method using $HgCo(NCS)_4$ for calibration. Infrared spectra were obtained using Grubb Parsons GS4 and DM4 spectrometers and Nujol and hexachlorobutadiene mulls. Electronic spectra were measured on a Unicam SP 500 spectrometer with reflectance attachment.

Carbon, hydrogen, and nitrogen analyses were performed by the Australian Microanalysis Service, Melbourne, Australia.

$Cu_4OCl_6(2\text{-mepy})_4 \cdot H_2O$.—2-Methylpyridine (0.72 g) in methanol (5 ml) was added to a solution of copper(II) chloride dihydrate (0.85 g) in methanol (30 ml). Dark olive green leaflets formed immediately and the mixture was allowed to stand for 2 hr. The crystals were filtered off and washed with methanol; yield 0.8 g. *Anal.* Calcd for $C_{24}H_{30}Cl_6Cu_4N_4O_2$: C, 33.0; H, 3.5; Cl, 24.4; Cu, 29.1; N, 6.4. Found: C, 32.9; H, 3.5; Cl, 24.7; Cu, 29.2; N, 6.1. The magnetic moment was 1.90 BM at 24°.

$[CuCl(OCH_3)(2\text{-mepy})]_2$.—$Cu_4OCl_6(2\text{-mepy})_4 \cdot H_2O$ (0.5 g) was dissolved in boiling methanol (75 ml) containing 2-methylpyridine (0.75 ml). On cooling, green needles slowly crystallized and after some hours were filtered off. Care was taken to draw air through the crystals for only a short time as decomposition readily occurred on the surface; yield 0.33 g. *Anal.* Calcd for $C_{14}H_{20}Cl_2Cu_2N_2O_2$: C, 37.7; H, 4.5; Cl, 15.9; Cu, 28.5; N, 6.3. Found: C, 36.8; H, 4.5; Cl, 16.2; Cu, 28.4; N, 6.3. The magnetic moment was 0.62 BM at 30°.

Reaction of $CuCl_2$ with 2-Methylpyridine under Anhydrous Conditions.—The reaction described above for the preparation of $Cu_4OCl_6(2\text{-mepy})_4 \cdot H_2O$ was carried out under anhydrous conditions by the use of a vacuum system. Copper(II) chloride dihydrate was dehydrated by heating at 110°, 2-methylpyridine was dried over calcium hydride, and methanol was dried by reaction with magnesium. A green solution was formed on mixing the methanol solutions and within 1 hr crystals of $[CuCl(OCH_3)(2\text{-mepy})]_2$ commenced to form slowly. After standing overnight the sealed reaction tube was opened and the crystals were filtered off (0.2 g from 0.92 g of $CuCl_2 \cdot 2H_2O$).

Reaction of $CuCl_2 \cdot 2H_2O$ with 2-Methylpyridine in the Absence of Oxygen.—Dissolved oxygen was removed from the reagents used in the above preparation of $Cu_4OCl_6(2\text{-mepy})_4 \cdot H_2O$ by degassing the methanol solutions in a vacuum system. On mixing the solutions $Cu_4OCl_6(2\text{-mepy})_4 \cdot H_2O$ was formed in the same yield.

X-Ray Data.—Crystals of $Cu_4OCl_6(2\text{-mepy})_4 \cdot H_2O$ (or $Cu_4OCl_6(2\text{-mepy})_4$) belong to the monoclinic system and form as very thin leaflets with {100} as the main faces. The unit cell dimensions, measured from Weissenberg photographs with superimposed powder lines of silicon ($a = 5.4305$ Å), are $a = 12.73 \pm 0.02$, $b = 12.07 \pm 0.02$, $c = 21.54 \pm 0.03$ Å, $\beta = 90.7 \pm 0.2°$, $V = 3309$ Å^3. The systematic absences were $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$, corresponding to space group $P2_1/c$ (no. 14). Density measurements, by flotation in mixtures of n-propyl iodide and carbon tetrachloride, gave a value of $d_m = 1.73 \pm 0.01$ g cm^{-3} compared to calculated values $d_x = 1.75$ g cm^{-3} for four molecules of $Cu_4OCl_6(2\text{-mepy})_4 \cdot H_2O$ per unit cell and $D_x = 1.72$ g cm^{-3} for $Cu_4OCl_6(2\text{-mepy})_4$. The crystal used for intensity measurements was a rectangular fragment measuring approximately 0.04 mm in the a direction and 0.06 mm in the c direction, cut from a hexagonal platelet and mounted along its long dimension (*ca.* 0.2 mm) which corresponded to the b direction. Data for seven layers hKl (K = 0–6) were collected from multiple-film equiinclination Weissenberg photographs recorded with Cu Kα radiation. Intensities were estimated visually against a scale of timed exposures of a reflection from the same crystal, averaging over equivalent reflections and correcting empirically for spot shape on upper layer photographs (by estimating the spot area with the aid of a graduated eyepiece). The intensities were corrected for Lorentz and polarization effects but no absorption correction was made. The linear absorption coefficient for Cu Kα radiation is 76.8 cm^{-1} and the maximum and minimum transmission coefficients were estimated to be

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[1] (a) D. P. Graddon, R. A. Schulz, E. C. Watton, and D. G. Weedon, *Nature*, **198**, 2699 (1963); (b) W. R. McWhinnie, *J. Chem. Soc.*, 2959 (1964); (c) C. M. Goldstein, E. F. Mooney, A. Anderson, and H. A. Gebbie, *Spectrochim. Acta*, **21**, 105 (1965).

[2] V. F. Duckworth, D. P. Graddon, N. C. Stephenson, and E. C. Watton, *Inorg. Nucl. Chem. Lett.*, **3**, 557 (1967).

approximately 0.77 and 0.65. The F_o values of the various layers were brought to a common scale by reference to *hk*0 data from another crystal (of approximate dimensions 0.04 × 0.05 × 0.1 mm). Approximate values of an overall temperature factor ($B = 3.0$) and a scale factor for placing the data on an absolute scale were derived from a Wilson plot. The intensity data were not very extensive, probably because of the small size and flaky habit of the crystals, and the 1950 independent observed reflections represent only 50–55% of the possible total in the recorded layers. Attempts to grow larger crystals produced polycrystalline specimens.

Determination and Refinement of the Structure.—The analysis was initiated on the basis of the empirical formula $Cu_2Cl_3ON_2C_{12}H_{15}$, assuming two dimeric molecules Cu_2Cl_3OH(2-mepy)$_2$ in the asymmetric unit. A three-dimensional Patterson synthesis was calculated, with the F_o^2 values modified by a factor exp ($2B \sin^2 \theta/\lambda^2$), and from its Harker section $P(u, {}^1/_2, w)$ and Harker line $P(0, v, {}^1/_2)$, the positions of four heavy atoms situated at the corners of a nearly regular tetrahedron with interatomic distances of the order of 3 Å were deduced. Assuming these to be copper atoms, it was apparent that the molecule must be tetrameric rather than dimeric as originally expected. An electron density distribution, based on the contributions of the four copper atoms, showed the positions of the six chlorine atoms in a rather distorted octahedral arrangement approximately concentric with the tetrahedron of copper atoms. Successive Fourier and difference syntheses with a progressively increasing number of contributing light atoms revealed the nitrogen and carbon atoms of the 2-methylpyridine rings but no peaks could be detected in any reasonable positions for the two expected hydroxide oxygen atoms. However, difference maps consistently showed a peak (*ca.* 5 e$^-$ Å^{-3}) at the center of the Cu_4 tetrahedron, somewhat higher than the nitrogen peaks (*ca.* 4 e$^-$ Å^{-3}). This peak was therefore assumed to be due to oxygen, revealing a central unit Cu_4OCl_6, similar to those in $Cu_4OCl_6((C_6H_5)_3PO)_4$[3] and $Cu_4OCl_6(py)_4$.[4] The infrared data and to some extent also the results of the chemical analysis seemed to require a molecular composition Cu_4OCl_6(2-mepy)$_4 \cdot H_2O$, but, although peaks due to all 24 carbon atoms showed up quite clearly, there was no indication of a second oxygen peak (hydrate oxygen) in either the Fourier or difference distributions. The analysis was therefore continued assuming Cu_4OCl_6(2-mepy)$_4$ as the contents of the asymmetric unit, the reliability index $R = (\Sigma|F_o - |F_c||)/\Sigma F_o$, calculated with the coordinates of the 39 atoms in the unit, being 0.19 at this stage.

The structure was then refined by full-matrix least-squares calculations, minimizing the function $\Sigma w(kF_o - |F_c|)^2$. Initially unit weighting was used, reflections with $|F_c| < 0.5kF_o$ and with $|F_o - |F_c|/k| > 20$ being given zero weights. The atomic scattering factors used were those given for neutral atoms in "International Tables for X-Ray Crystallography," 1962, with the real part of the anomalous dispersion correction (−2.1 e$^-$) applied to the copper scattering curve. Two cycles, in which the positional and isotropic thermal parameters of all atoms and the overall scale factor were varied, reduced R to 0.13. Adjustment of interlayer scale factors to give $\Sigma F_o = \Sigma|F_c|$ and correction of some errors in the intensity data resulted in $R = 0.11$, and, in three further cycles, the isotropic refinement converged to $R = 0.10$ for 1824 measured reflections. Finally, two refinement cycles were calculated in which the overall scale factor, coordinates of all atoms, and anisotropic thermal parameters for the copper, chlorine, oxygen, and nitrogen atoms were varied, with the isotropic temperature factors of the carbon atoms held constant at the values obtained in the last isotropic cycle. The resulting R value was 0.082 with all parameter shifts in the last cycle less than half the corresponding standard deviations. The final refinement cycles (one isotropic, two anisotropic) were calculated using a weighting factor $1/F_o^2$, with a maximum value of $1/(2.25F_{min})^2$, F_{min} being the average minimum observable structure factor. Parallel calculations using unit weighting with the rejection routine described above gave an identical value of R and no significant differences in the final positional and thermal parameters.

Because of the relatively high standard deviations of the coordinates of the carbon atoms (*ca.* 0.04 Å), it was considered that anisotropic refinement of the carbon thermal parameters would have little physical meaning. For the same reason, no serious attempts were made to locate the hydrogen atoms. A difference map, calculated after the final least-squares cycle, showed no peaks higher than 0.8 e$^-$ Å^{-3} compared to 2–3 e$^-$ Å^{-3} for carbon atoms in the initial difference syntheses, most of the higher positive regions corresponding to possible hydrogen atom sites.

The final positional parameters, together with the isotropic temperature factors of the carbon atoms, are given in Table I and the anisotropic thermal parameters of the copper, chlorine, oxygen, and nitrogen atoms in Table II. Table III lists the observed and final calculated structure factors.

TABLE I

FINAL POSITIONAL PARAMETERS FOR ALL ATOMS AND ISOTROPIC TEMPERATURE PARAMETERS FOR CARBON ATOMS FOR Cu_4OCl_6(2-mepy)$_4$[a]

Atom	x	y	z	B, Å^2
Cu(1)	0.2125 (2)	0.2519 (3)	0.2223 (1)	
Cu(2)	0.1818 (2)	0.2322 (3)	0.0804 (1)	
Cu(3)	0.4025 (2)	0.2082 (3)	0.1410 (1)	
Cu(4)	0.2474 (2)	0.0208 (4)	0.1622 (1)	
Cl(1)	0.3489 (5)	0.3734 (6)	0.1994 (3)	
Cl(2)	0.0573 (4)	0.3064 (6)	0.1455 (2)	
Cl(3)	0.3518 (4)	0.2389 (6)	0.0342 (2)	
Cl(4)	0.1557 (4)	0.0131 (6)	0.0678 (2)	
Cl(5)	0.4245 (4)	0.0504 (6)	0.2043 (3)	
Cl(6)	0.1407 (4)	0.0866 (5)	0.2571 (2)	
O	0.2587 (9)	0.1729 (14)	0.1504 (5)	
N(1)	0.1739 (12)	0.3420 (15)	0.2973 (6)	
N(2)	0.1055 (12)	0.2888 (16)	0.0078 (7)	
N(3)	0.4448 (13)	0.7423 (17)	0.3726 (8)	
N(4)	0.2423 (12)	0.8597 (18)	0.1788 (7)	
C(1)	0.3172 (18)	0.2427 (23)	0.3516 (10)	6.4 (7)
C(2)	0.2344 (16)	0.3318 (20)	0.3514 (9)	4.8 (6)
C(3)	0.2088 (16)	0.3965 (20)	0.4020 (9)	4.6 (6)
C(4)	0.1305 (17)	0.4730 (22)	0.3977 (10)	5.6 (6)
C(5)	0.0728 (16)	0.4906 (20)	0.3395 (9)	4.7 (5)
C(6)	0.1001 (17)	0.4172 (21)	0.2907 (9)	4.6 (5)
C(7)	0.2013 (21)	0.4699 (25)	0.0177 (12)	7.8 (8)
C(8)	0.1223 (16)	0.1109 (26)	0.4868 (10)	4.8 (6)
C(9)	0.0664 (19)	0.0668 (23)	0.4335 (11)	6.5 (7)
C(10)	0.0060 (19)	0.6359 (26)	0.0929 (12)	6.9 (7)
C(11)	0.0322 (17)	0.7377 (24)	0.0689 (10)	6.1 (6)
C(12)	0.0317 (15)	0.2753 (20)	0.4819 (9)	4.2 (5)
C(13)	0.4315 (18)	0.5738 (23)	0.4361 (10)	6.1 (7)
C(14)	0.3851 (16)	0.6784 (22)	0.4075 (10)	5.1 (7)
C(15)	0.2793 (16)	0.7110 (21)	0.4211 (10)	5.2 (6)
C(16)	0.2433 (19)	0.8046 (25)	0.3933 (11)	6.5 (7)
C(17)	0.3024 (18)	0.8687 (22)	0.3552 (11)	6.2 (7)
C(18)	0.4104 (18)	0.8356 (25)	0.3444 (10)	5.6 (6)
C(19)	0.3852 (20)	0.8306 (25)	0.1031 (12)	7.7 (7)
C(20)	0.3079 (20)	0.7855 (29)	0.1521 (12)	6.8 (7)
C(21)	0.3100 (21)	0.6753 (32)	0.1701 (13)	8.3 (8)
C(22)	0.2342 (22)	0.6392 (28)	0.2143 (13)	8.5 (8)
C(23)	0.1667 (18)	0.7153 (26)	0.2384 (11)	6.3 (7)
C(24)	0.1701 (18)	0.8262 (26)	0.2200 (11)	6.0 (7)

[a] Numbers in parentheses are estimated standard deviations in the last digit(s).

The following FORTRAN programs, modified for the IBM 360/50 computer, were used: MU-FR3 (White, 1966) for Patterson and Fourier syntheses; ORFLS (Busing, Martin, and Levy, 1962) for structure factor calculations and least-squares refinement; DISTAN (Shoemaker, 1963) for interatomic distances and angles.

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(3) J. A. Bertrand and J. A. Kelley, *J. Amer. Chem. Soc.*, **88**, 4746 (1966); J. A. Bertrand, *Inorg. Chem.*, **6**, 495 (1967).

(4) B. T. Kilbourn and J. D. Dunitz, *Inorg. Chim. Acta*, **1**, 209 (1967).

TABLE II

Anistropic Thermal Parameters (x10^4) for Copper, Chlorine, Oxygen and Nitrogen Atoms with Standard Deviations (x10^4) in Parentheses[a]

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}	Equivalent isotropic B
Cu(1)	65(2)	62(5)	18(1)	0(2)	0(1)	0(1)	3.8
Cu(2)	61(2)	61(5)	16(1)	1(2)	-2(1)	7(1)	3.5
Cu(3)	52(2)	69(5)	20(1)	-3(2)	-2(1)	2(1)	3.7
Cu(4)	68(2)	48(7)	21(1)	-1(2)	-5(1)	4(1)	3.7
Cl(1)	94(5)	79(9)	41(2)	-20(5)	10(2)	-17(3)	6.1
Cl(2)	73(4)	136(9)	20(1)	37(4)	2(2)	7(2)	5.5
Cl(3)	65(4)	123(9)	22(1)	-8(4)	1(2)	9(2)	5.1
Cl(4)	89(4)	83(9)	19(1)	-22(4)	-5(2)	5(2)	4.7
Cl(5)	70(4)	90(9)	35(2)	11(4)	-14(2)	14(3)	5.4
Cl(6)	96(4)	67(8)	19(1)	-4(4)	7(2)	5(2)	4.5
O	67(10)	59(23)	11(3)	13(10)	0(4)	-5(5)	3.3
N(1)	64(12)	96(23)	13(4)	9(12)	-5(5)	-6(6)	4.0
N(2)	74(13)	48(23)	24(4)	-32(12)	-5(6)	4(7)	4.0
N(3)	91(14)	55(25)	30(4)	-4(14)	-2(6)	10(8)	4.9
N(4)	79(13)	93(31)	16(4)	14(13)	-1(6)	0(8)	4.5

Root-Mean-Square Amplitudes of Vibration (Å)[b]

	Major axis	Median axis	Minor axis
Cu(1)	0.231 (0.998, 0.012,-0.056)	0.214 (-0.006, 0.994, 0.110)	0.207 (0.057,-0.110, 0.992)
Cu(2)	0.224 (0.975,-0.103,-0.197)	0.217 (0.181, 0.882, 0.435)	0.189 (0.129,-0.459, 0.879)
Cu(3)	0.227 (-0.192, 0.920, 0.341)	0.218 (-0.296,-0.386, 0.874)	0.204 (0.936, 0.067, 0.347)
Cu(4)	0.242 (0.901,-0.065,-0.428)	0.218 (0.432, 0.185, 0.883)	0.187 (-0.022, 0.981,-0.195)
Cl(1)	0.319 (0.316,-0.293, 0.902)	0.276 (0.916,-0.154,-0.371)	0.231 (0.248, 0.943, 0.219)
Cl(2)	0.325 (0.301, 0.950, 0.080)	0.236 (0.953,-0.297,-0.054)	0.215 (0.027,-0.093, 0.995)
Cl(3)	0.303 (-0.080, 0.986, 0.147)	0.231 (0.986, 0.057, 0.154)	0.223 (-0.144,-0.157, 0.977)
Cl(4)	0.281 (0.875,-0.460,-0.153)	0.238 (0.474, 0.877, 0.078)	0.210 (0.098,-0.140, 0.985)
Cl(5)	0.298 (-0.277, 0.321, 0.906)	0.259 (0.529, 0.838,-0.135)	0.224 (0.802,-0.442, 0.401)
Cl(6)	0.282 (0.992,-0.044, 0.121)	0.226 (-0.013, 0.898, 0.440)	0.205 (-0.128,-0.438, 0.890)
O	0.239 (0.930, 0.364,-0.043)	0.206 (-0.366, 0.914,-0.178)	0.159 (-0.026, 0.181, 0.983)
N(1)	0.268 (0.201, 0.974,-0.103)	0.228 (0.970,-0.213,-0.117)	0.171 (0.136, 0.076, 0.988)
N(2)	0.260 (0.850,-0.360,-0.385)	0.233 (0.364,-0.127, 0.923)	0.174 (0.381, 0.924,-0.023)
N(3)	0.275 (0.865,-0.123,-0.487)	0.266 (0.501, 0.157, 0.851)	0.198 (0.029, 0.980,-0.197)
N(4)	0.269 (0.568, 0.823,-0.021)	0.247 (0.822,-0.568,-0.027)	0.191 (0.034, 0.002, 0.999)

[a] The anisotropic temperature factors are defined by $T = \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{13}kl)]$. [b] Direction cosines of the principal axes relative to the crystallographic axes a, b, c, repectively, are given in parentheses.

Results and Discussion

Preparations, Properties, and Infrared Spectra.—Using methanol as solvent the reaction of copper(II) chloride dihydrate with 2-methylpyridine in the molar ratio 1:1.5–1:2 yields only dark olive green leaflets of μ_4-oxo-hexa-μ-chloro-tetrakis[(2-methylpyridine)copper(II)] hydrate, $Cu_4OCl_6(2\text{-mepy})_4 \cdot H_2O$ (I). The empirical formula of this compound was deduced from analytical data and the presence of water was indicated by the infrared spectrum, Table IV, which has a set of absorption bands in the region 3350–3550 cm^{-1}. The intensity of these bands is of the same order as that of the C–H stretching frequencies in the region of 3300 cm^{-1} and they can only be attributed to water in the crystal lattice. The X-ray structure analysis of I established a molecular structure similar to that of $Cu_4OCl_6(TPPO)_4$[3] (TPPO = triphenylphosphine oxide) and $Cu_4OCl_6(py)_4$[4] but did not reveal the presence of water molecules. Therefore we can only conclude that the water is in a disordered state and it is possible that there is less than one molecule per molecule of the complex. There is no indication that water is bonded to any of the four copper atoms in the molecule.

Compound I can be recrystallized from methanol containing a small amount of 2-methylpyridine, but as this is increased, the color of the solution changes from olive green to green and a second green compound crystallizes as needles. This compound, which is somewhat unstable, surface decomposition occurring readily, was found to be di-μ-methoxo-bis[chloro(2-methylpyridine)copper(II)], $[CuCl(OCH_3)(2\text{-mepy})]_2$ (II), from analytical data, the infrared spectrum, and an X-ray structure determination. The structure consists of centrosymmetric dimeric units $[CuCl(OCH_3)(2\text{-mepy})]_2$ with methoxy groups bridging the copper atoms and these units form infinite chains through long Cu–Cl bonds (2.94 ± 0.004 Å compared to 2.27 ± 0.004 Å within the units). Thus the compound would be more accurately formulated as $[Cu_2Cl_2(OCH_3)_2(2\text{-mepy})_2]_n$ and each copper atom has distorted tetragonal-pyramidal coordination consisting of one chlorine, one nitrogen, and two oxygen atoms in a distorted plane with a second chlorine atom of another dimeric unit completing the pyramidal arrangement. The structure, determined from 847 photographically recorded reflections and refined to $R = 0.073$, will be described fully in a later paper.

The infrared spectrum of II, Table IV, shows no absorption bands in the region of 3500 cm^{-1}, while there is a very strong band at 1055 cm^{-1} that is not present in the spectrum of I and is attributed to the C–O stretching mode of the methoxy group. This strong absorption band obscures the CH_3 rocking mode of the 2-mepy ligand, which is also obscured in the spectrum of I by the bands due to ν_{18a} and ν_1, although it is well-defined at 1043 cm^{-1} in the spectrum of $Cu(2\text{-mepy})_2Cl_2$.[1c] Possible assignments are given for all bands in the spectra of I and II but from these limited data bands in the region of 230–350 cm^{-1} are not assigned specifically to Cu–Cl or Cu–N vibrations. At about 550 cm^{-1} a strong band is observed in the spectrum of II and a set of medium to strong bands in that of I compared to only a weak band due to ν_{6a} of the 2-methylpyridine ligand in the spectra of complexes such as $Cu(2\text{-mepy})_2Cl_2$ and tetrahedral $M(2\text{-mepy})_2X_2$.[5] This difference is attributed to a copper–oxygen stretching mode also occurring in this region. Other bands due to such a vibration would also be expected but have not been identified.

Magnetism.—Compound I has a magnetic moment of 1.90 BM at room temperature, somewhat lower than those reported for the TPPO complex,[3] $Cu_4OCl_{10}^{4-}$,[3] and $Cu_4OBr_6(py)_4$,[6] it being assumed that the last two compounds have the same type of structure.[7] In contrast, the moment of II is low, 0.6 BM, and interaction between the copper atoms leading to coupling of spins must take place through orbitals of the bridging oxygen

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[5] N. S. Gill and H. J. Kingdon, *Aust. J. Chem.*, **19**, 2197 (1966).

[6] C. M. Harris and E. Sinn, *Inorg. Nucl. Chem. Lett.*, **5**, 125 (1969).

[7] After this paper had been submitted for publication, the structure of $[(CH_3)_4N]_4[Cu_4OCl_{10}]$ was published by J. A. Bertrand and J. A. Kelley, *Inorg. Chem.*, **8**, 1982 (1969), confirming this assumption. It has also been reported (P. W. Ball, *Coord. Chem. Rev.*, **4**, 361 (1969)) that the magnetic moment of the TPPO complex is 1.87 BM rather than 2.2 BM.[3]

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS [$F(000)$ = 1704]

K = 0

h	l	F_o	$\|F_c\|$
1	0	73	95
2	0	301	325
3	0	109	103
4	0	78	85
5	0	219	226
6	0	70	69
7	0	25	14
10	0	27	24
12	0	25	37
0	2	185	194
0	4	158	153
0	6	30	27
0	8	23	26
0	10	103	92
0	12	76	73
0	14	167	165
0	16	90	95
0	18	48	47
1	2	263	237
1	4	265	250
1	6	329	312
1	8	28	28
1	10	29	30
1	12	237	219
1	14	63	57
1	16	33	33
1	22	32	34
-1	2	369	367
-1	4	34	28
-1	6	42	48
-1	8	43	38
-1	14	101	97
-1	16	52	51
-1	22	61	59
2	2	195	191
2	4	183	187
2	6	57	50
2	8	147	142
2	10	142	130
2	14	72	66
2	16	65	64
2	18	79	83
2	22	24	37

h	l	F_o	$\|F_c\|$
0	6	19	21
0	7	44	35
0	8	22	15
0	9	111	[illegible]
0	10	63	57
0	11	29	21
0	12	114	112
0	13	39	40
0	14	39	38
0	16	81	95
0	19	29	35
0	20	28	42
0	21	27	40
0	22	27	28
1	0	305	331
1	1	144	162
1	2	133	143
1	3	35	42
1	4	71	71
1	5	51	40
1	6	51	52
1	7	52	51
1	8	23	18
1	9	83	80
1	10	91	82
1	11	155	152
1	12	21	20
1	13	31	28
1	14	119	123
1	16	64	70
1	18	27	35
1	23	22	25
-1	1	79	55
-1	2	83	90
-1	3	24	15
-1	4	55	54
-1	5	45	47
-1	6	47	40
-1	7	30	21
-1	8	43	34
-1	9	17	19
-1	10	45	34
-1	11	115	102
-1	14	62	63
-1	16	49	45
-1	18	47	45

TABLE IV

INFRARED SPECTRA (CM^{-1})

Assignment[a]	2-methylpyridine (liquid)	$Cu_4OCl_6(2\text{-mepy})_4 \cdot xH_2O$	$[CuCl(OCH_3)(2\text{-mepy})]_2$
O-H str		3562, 3451, 3355	
2[b]	3083	3106	3106
7,20a	3062, 3049	3077	3076
20b	3014	3043	3030
CH_3 antisym str	2960	2984	2986, 2948
CH_3 sym str	2927	2932	2913, 2871
CH_3 str (OCH_3)			2799
8a	1592	1613	1610, 1589
8b	1572	1571	1571
19a	1477	1486	1492
19b	1449	1452	1457
CH_3 antisym def	1433	1431	1432
14	1376	1387	1379
CH_3 sym def			1361
3	1291	1302	1308
13	1238	1239	1240
9a	1151	1158	1160, 1152
18b	1103	1111	1110
18a	1050	1063	1063
CH_3 rock (OCH_3)			1055
CH_3 rock	1042		-
1	998	1034, 1031	1030
12	800	803	803
10	754	781, 769, 765	760, 757
4	732	732	724
6b	629	656	653
6a	547	591, 573	
Cu-O str		564, 552	sh, 539[c], sh
11	470	478	476
16a	402	442, 432	431
15	357	396	393
Cu-ligand str		266, 248	356, 271, 233

[a] Assignment of bands of 2-methylpyridine follows that of Goldstein, *et al.*[10] [b] x of ν_x of 2-methylpyridine. [c] Very broad band with two shoulders.

atoms of the methoxy groups since the Cu–Cu distance in the dimeric unit is large, 3.02 Å.

Electronic Spectra.—Reflectance spectra determined in the range 10,000–20,300 cm^{-1} showed one absorption band for each compound. This band, which is attributed to d–d transitions, lies in the near-infrared region, is very broad, and extends well into the visible region. The maxima are at 13,600 cm^{-1} for I and 14,300 cm^{-1} for II. Another band, most likely due to a charge-transfer transition, occurs well into the ultraviolet region, and in the case of I a shoulder on this band is observed at 23,300 cm^{-1}, while in the case of II a small maximum is observed at 26,300 cm^{-1}. Comparison with the reflectance spectrum of $Cu_4OCl_6(TPPO)_4$[3] shows that the d–d band of I is at a higher energy than those of the former as would be expected when a ligand is changed from an oxygen-bonded to a nitrogen-bonded one.

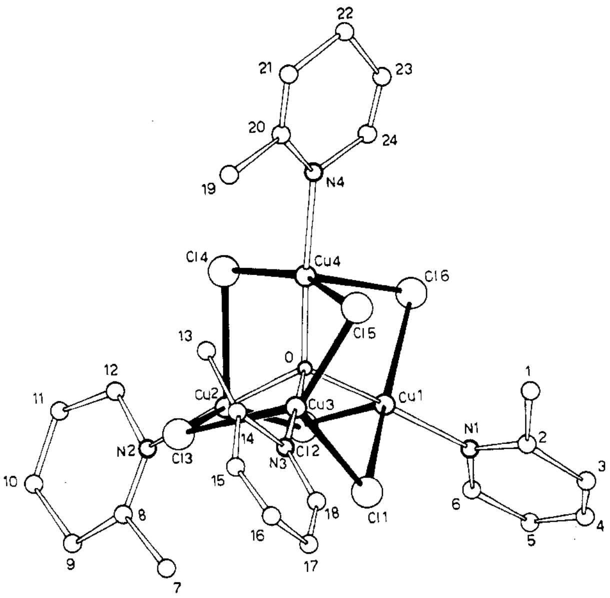

Figure 1.—Perspective drawing of the $Cu_4OCl_6(2\text{-mepy})_4$ molecule. The carbon atoms are designated by their numbers.

Structure of $Cu_4OCl_4(2\text{-mepy})_4$.—The structure of the tetrameric molecule is shown in Figure 1 and the packing of molecules in the unit cell in Figure 2. The central unit Cu_4OCl_6 is of the same type as those in

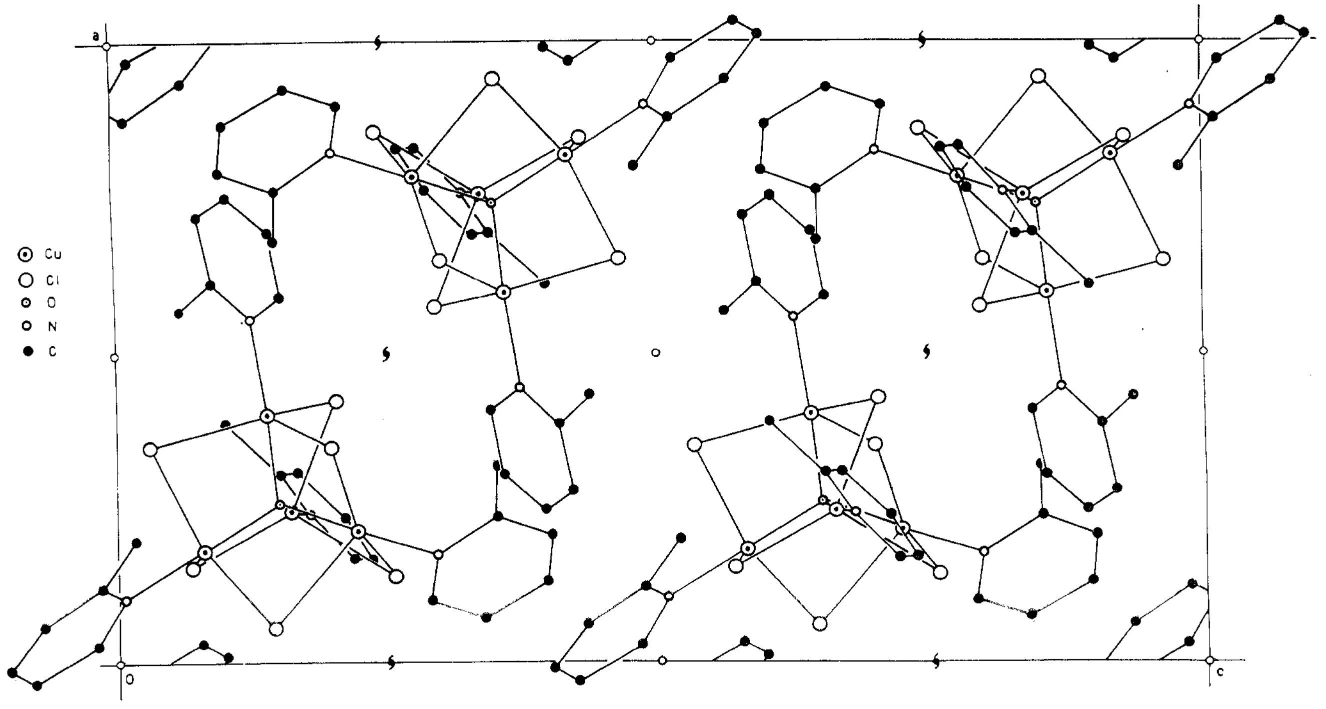

Figure 2.—Contents of the unit cell projected on the *ac* plane.

$Cu_4OCl_6(TPPO)_4$[3] and in $Cu_4OCl_6(py)_4$,[4] with the copper atoms disposed tetrahedrally around a central oxygen atom and bridged in pairs by chlorine atoms. In the TPPO complex,[3] the Cu_4OCl_6 cluster has exact $\bar{4}3m$ symmetry, the chlorine atoms forming an octahedron concentric with the Cu_4 tetrahedron, with the Cu–O bonds along the threefold axes and each copper atom coordinated to three chlorine atoms at distances of 2.38 Å, the central oxygen atom and the oxygen atom of the triphenylphosphine oxide at the vertices of a trigonal bipyramid. In the structure of $Cu_4OCl_6(py)_4$[4] the central unit is somewhat distorted and the distortion is still more pronounced in the present structure of $Cu_4OCl_6(2\text{-mepy})_4$ as might be expected considering the lower symmetry of the 2-methylpyridine ligand. Interatomic distances and angles for the central unit of $Cu_4OCl_6(2\text{-mepy})_4$ are listed in Tables V and VI.

TABLE V

INTERATOMIC DISTANCES IN THE $Cu_4OCl_6N_4$ CLUSTER (Å)[a]

Cu(1)–Cl(1)	2.329 (8)	Cu(1)–Cu(4)	3.109 (5)
Cu(1)–Cl(2)	2.644 (8)	Cu(2)–Cu(3)	3.096 (5)
Cu(1)–Cl(6)	2.324 (8)	Cu(2)–Cu(4)	3.206 (6)
Cu(2)–Cl(2)	2.310 (8)	Cu(3)–Cu(4)	3.041 (6)
Cu(2)–Cl(3)	2.394 (8)	O–Cl(1)	2.87 (2)
Cu(2)–Cl(4)	2.679 (8)	O–Cl(2)	3.03 (2)
Cu(3)–Cl(1)	2.458 (8)	O–Cl(3)	2.90 (2)
Cu(3)–Cl(3)	2.411 (8)	O–Cl(4)	2.92 (2)
Cu(3)–Cl(5)	2.357 (8)	O–Cl(5)	2.81 (2)
Cu(4)–Cl(4)	2.335 (8)	O–Cl(6)	2.95 (2)
Cu(4)–Cl(5)	2.445 (8)	Cl(1)–Cl(2)	3.96 (1)
Cu(4)–Cl(6)	2.593 (8)	Cl(1)–Cl(3)	3.91 (1)
Cu(1)–O	1.92 (2)	Cl(1)–Cl(5)	4.02 (1)
Cu(2)–O	1.93 (2)	Cl(1)–Cl(6)	4.54 (1)
Cu(3)–O	1.89 (2)	Cl(2)–Cl(3)	4.55 (1)
Cu(4)–O	1.86 (2)	Cl(2)–Cl(4)	4.12 (1)
Cu(1)–N(1)	2.01 (2)	Cl(2)–Cl(6)	3.73 (1)
Cu(2)–N(2)	1.96 (2)	Cl(3)–Cl(4)	3.77 (1)
Cu(3)–N(3)	2.01 (2)	Cl(3)–Cl(5)	4.40 (1)
Cu(4)–N(4)	1.98 (2)	Cl(4)–Cl(5)	4.51 (1)
Cu(1)–Cu(2)	3.085 (5)	Cl(4)–Cl(6)	4.18 (1)
Cu(1)–Cu(3)	3.048 (5)	Cl(5)–Cl(6)	3.83 (1)

[a] Numbers in parentheses in Tables V and VI are standard deviations in the last significant digit, calculated from standard deviations of the atomic coordinates.

TABLE VI

BOND ANGLES IN THE $Cu_4OCl_6N_4$ CLUSTER (DEG)

Cl(1)–Cu(1)–Cl(2)	105.3 (4)	N(1)–Cu(1)–Cl(6)	95.9 (7)
Cl(1)–Cu(1)–Cl(6)	155.0 (4)	N(2)–Cu(2)–Cl(2)	90.7 (7)
Cl(2)–Cu(1)–Cl(6)	97.0 (4)	N(2)–Cu(2)–Cl(3)	95.6 (7)
Cl(2)–Cu(2)–Cl(3)	150.4 (4)	N(2)–Cu(2)–Cl(4)	101.8 (7)
Cl(2)–Cu(2)–Cl(4)	111.0 (4)	N(3)–Cu(3)–Cl(1)	100.6 (7)
Cl(3)–Cu(2)–Cl(4)	95.9 (4)	N(3)–Cu(3)–Cl(3)	94.5 (7)
Cl(1)–Cu(3)–Cl(3)	106.9 (4)	N(3)–Cu(3)–Cl(5)	98.1 (7)
Cl(1)–Cu(3)–Cl(5)	113.0 (4)	N(4)–Cu(4)–Cl(4)	95.8 (7)
Cl(3)–Cu(3)–Cl(5)	134.8 (4)	N(4)–Cu(4)–Cl(5)	96.3 (7)
Cl(4)–Cu(4)–Cl(5)	141.0 (4)	N(4)–Cu(4)–Cl(6)	98.0 (7)
Cl(4)–Cu(4)–Cl(6)	116.0 (4)	O–Cu(1)–N(1)	175.7 (9)
Cl(5)–Cu(4)–Cl(6)	98.8 (4)	O–Cu(2)–N(2)	178.3 (9)
O–Cu(1)–Cl(1)	84.4 (6)	O–Cu(3)–N(3)	177.5 (9)
O–Cu(1)–Cl(2)	81.6 (6)	O–Cu(4)–N(4)	176.4 (9)
O–Cu(1)–Cl(6)	87.6 (6)	Cu(1)–O–Cu(2)	106.8 (8)
O–Cu(2)–Cl(2)	90.8 (6)	Cu(1)–O–Cu(3)	106.3 (8)
O–Cu(2)–Cl(3)	83.4 (6)	Cu(1)–O–Cu(4)	110.9 (8)
O–Cu(2)–Cl(4)	76.9 (6)	Cu(2)–O–Cu(3)	108.4 (8)
O–Cu(3)–Cl(1)	81.6 (6)	Cu(2)–O–Cu(4)	115.8 (8)
O–Cu(3)–Cl(3)	83.6 (6)	Cu(3)–O–Cu(4)	108.3 (8)
O–Cu(3)–Cl(5)	82.2 (6)	Cu(1)–Cl(1)–Cu(3)	79.0 (3)
O–Cu(4)–Cl(4)	87.7 (6)	Cu(1)–Cl(2)–Cu(2)	76.7 (3)
O–Cu(4)–Cl(5)	80.4 (6)	Cu(2)–Cl(3)–Cu(3)	80.2 (3)
O–Cu(4)–Cl(6)	81.2 (6)	Cu(2)–Cl(4)–Cu(4)	79.2 (3)
N(1)–Cu(1)–Cl(1)	91.1 (7)	Cu(3)–Cl(5)–Cu(4)	78.5 (3)
N(1)–Cu(1)–Cl(2)	100.4 (7)	Cu(1)–Cl(6)–Cu(4)	78.2 (3)

The Cu_4O tetrahedron is reasonably regular, the Cu–Cu distances being between 3.05 and 3.21 Å, each ±0.005–0.006 Å, and the Cu–O–Cu angles varying from 106.3 to 115.8°, each ±0.8°. All Cu–O and Cu–N bond distances have the usual values but the fivefold coordination around the copper atoms is rather irregular, the extent of distortion from a trigonal-bipyramidal arrangement being different for the four copper atoms. For Cu(1), the bonds Cu(1)–Cl(1) and Cu(1)–Cl(6) (2.329 ± 0.008 and 2.324 ± 0.008 Å) are considerably shorter than the values reported for $Cu_4OCl_6(TPPO)_4$[3] and the angle between these bonds is 155.0 ± 0.4°. The coordination is thus intermediate between a trigonal bipyramid and a tetragonal pyramid with Cl(1), O, Cl(6), and N(1) as the base and Cl(2) (at 2.64 Å from Cu(1)) as the apex. The coordination around Cu(2) and Cu(4) is similar and it appears that, for these three copper atoms, the distortion of the trigonal-bipyramidal coordination is at least partly due to steric interference by the methyl group of the 2-methylpyridine bonded to each copper atom. The chlorine atoms forming the shorter bonds, with the larger angle between them, are in each case those nearest the respective methyl carbon atoms C(1), C(7), and C(19). The relevant C–Cl approach distances (Å) are: C(1)–Cl(1) = 3.66, C(1)–Cl(6) = 3.55, C(7)–Cl(2) = 3.87, C(7)–Cl(3) = 3.40, C(19)–Cl(4) = 3.73, C(19)–Cl(5) = 3.46 (±0.03 Å). It might be expected that the proximity of the methyl carbon atom C(13) to Cl(3) and Cl(5), at 3.45 ± 0.03 and 3.56 ± 0.03 Å, respectively, would cause the same kind of distortion in the coordination around Cu(3). However, the environment of Cu(3) is less distorted than those of the other copper atoms, as can be seen from the observed bond distances and angles (Tables V and VI). This could perhaps be explained by the fact that Cl(3) and Cl(5) are also close to C(7) and C(19), respectively, which might oppose to some extent the distorting effect of C(13) on these two chlorine atoms. A more detailed quantitative evaluation of the steric effects of the methyl groups is not possible from the present results since the quality of the data was not sufficiently good to locate the methyl hydrogen atoms or to decide whether the methyl groups are fixed or rotating. This also prevents a quantitative examination of intermolecular contacts, which could be partly responsible for the distortion of the Cu_4OCl_6 cluster, but, from inspection of the intermolecular C–C and C–Cl distances, it appears that the main reason for the distortion is intramolecular steric effects of the methyl groups, compared to $Cu_4OCl_6(py)_4$,[4] for which it was suggested that the observed distortion is due mainly to intermolecular interactions. Steric hindrance was also assumed to be the cause of Cu(2-

mepy)$_2$Cl$_2$[2] adopting a structure different from that of Cu(py)$_2$Cl$_2$,[8] the close approach of the methyl groups to the sixth coordination position about the metal leading to a distorted tetragonal-pyramidal arrangement.

The 2-methylpyridine molecules are not appreciably distorted and the bond distances and angles do not deviate appreciably from the accepted values. The C–N bond distances have an average value of 1.34 Å and range from 1.31 to 1.39 Å, the average value of the aromatic C–C distances is 1.40 Å, with a range of 1.36–1.46 Å, and the four C–C bonds to the methyl carbon atoms C(1), C(7), C(13), and C(19) are 1.51, 1.55, 1.52, and 1.55 Å. The standard deviations are between 0.03 and 0.04 Å for C–N distances and between 0.04 and 0.05 Å for C–C distances. The bond angles within the aromatic rings range from 115 to 124°, with an average value of 120°, and the eight angles involving the methyl carbon atoms have a range of 115–125°, with an average of 120°, all standard deviations being between 3 and 4°.

The aromatic rings are essentially planar, the average deviations of the atoms from the mean ring planes being *ca.* 0.02 Å, while the largest deviation is 0.04 Å which is of the order of the maximum standard deviation of the coordinates of the carbon atoms. The methyl carbon atoms C(1), C(7), C(13), and C(19) are displaced by 0.02, 0.12, 0.03, and 0.06 Å from the planes of the respective rings. The deviations of C(7) and C(19) may simply indicate an underestimate of coordinate errors, but, for both atoms, the displacement is to the opposite side of the ring plane from the nearest chlorine atoms.

It has not been possible to reach a definite conclusion regarding the presence of water of crystallization in the structure. Since no hydrate oxygen atoms could be located from the X-ray structure analysis, it must be assumed that the water of crystallization is in a disordered state. From the molecular packing, the only sites which could accommodate water molecules appear to be on either side of the screw axes at $^1/_2$, y, $^1/_4$ and $^1/_2$, y, $^3/_4$ and near the symmetry centers at $^1/_2$, 0, $^1/_2$ and $^1/_2$, $^1/_2$, 0. Water molecules in the former sites could conceivably have some effect on the positions of Cl(1) and Cl(5), contributing to the distortion of the molecule, but there was no evidence whatsoever of any residual electron density in this region. The small peaks (*ca.* 0.8 e^- Å^{-3}) observed on the two symmetry centers in difference maps are much lower than would be expected for oxygen atoms. Water molecules on the symmetry centers would account for only 0.5 H_2O per molecule of Cu$_4$OCl$_6$(2-mepy)$_4$ and, moreover, would have to exhibit complete rotational disorder.

Source of Oxygen in Cu$_4$OCl$_6$(2-mepy)$_4$.—Although several complexes of the type Cu$_4$OCl$_6$L$_4$ have now been described, the source of the oxygen atom in the Cu$_4$O cluster has not been identified. It could originate in an oxygen or water molecule, since neither species were excluded in any preparation or in some other oxygenated species in each case Variation of the reaction conditions has now shown that the oxygen atom in I originates in water. The reaction of copper(II) chloride with 2-methylpyridine in methanol using the same quantities as in the preparation of I but under anhydrous conditions and with the removal of dissolved oxygen led to the formation of II directly. Only a small amount of II crystallized from the volume of solvent used and when the mother liquor was exposed to the atmosphere the color changed from green to dark olive green and I crystallized out owing to its lower solubility, thus showing that either oxygen or water was the source of the oxygen atoms. When only oxygen was removed from the reagents, I was obtained in the same yield as when the methanolic solutions of copper(II) chloride dihydrate and 2-methylpyridine were mixed under normal conditions.

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(8) J. D. Dunitz, *Acta Crystallogr.*, **10**, 307 (1957).