Thus, overall, the cis complex appears to be subject to more internal strain than a comparable trans complex. In addition, the oxalate ligand, having a bite of only 80°, allows the N–Ru–N bond angle for the equatorial pyridine rings to expand to 98°. Thus if the oxalate ligand were replaced by two chlorine atoms, the resultant cis complex, requiring a larger Cl–Ru–Cl angle, would certainly be more crowded and thus would be expected to be unstable relative to the trans complex.

Acknowledgments.—This work was supported by a grant from the National Research Council of Canada. B. R. L. acknowledges financial assistance received from an Ontario Government fellowship. We are indebted to Dean A. D. Allen for his active encouragement and support.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
TEXAS CHRISTIAN UNIVERSITY, FORTH WORTH, TEXAS

The Crystal and Molecular Structure of Dichlorobis(4-methylpyridine 1-oxide)copper(II), Yellow Modification

BY D. R. JOHNSON AND W. H. WATSON*

Received September 11, 1970

The crystal structure of the yellow modification of dichlorobis(4-methylpyridine 1-oxide)copper(II), $[(C_6H_7NO)_2CuCl_2]_2$, has been determined by single-crystal X-ray diffraction methods. Counter methods were used to collect 1469 nonzero reflections. The complex crystallizes in the monoclinic space group $P2_1/n$ with two dimeric molecules per unit cell. The cell dimensions are $a = 7.368$ (10), $b = 19.857$ (5), $c = 10.773$ (5) Å, and $\beta = 111°\ 25\ (10)'$. The observed and calculated densities are 1.60 and 1.59 g cm^{-3}, respectively. The structure was refined by least-squares methods to a conventional R factor of 0.061%. The molecules consist of oxygen-bridged dimer units. The coordination around the copper ion may be described as a highly distorted square-based pyramid with a chlorine atom at the apical site at a distance of 2.354 (3) Å. The oxygen bridging system contains unequal Cu–O bond lengths of 1.957 (6) and 2.153 (6) Å, and the magnetic moment should be larger than those observed for the 1:1 dimeric species. The unstable dimeric molecule of the yellow modification is postulated to be an intermediate in the formation of the thermodynamically stable trans 2:1 monomer.

Introduction

The various types of 2:1 aromatic *N*-oxide complexes of copper(II) have been discussed in previous papers.[1,2] The infrared spectra have been reported for many of these complexes, and copper(II) coordination geometries were predicted from a consideration of the metal–chlorine stretching modes.[3] The green form of the 2:1 4-methylpyridine 1-oxide complex was shown to have a trans square-planar geometry about the copper(II) ions.[2] The monomers are isolated units which show little intramolecular steric interaction and exhibit normal magnetic moments from 77°K to well above room temperature. This form is thermodynamically the most stable, and all 2:1 green crystalline forms are predicted to be trans square planar.

The yellow form of the dichlorobis(2,6-dimethylpyridine 1-oxide)copper(II) complex was shown to have a geometry intermediate between tetrahedral and cis square planar.[4] This is consistent with the prediction of Hatfield and Morrison[5] based upon the diffuse reflectance spectrum of dibromobis(2,6-dimethylpyridine 1-oxide)copper(II). The magnetic moments of these two complexes were normal. In general, only small quantities of the yellow form can be prepared, and the infrared spectra and magnetic moments of only a few of the complexes have been reported. The dichlorobis(pyridine 1-oxide) copper(II) complex has been shown to be an oxygen-bridged dimer,[6] and the complex has a magnetic moment around 0.5 BM.[7] The corresponding bromide and dibromobis(4-methylpyridine 1-oxide)copper(II) complexes have magnetic moments of 1.4[7] and 1.33[8] BM, respectively. Since the 1:1 dimeric bromide complexes usually have lower magnetic moments than the corresponding chloride complexes, these intermediate moments are not consistent with the known structures in this series. A dimeric structure was predicted,[2] but some significant differences in geometry must exist.

We wish to report the structure of the yellow form of dichlorobis(4-methylpyridine 1-oxide)copper(II) and rationalize the physical properties in terms of this structure.

Experimental Section

Small quantities of the yellow 2:1 complex were prepared by mixing an excess of 4-methylpyridine 1-oxide with the 1:1 complex in boiling ethanol. The solution was allowed to evaporate slowly at room temperature, and a few yellow crystals were found together with a large excess of the green form. Attempts to improve the yield of yellow modification were unsuccessful. The crystals were unstable, and the small quantities of sample hindered the complete chemical and physical characterization of this material.

The yellow complex was irreversibly converted to the green form above 73°, and the converted green form retained its color on returning to room temperature. An infrared spectrum was obtained of the yellow form pressed into a KBr pellet. Two

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[1] W. H. Watson, *Inorg. Chem.*, **8**, 1879 (1969).

[2] D. R. Johnson and W. H. Watson, submitted for publication.

[3] R. Whyman and W. E. Hatfield, *Inorg. Chem.*, **6**, 1859 (1967).

[4] R. S. Sager and W. H. Watson, *ibid.*, **8**, 308 (1969).

[5] W. E. Hatfield and J. C. Morrison, *ibid.*, **5**, 1390 (1966).

[6] J. C. Morrow, presented at the National Meeting of the American Crystallographic Association, Gatlinburg, Tenn., June 1965.

[7] S. J. Gruber, C. M. Harris, E. Kokot, S. L. Lenzer, T. N. Lockyer, and E. Sinn, *Aust. J. Chem.*, **20**, 2403 (1967).

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

N–O stretching bands at 1200 and 1222 cm^{-1} were observed. This indicates the presence of two distinct types of *N*-oxide ligands in the complex. The far-infrared spectrum of the complex was not resolved sufficiently to obtain accurate frequencies for the copper–chlorine vibrational modes. Hatfield and Whyman reported copper–chlorine modes at 339, 316, and 296 cm^{-1} for the green modification of the dichlorobis(4-methylpyridine 1-oxide)copper(II) complex.[3] Only the band at 339 cm^{-1} is associated with the green trans square-planar complex, and the remaining two bands probably can be assigned to the yellow form. The two frequencies 316 and 296 cm^{-1} are consistent with those observed for the yellow form of dichlorobis(2,6-pyridine 1-oxide)copper(II), 319 and 297 cm^{-1}, and dichlorobis(2,4,6-trimethylpyridine 1-oxide)copper(II), 317 and 303 cm^{-1}.

A yellow plateletlike crystal having the dimensions 0.25 × 0.06 × 0.98 mm was used in collecting all intensity data. The crystal was mounted with the long axis coincident with the spindle axis of the instrument. The unit cell parameters were determined at room temperature from an *a* axis rotation and an $0kl$ Weissenberg photograph, both calibrated with superimposed NaCl powder lines, $a = 5.6402$ Å. The photographs were obtained using zirconium-filtered Mo Kα radiation.

Crystal Data

$[(CH_3C_5H_4NO)_2CuCl_2]_2$, mol wt 705.4, crystallizes in the monclinic space group $P2_1/n$ with $a = 7.368$ (10), $b = 19.857$ (5), $c = 10.773$ (5) Å, $\beta = 111°\ 25$ (10)′ $Z = 2$, $V = 1468.3$ Å^3, $\mu = 19.00$ cm^{-1} (Mo Kα), $d_{\text{obsd}} = 1.60$ g cm^{-3}, and $d_{\text{calcd}} = 1.59$ g cm^{-3}. The systematic absences are: $0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$ (observed on $hk0$ and $h0l$ precession and $0kl$ Weissenberg photographs). The errors in the cell edges are the average deviations calculated from measurements of several higher angle reflections or layer lines. The error in the angle is the average deviation calculated from several measurements of the same angle. The density was measured by the flotation technique using a mixture of chloroform and bromoform.

Three-dimensional intensity data were collected through the seventh level ($0kl$–$7kl$) with a Philips PAILRED diffractometer using equiinclination geometry and a continuous ω-scan technique. Mo Kα radiation (λ 0.71069 Å) and a silicon monochromator crystal [$d(111) = 3.1355$ Å] were used. The ω-scan range varied from 2.0° for the zero level to 4.0° for the seventh level and a scan speed of 0.5°/min was used throughout. In general all of the nonequivalent reflections of the types hkl and $hk\bar{l}$ were scanned up to a 2θ limit of 51.6°. For the zero level, where $0kl = 0k\bar{l}$, the equivalent reflections were averaged to give one unique set of data. Several reference reflections were monitored throughout the data collection period, and the intensities decreased by 15% during this time. The zero-level data were retaken and the decrease in intensity was uniform for all reflections. Since the complex is thermodynamically unstable, the deterioration upon exposure to X-rays was expected. The standard reflections were used initially to scale the levels together.

A total of 2213 nonequivalent reflections were obtained, of which 1459 were tabulated as having an observed intensity. An intensity was designated as observed if the intensity was greater than twice the calculated standard deviation for the reflection. The raw data were reduced to the structure factors using a standard data reduction program with Lorentz and polarization corrections applied to the data.[9] Standard deviations for the structure factors were assigned on the basis of counting statistics. Included in the standard deviation is a term for instrument instability which was chosen as 3% of the magnitude of the observed raw intensity. The standard deviation is given by

$$\sigma(F_o) = \frac{1}{2\sqrt{Lp}}\sqrt{\frac{N_S + RN_B + (0.03I_0)^2}{I_0}}$$

$$I_0 = K(N_S - RN_B)$$

where N_S is the total count obtained during a scan cycle, N_B is the total background count, R is a constant which scales the background count time to the total scan time, I_0 is the raw magnitude of the peak, and K is a scaling constant for the raw data.

If a cylindrical shape is assumed for the crystal, the maximum error introduced in the structure factor by neglecting the absorption correction is approximately 11%. An absorption correction program for Weissenberg geometry[10] was used to make the necessary corrections. The program is general and depends upon the equations of the crystal faces and not on the crystal class. The maximum and minimum transmission factors for the intensity were calculated as 0.891 and 0.640, respectively.

The scattering factors of Cromer and Waber[11] were used for all nonhydrogen atoms. The scattering factors of copper and chlorine were corrected for the real part of the anomalous dispersion using the values of Cromer.[12] The hydrogen scattering factors were those calculated by Stewart, Davidson, and Simpson.[13]

Structure Determination

A three-dimensional Patterson map was calculated with the origin peak removed. Evaluation of the Harker planes and Harker lines from the map indicated the vector (0.05, 0.12, 0.16) was a copper–copper vector. This places two copper atoms within approximately 3 Å of each other, which is consistent with a dimeric structure for the complex. Further evaluation of the map gave the chlorine atomic positions as (0.29 0.07, 0.27) and (−0.02, 0.18, −0.08). The vectors generated from the assignment of these heavy-atom positions accounted for all of the large peaks in the map.

The positions of the heavy atoms were used to calculate structure factors for the 894 reflections with $(\sin\theta)/\lambda \leqslant 0.45$, and a conventional R value of 0.47 was obtained, where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. A three-dimensional Fourier map was computed using the calculated phases from structure factors if $2F_c \geqslant F_o$. Reasonable positions for two oxygen and two nitrogen atoms were found, and a structure factor calculation based on the coordinates of a copper atom and two chlorine, two oxygen, and two nitrogen atoms yielded an $R = 0.44$ for the 894 reflections. Two cycles of least-squares refinement with isotropic temperature factors improved the agreement to $R = 0.37$. Tentative coordinates for several ring carbon atoms were

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(9) A listing of all computer programs may be found in the Ph.D. dissertation of N. R. Stemple, Texas Christian University, 1970.

(10) J. A. Ibers, Northwestern University, absorption correction program for Weissenberg geometry; modified for the IBM 1800 by N. R. Stemple, Texas Christian University, 1969.

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

(12) D. T. Cromer, *ibid.*, **18**, 17 (1965).

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

included in a structure factor calculation, and R dropped to 0.30. A new three-dimensional Fourier map revealed the positions of the remaining nonhydrogen atoms. A structure factor calculation which included all of the atomic positions gave $R = 0.22$ for the 894 reflections.

Anisotropic temperature factors were assigned to the copper atom. Three cycles of full-matrix least-squares refinement reduced the R factor to $R = 0.087$. R(wtd) was calculated as 0.079 at the conclusion of the refinement. R(wtd) is defined as $R(\text{wtd}) = \Sigma w||F_o| - |F_c||/\Sigma w|F_o|$. The weighting scheme used in the refinement was $w = [1/\sigma(F_o)]^2$.

Refinement with anisotropic thermal parameters assigned to the chlorine atoms yielded $R = 0.076$ and $R(\text{wtd}) = 0.066$ for the same 894 reflections. The inclusion of anisotropic thermal parameters for the chlorine atoms was found to be significant at the $\alpha = 0.005$ level based on Hamilton's significance test.[14]

Anisotropic thermal parameters were assinged to all the remaining atoms, and three cycles of full-matrix refinement were carried out for the 1469 observed reflections. The R factor dropped from $R = 0.102$ to $R = 0.083$ at the conclusion of the refinement. All of the last shifts were less than the estimated standard deviations of the parameters, which were calculated from the inverse of the normal-equations matrix.

Bond lengths calculated from the final positional parameters indicated a variation in the C–C bond lengths of one of the ring systems. The calculated C–C bond lengths for this ring were C(8)–C(9) = 1.28, C(9)–C(10) = 1.39, C(10)–C(11) = 1.41, and C(11)–C(12) = 1.30 Å. Two of the bond lengths are much shorter than expected. A three-dimensional difference Fourier technique[15] was used to examine the positions of the atoms in the distorted ring. New parameters always refined to the original positions. All other bond lengths were within 2σ of the expected values.

Since the carbon atoms did not refine to chemically reasonable positions, the data were analyzed for systematic errors. Plots of the function $Q_s = \Sigma(|F_o| - |F_c|)/\sigma(F_o)$ for incremental ranges of F_o, $(\sin\theta)/\lambda$, h, k, and l indicated the presence of systematic errors in level scaling and as a function of the Bragg angle θ. The least-squares program refines only an overall scale factor, and the errors in scaling of the levels are not minimized during refinement unless they can be absorbed by the temperature factors. The θ dependence was found to be associated with an instrument error which depended upon the counter angle. This was traced to a faulty part which was replaced.

The data could be corrected to provide proper scaling and to compensate for the instrument malfunction. The forms of the corrections were determined from the plots of the Q_s function for incremental ranges of h and $\sin 2\psi$, where h is the rotation axis index and 2ψ is the counter angle for a particular reflection. The maximum corrections were 7% for scaling of the levels and 5% for the errors associated with the counter angle. A re-collection of some data indicated the instrument error correction was adequate.

Least-squares refinement with all atoms and anisotropic thermal parameters yielded $R = 0.052$ and $R(\text{wtd}) = 0.049$ for 1210 reflections of the corrected data set. This may be compared with $R = 0.063$ and $R(\text{wtd}) = 0.059$ for the uncorrected set. The C–C bond lengths which had been too short were now observed as C(8)–C(9) = 1.37 and C(11)–C(12) = 1.39 Å. All other bond lengths changed by less than two standard deviations.

The structural model is chemically reasonable, and the data corrections appear to be justified. The complex is an unstable intermediate which decomposes slowly upon exposure to X-rays, and some peculiarities might be expected to occur in the anisotropic temperature factors. The thermal parameters of O(1), which is located at the point of bond breaking, are abnormal; however, the thermal parameters probably have absorbed some of the inaccuracies in the data and physical interpretation may be questionable.

Ring hydrogen positions were calculated by assuming the hydrogen atoms were in the plane of the ring at a distance of 1.08 Å from the carbon atoms. The inclusion of the ring hydrogen atoms in the structure factor calculation yielded $R = 0.050$ and $R(\text{wtd}) = 0.048$ for 1210 reflections. The addition of the hydrogen atoms to the model was significant at the $\alpha = 0.01$ level. Calculation of the structure factors for all 1469 observed reflections gave $R = 0.061$ and $R(\text{wtd}) = 0.052$. Those reflections initially assigned a zero magnitude generally were found to have a calculated magnitude less than the observed minimum. The final observed and calculated structure factors are given in Table I.

A final three-dimensional difference Fourier map was calculated and the largest peak was 0.5 e$^-$/Å^3. Some peaks about the methyl carbon atoms were observed and might correspond to methyl hydrogen atoms, but no attempt was made to assign these positions.

All shifts of the parameters during the final cycle of full-matrix refinement were less than one-seventh of the estimated standard deviations of the parameters. The final positional and thermal parameters are given in Table II. The estimated standard deviations of the parameters were calculated from the inverse of the normal-equations matrix of the last least-squares cycle.

Discussion

The calculated bond lengths and bond angles are given in Table III. Also included in the table are several nonbonding distances which determine the packing in the unit cell. Figures 1 and 2 are projections of the unit cell along the crystallographic a and c axes, and the numbering of the atoms can be related to these figures.

Several features distinguish this structure from previously reported oxygen-bridged dimeric copper(II) complexes of aromatic *N*-oxides.[16-19] The two Cu–O bonds in the bridging system are significantly different, 1.957 (6) and 2.153 (6) Å. The copper(II) ion is five-coordinate with chlorine atom Cl(1) more tightly bonded in the apical site of a square-based pyramidal

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[14] W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

[15] J. Ladell and J. L. Katz, *ibid.*, **7**, 460 (1954).

[16] (a) R. S. Sager, R. J. Williams, and W. H. Watson, *Inorg. Chem.*, **6**, 951 (1967); (b) *ibid.*, **8**, 694 (1969).

[17] R. S. Sager and W. H. Watson, *ibid.*, **7**, 2035 (1968).

[18] J. C. Morrow, Presented at the National Meeting of the American Crystallographic Association, Gatlinburg, Tenn., June 1965.

[19] S. Scavnicar and B. Matkovic, *Acta Crystallogr., Sect. B*, **25**, 2046 (1969).

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR DICHLOROBIS(4-METHYLPYRIDINE 1-OXIDE)COPPER(II)

K	L	|10FO|	10FC
	H = 0		
0	2	305	322
0	3	**	0
0	4	166	215
0	5	**	0
0	6	665	-674
0	7	**	0
0	8	210	-206
0	9	**	0
0	10	191	-208
0	11	**	0
1	2	70	196
1	3	742	735
1	4	156	138
1	5	939	-922
1	6	391	409
1	7	190	-201
1	8	113	126
1	9	266	-275
1	10	162	146
1	11	103	102
2	2	570	-597
2	3	73	63
2	4	**	29
2	5	322	-320
2	6	495	-495
2	7	138	130
2	8	114	-90
2	9	240	257
2	10	**	71
3	0	**	0
3	1	528	463
3	2	610	-609
3	3	178	-139
3	4	633	-656
3	5	84	-71
3	6	179	-177
3	7	**	20
3	8	**	89
3	9	**	16
3	10	352	352
4	0	974	-954
4	1	71	-76
4	2	301	283
4	3	426	-456
4	4	185	178
4	5	587	-594
4	6	**	10
4	7	**	31
4	8	138	132
4	9	156	185
4	10	132	130
5	1	625	-612
5	2	668	-641
5	3	**	29
5	4	472	-497
5	5	426	443
5	6	217	-205
5	7	187	204
5	8	**	41
5	9	88	107
5	10	202	199
6	0	1237	-1180
6	1	107	-103
6	2	322	282
6	3	**	14
6	4	617	593
6	5	223	-236
6	6	495	506
6	7	164	171
6	8	106	97
6	9	141	164
6	10	**	30
7	1	630	-602
7	2	864	811
7	3	117	109
7	4	245	255
7	5	603	600
7	6	351	344
7	7	251	244
7	8	**	52
7	9	182	183
7	10	102	101
8	0	1273	-1318
8	1	207	224
8	2	335	-336
8	3	897	884
8	4	305	-319
8	5	299	308
8	6	502	501
8	7	**	89
8	8	233	240
8	9	117	-112
8	10	**	4
9	0	**	0
9	1	645	-613
9	2	591	580
9	3	423	-412
9	4	358	399
9	5	313	312
9	6	190	183
9	7	98	97
9	8	174	-158
9	9	117	70
9	10	166	-165
10	0	318	-344
10	1	274	305
10	2	244	221
10	3	319	333
10	4	163	-159
10	5	280	290
10	6	274	262
10	7	152	-145
10	8	91	-79
10	9	173	-188
11	0	**	0
11	1	644	639
11	2	381	401
11	3	92	66
11	4	341	363
11	5	**	19
11	6	**	71
11	7	135	-120
11	8	130	-110
11	9	87	-82
12	0	537	546
12	1	394	388
12	2	602	621
12	3	199	209
12	4	95	-88
12	5	467	492
12	6	200	-202
12	7	164	-158
12	8	307	-319
12	9	**	21
13	0	**	0
13	1	421	424
13	2	**	45
13	3	94	82
13	4	366	380
13	5	220	-210
13	6	111	100
13	7	300	-304
13	8	180	163
14	0	255	257
14	1	159	142
14	2	168	183
14	3	253	-277
14	4	92	-36
14	5	135	137
14	6	285	-296
14	7	**	43
14	8	156	-162
15	0	**	0
15	1	83	18
15	2	255	-264
15	3	150	169
15	4	**	76
15	5	224	-217
15	6	158	-154
15	7	185	-207
16	0	165	178
16	1	200	-191
16	2	152	-133
16	3	342	-348
16	4	**	10
16	5	219	-219
16	6	**	62
16	7	**	79
17	0	**	0
17	1	**	17
17	2	333	-349
17	3	169	166
17	4	329	-341
17	5	**	6
17	6	**	14
18	0	**	27
18	1	180	-193
18	2	**	30
18	3	114	-79
18	4	116	99
18	5	106	-67
18	6	**	49
19	1	240	-264
19	2	**	9
19	3	207	-225
19	4	95	40
19	5	**	80
20	0	299	-313
20	1	**	6
20	2	319	-340
20	3	**	50
20	4	**	12
21	0	**	0
21	1	180	-174
21	2	**	6
	H = 1		
0	-10	**	0
0	-9	430	-426
0	-8	**	0
0	-7	809	-807
0	-6	**	0
0	-5	**	36
0	-4	**	0
0	-3	**	30
0	-2	**	0
0	1	1409	1369
0	2	**	0
0	3	691	694
0	4	**	0
0	5	547	-594
0	6	**	0
0	7	194	-191
0	8	**	0
0	9	**	42
0	10	**	0
1	-11	133	-110
1	-10	181	-179
1	-9	159	-164
1	-8	332	-344
1	-7	148	-163
1	-6	507	-499
1	-5	89	86
1	-4	**	32
1	-3	123	-116
1	-2	645	662
1	-1	398	403
1	0	1246	1350
1	1	855	-851
1	2	884	902
1	3	373	-368
1	4	**	89
1	5	**	5
1	6	327	-328
1	7	**	50
1	8	320	-329
1	9	200	194
1	10	96	88
2	-11	105	61
2	-10	338	-330
2	-9	**	10
2	-8	264	-264
2	-7	425	-411
2	-6	193	196
2	-5	**	75
2	-4	169	160
2	-3	611	-585
2	-2	518	592
2	-1	817	755
2	0	386	-404
2	1	958	882
2	2	126	-120
2	3	207	239
2	4	530	-544
2	5	367	-381
2	6	426	444
2	7	158	-163
2	8	157	141
2	9	**	32
2	10	148	149
3	-11	224	-216
3	-10	94	-83
3	-9	140	-107
3	-8	103	48
3	-7	**	63
3	-6	321	-296
3	-5	627	610
3	-4	577	-539
3	-3	825	766
3	-2	595	-603
3	-1	503	427
3	0	615	-676
3	1	1044	-982
3	2	87	100
3	3	1204	-1221
3	4	308	318
3	5	207	179
3	6	**	82
3	7	**	55
3	8	**	24
3	9	222	218
3	10	110	96
4	-10	145	-136
4	-9	95	78
4	-8	193	197
4	-7	94	-117
4	-6	859	843
4	-5	85	63
4	-4	514	522
4	-3	98	-174
4	-2	1654	1647
4	-1	196	-128
4	0	1422	-1461
4	1	1052	-1027
4	2	1003	-1042
4	3	197	190
4	4	1045	-1053
4	5	224	218
4	6	96	-111
4	7	**	15
4	8	**	48
4	9	**	4
4	10	182	206
5	-10	**	13
5	-9	227	-228
5	-8	264	283
5	-7	**	54
5	-6	274	268
5	-5	888	867
5	-4	365	363
5	-3	736	761
5	-2	102	-106
5	-1	410	-358
5	0	621	622
5	1	320	304
5	2	146	172
5	3	1139	-1156
5	4	430	427
5	5	**	34
5	6	321	332
5	7	210	-207
5	8	117	107
5	9	246	222
6	-10	**	62
6	-9	**	16
6	-8	227	-228
6	-7	566	565
6	-6	224	205
6	-5	182	-183
6	-4	147	-126
6	-3	247	306
6	-2	529	508
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11	7	180	-210
12	-10	126	148
12	-9	163	-177
12	-8	108	-94
12	-7	367	-365
12	-6	**	77
12	-5	**	87
12	-4	416	-391
12	-3	332	338
12	-2	**	72
12	-1	642	602
12	0	**	111
12	1	376	370
12	2	350	375
12	3	237	234
12	4	**	47
12	5	169	-213
12	6	**	35
12	7	120	-137
13	-9	**	20
13	-8	177	-178
13	-7	**	127
13	-6	250	-244
13	-5	**	42
13	-4	**	48
13	-3	145	-163
13	-2	368	345
13	-1	259	-228
13	0	428	415
13	1	255	247
13	2	141	104
13	3	**	13
13	4	191	-171
13	5	215	240
13	6	168	-183
14	-9	140	-155
14	-8	**	63
14	-7	216	-192
14	-6	228	219
14	-5	192	-200
14	-4	**	37
14	-3	**	45
14	-2	**	46
14	-1	275	279
14	0	222	-235
14	1	**	149
14	2	**	78
14	3	320	-332
14	4	**	55
14	5	193	-178
14	6	**	27
15	-8	136	-115
15	-7	113	139
15	-6	111	-137
15	-5	200	209
15	-4	**	12
15	-3	337	343
15	-2	**	97
15	-1	190	-220
15	0	225	217
15	1	109	-113
15	2	**	52
15	3	316	-309
15	4	164	-146
15	5	**	29
16	-8	**	38
16	-7	**	104
16	-6	347	323
16	-5	139	-122
16	-4	388	398
16	-3	**	22
16	-2	150	113
16	-1	180	197
16	0	155	-134
16	1	**	76
16	2	364	-356
16	3	**	26
16	4	**	76
16	5	**	22
17	-7	263	274
17	-6	**	16
17	-5	300	308
17	-4	121	147
17	-3	269	251
17	-2	121	-75
17	-1	115	-144
17	0	**	129
17	1	238	-263
17	2	**	31
17	3	243	-234
17	4	**	86
18	-6	**	59
18	-5	**	43
18	-4	196	186
18	-3	**	99
18	-2	**	100
18	-1	**	51
18	0	135	-154
18	1	**	17
18	2	166	-179
18	3	**	32
19	-5	**	19
19	-4	**	30
19	-3	**	16
19	-2	155	-136
19	-1	**	18
19	0	115	-153
19	1	**	122
19	2	**	108
20	-4	**	12
20	-3	**	12
20	-2	**	81
20	-1	323	-399
20	0	**	22
20	1	**	145
	H = 4		
0	-11	**	0
0	-10	190	-172
0	-9	**	0
0	-8	299	-271
0	-7	**	0
0	-6	392	-391
0	-5	**	0
0	-4	56	48
0	0	710	726
0	1	**	0
0	2	219	219
0	3	**	0
0	4	468	-457
0	5	**	0
0	6	101	91
0	7	**	0
1	-12	136	-95
1	-11	99	-97
1	-10	**	80
1	-9	**	69
1	-8	**	52
1	-7	505	-517
1	-6	**	51
1	-5	122	-121
1	-4	290	278
1	-3	400	414
1	-1	1001	1013
1	0	373	-369
1	1	363	-333
1	2	**	41
1	3	**	8
1	4	**	32
1	5	341	-358
1	6	152	139
1	7	97	-81
2	-12	153	116
2	-11	281	-275
2	-10	**	68
2	-9	245	-246
2	-8	102	-128
2	-7	**	13
2	-6	343	-361
2	-5	520	543
2	-4	56	58
2	-3	56	87
2	-2	203	182
2	-1	135	-151
2	0	73	-69
2	1	173	-186
2	2	274	-272
2	3	185	-187
2	4	373	-361
2	5	**	57
2	6	**	72
2	7	**	60
3	-12	235	-199
3	-11	111	164
3	-10	241	-225
3	-9	**	62
3	-8	**	1
3	-7	**	27
3	-6	623	626
3	-5	84	-93
3	-4	544	557
3	-3	481	-463
3	-2	189	200
3	-1	129	-128
3	0	448	-470
3	1	227	-245
3	2	196	-183
3	3	89	-65
3	4	395	-402
3	5	116	-107
3	6	**	10
3	7	124	127
4	-12	**	36
4	-11	304	-299
4	-10	154	192
4	-9	198	-196
4	-8	251	251
4	-7	320	327
4	-6	**	12
4	-5	1198	1239
4	-4	**	5
4	-3	477	509
4	-2	483	-498
4	-1	**	26
4	0	191	-202
4	1	529	-538
4	2	106	-102
4	3	295	-292
4	4	108	100
4	5	232	-239
4	6	**	23
4	7	**	96
5	-11	**	87
5	-10	224	-215
5	-9	**	20
5	-8	151	-177
5	-7	324	344
5	-6	752	755
5	-5	**	36
5	-4	395	388
5	-3	263	-262
5	-2	570	593
5	-1	396	-390
5	0	270	-281
5	1	89	70
5	2	186	-191
5	3	97	64
5	4	422	-422
5	5	125	118
5	6	164	164
5	7	**	83
6	-11	183	-164
6	-10	123	136
6	-9	140	157
6	-8	**	54
6	-7	177	-171
6	-6	303	310
6	-5	300	319
6	-4	134	-121
6	-3	187	-172
6	-2	444	-435
6	-1	210	230
6	0	224	-218
6	1	257	-260
6	2	218	228
6	3	106	-119
6	4	357	358
6	5	**	62
6	6	161	161
6	7	**	50
7	-11	**	61
7	-10	**	30
7	-9	288	283
7	-8	**	52
7	-7	374	386
7	-6	**	46
7	-5	**	64
7	-4	562	-585
7	-3	203	-212
7	-2	**	30
7	-1	765	-794
7	0	94	-93
7	1	143	148
7	2	221	243
7	3	**	78
7	4	**	74
7	5	394	395
7	6	152	129
7	7	**	18
8	-11	**	43
8	-10	189	163
8	-9	**	118
8	-8	278	279
8	-7	**	91
8	-6	391	404
8	-5	364	-367
8	-4	534	-534
8	-3	338	-342
8	-2	365	-364
8	-1	197	204
8	0	510	-493
8	1	264	274
8	2	**	87
8	3	142	143
8	4	150	161

geometry than has been observed previously, Cu–Cl(1) = 2.354 (3) Å. There is no chloride ion bridging between adjacent dimers.

A projection of the structure along the normal to the copper–oxygen bridging plane is shown in Figure 3. The geometry about the copper ion approximates a highly distorted square-based pyramid. Cl(1) occupies the apical site of the pyramid, and the three oxygen atoms and the other chlorine atom form the distorted basal plane. A unit-weighted least-squares plane fitted to the basal atoms indicates a distorted geometry, and all atoms are found to be more than 0.2 Å out of the plane, which is a deviation greater than would be expected from the estimated standard deviations of the positional parameters. A plane defined by the three oxygen atoms is represented by the equation

TABLE I (*Continued*)

K	L	|10FO|	10FC
8	5	198	205
8	6	**	40
8	7	**	36
9	−10	308	293
9	−9	173	157
9	−8	**	25
9	−7	95	95
9	−6	237	−259
9	−5	143	−129
9	−4	413	−416
9	−3	216	195
9	−2	**	15
9	−1	634	−636
9	0	246	246
9	1	94	−56
9	2	189	166
9	3	131	−141
9	4	136	161
9	5	198	191
9	6	121	−116
10	−10	**	20
10	−9	173	163
10	−8	123	91
10	−7	131	104
10	−6	**	33
10	−5	398	−406
10	−4	**	7
10	−3	200	−208
10	−2	**	18
10	−1	**	56
10	0	117	−91
10	1	328	319
10	2	**	57
10	3	123	89
10	4	134	118
10	5	**	59
10	6	**	51
11	−10	206	209
11	−9	157	−160
11	−8	**	109
11	−7	**	40
11	−6	185	−189
11	−5	**	21
11	−4	**	30
11	−3	218	231
11	−2	178	−194
11	−1	237	233
11	0	283	254
11	1	224	196
11	2	234	221
11	3	**	18
11	4	170	156
11	5	**	34
11	6	136	−154
12	−10	197	−204
12	−9	**	10
12	−8	273	−253
12	−7	**	8
12	−6	232	−218
12	−5	171	−161
12	−4	210	227
12	−3	187	−200
12	−2	370	359
12	−1	**	42
12	0	356	329
12	1	128	107
12	2	**	40
12	3	202	197
12	4	**	61
12	5	**	15
13	−9	244	−217
13	−8	**	14
13	−7	246	−220
13	−6	282	−266
13	−5	98	35
13	−4	**	13
13	−3	293	278
13	−2	315	−310
13	−1	284	304
13	0	**	48
13	1	160	144
13	2	**	17
13	3	200	−182
13	4	**	75
13	5	191	−193
14	−9	**	68
14	−8	212	−201
14	−7	**	30
14	−6	**	14
14	−5	**	20
14	−4	150	128
14	−3	197	195
14	−2	131	102
14	−1	**	103
14	0	122	66
14	1	**	26
14	2	**	51
14	3	**	34
14	4	176	−157
14	5	**	64
15	−8	**	68
15	−7	160	−143
15	−6	320	328
15	−5	**	9
15	−4	414	400
15	−3	**	77
15	−2	**	16
15	−1	**	50
15	0	**	16
15	1	**	93
15	2	294	−304
15	3	**	41
15	4	**	5
16	−8	106	−77
16	−7	306	277
16	−6	**	6
16	−5	277	266
16	−4	162	134
16	−3	440	443
16	−2	**	41
16	−1	132	−124
16	0	128	148
16	1	230	−223
16	2	**	51
16	3	291	−273
17	−7	**	14
17	−6	220	200
17	−5	**	60
17	−4	325	302
17	−3	108	53
17	−2	184	204
17	−1	179	160
17	0	112	−105
17	1	**	52
17	2	293	−270
17	3	154	138
18	−6	**	46
18	−5	171	165
18	−4	**	37
18	−3	176	189
18	−2	**	58
18	−1	**	15
18	0	**	46
18	1	129	−133
18	2	**	47
H = 5			
0	−11	231	−220
0	−10	**	0
0	−9	241	−242
0	−8	**	0
0	−7	448	−447
0	−6	**	0
0	−5	165	158
0	−1	719	750
0	0	61	0
0	1	107	109
0	2	**	0
0	3	153	−149
0	4	**	0
0	5	213	−180
0	6	**	0
0	7	180	−178
1	−12	**	27
1	−11	148	−135
1	−10	213	−203
1	−9	103	−77
1	−8	391	−371
1	−7	**	27
1	−6	**	54
1	−5	120	−123
1	−1	284	−316
1	0	177	180
1	1	**	55
1	2	126	145
1	3	120	−130
1	4	310	−309
1	5	**	117
1	6	**	16
1	7	**	62
2	−12	192	200
2	−11	**	64
2	−10	112	108
2	−9	**	52
2	−8	172	−159
2	−7	156	−156
2	−6	274	280
2	−5	79	66
2	−1	166	189
2	0	370	−382
2	1	**	41
2	2	174	−169
2	3	205	−190
2	4	141	137
2	5	93	−85
2	6	**	43
2	7	**	66
3	−12	**	66
3	−11	203	−217
3	−10	132	125
3	−9	**	8
3	−8	80	66
3	−7	305	300
3	−6	79	97
3	−5	330	324
3	−4	226	−225
3	−3	757	766
3	−2	**	44
3	−1	436	−461
3	0	262	−252
3	1	224	−220
3	2	133	−120
3	3	302	−300
3	4	199	−172
3	5	170	185
3	6	**	57
3	7	**	58
4	−12	240	−252
4	−11	**	79
4	−10	**	84
4	−9	108	131
4	−8	115	112
4	−7	107	112
4	−6	627	621
4	−5	**	27
4	−4	485	483
4	−3	241	−245
4	−2	178	191
4	−1	245	−266
4	0	259	−283
4	1	**	69
4	2	440	−455
4	3	**	23
4	4	**	19
4	5	**	28
4	6	102	−116
4	7	**	24
5	−12	**	48
5	−11	142	−145
5	−10	182	203
5	−9	102	−107
5	−8	316	303
5	−7	372	358
5	−6	132	150
5	−5	493	511
5	−4	**	24
5	−3	239	229
5	−2	423	−419
5	−1	347	−353
5	0	91	−93
5	1	**	26
5	2	128	169
5	3	215	−201
5	4	151	132
5	5	**	36
5	6	**	104
5	7	**	47
6	−12	131	−88
6	−11	**	89
6	−10	138	−146
6	−9	275	280
6	−8	95	118
6	−7	395	379
6	−6	162	170
6	−5	**	57
6	−4	214	207
6	−3	381	−400
6	−2	**	28
6	−1	264	−255
6	0	**	44
6	1	**	27
6	2	126	112
6	3	199	195
6	4	116	100
6	5	129	139
6	6	**	10
7	−11	**	15
7	−10	174	154
7	−9	195	−190
7	−8	333	319
7	−7	**	35
7	−6	**	52
7	−5	**	18
7	−4	120	−108
7	−3	267	−275
7	−2	488	−488
7	−1	**	16
7	0	175	−169
7	1	206	207
7	2	**	3
7	3	**	11
7	4	209	190
7	5	**	27
7	6	**	70
8	−11	119	158
8	−10	**	11
8	−9	234	244
8	−8	160	−161
8	−7	275	276
8	−6	213	−204
8	−5	**	50
8	−4	368	−348
8	−3	353	−351
8	−2	259	−250
8	−1	501	−483
8	0	254	242
8	1	207	−196
8	2	199	212
8	3	**	86
8	4	**	57
8	5	110	99
8	6	**	48
9	−11	**	88
9	−10	144	144
9	−9	93	106
9	−8	353	319
9	−7	**	17
9	−6	**	18
9	−5	225	−216
9	−4	83	60
9	−3	101	−55
9	−2	555	−525
9	−1	178	179
9	0	178	−200
9	1	275	259
9	2	288	−292
9	3	159	167
9	4	251	227
9	5	**	45
9	6	**	8
10	−11	146	73
10	−10	143	163
10	−9	168	−139
10	−8	**	18
10	−7	173	175
10	−6	**	93
10	−5	178	−180
10	−4	**	33
10	−3	119	131
10	−2	**	30
10	−1	**	23
10	0	333	332
10	1	**	105
10	2	200	163
10	3	**	34
10	4	**	57
10	5	**	19
10	6	**	70
11	−11	**	116
11	−10	151	−142
11	−9	186	170
11	−8	171	−163
11	−7	164	−163
11	−6	230	−223
11	−5	240	−222
11	−4	442	433
11	−3	**	29
11	−2	**	98
11	−1	257	263
11	0	355	354
11	1	**	20
11	2	118	−121
11	3	165	151
11	4	**	76
11	5	**	68
12	−10	**	64
12	−9	337	−307
12	−8	**	37
12	−7	**	104
12	−6	337	−305
12	−5	**	28
12	−4	**	67
12	−3	471	461
12	−2	**	51
12	−1	286	274
12	0	**	64
12	1	**	54
12	2	164	148
12	3	**	7
12	4	**	24
12	5	167	−89
13	−10	195	−176
13	−9	**	35
13	−8	287	−271
13	−7	147	−124
13	−6	103	−91
13	−5	**	40
13	−4	211	190
13	−3	**	63
13	−2	342	335
13	−1	183	180
13	0	217	197
13	1	**	65
13	2	**	41
13	3	126	119
13	4	**	82
13	5	**	27
14	−10	**	9
14	−9	170	139
14	−8	**	45
14	−7	321	297
14	−6	107	79
14	−5	**	57
14	−4	**	58
14	−3	215	214
14	−2	**	89
14	−1	146	151
14	0	**	88
14	1	**	65
14	2	**	31
14	3	149	−150
14	4	**	3
15	−9	**	22
15	−8	176	−142
15	−7	**	93
15	−6	**	11
15	−5	190	169
15	−4	**	59
15	−3	124	125
15	−2	239	204
15	−1	**	12
15	0	**	7
15	1	118	−122
15	2	**	6
15	3	**	71
16	−8	110	88
16	−7	**	101
16	−6	317	301
16	−5	**	57
16	−4	273	262
16	−3	**	41
16	−2	184	128
16	−1	**	68
16	0	**	80
16	1	**	53
16	2	141	−125
16	3	**	8
H = 6			
0	−10	290	−300
0	−9	**	0
0	−8	194	−168
0	−7	**	0
0	−6	111	105
0	−5	**	0
0	−2	534	561
0	−1	**	0
0	0	382	361
0	1	**	0
0	2	100	−112
0	3	**	0
0	4	99	−89
0	5	**	0
1	−11	130	−126
1	−10	174	−154
1	−9	314	−304
1	−8	**	43
1	−7	92	−96
1	−6	**	24
1	−5	130	130
1	−1	209	199
1	0	136	−128
1	1	198	196
1	2	**	80
1	3	217	−204
1	4	101	54
1	5	148	−72
2	−11	142	−160
2	−10	**	68
2	−9	**	80
2	−8	147	−149
2	−7	148	143
2	−6	**	71
2	−5	271	277
2	−2	133	136
2	−1	181	−179
2	0	**	52
2	1	317	−300
2	2	175	−182
2	3	**	42
2	4	**	18
2	5	**	13
3	−11	**	35
3	−10	217	217
3	−9	**	68
3	−8	281	263
3	−7	157	156
3	−6	258	250
3	−5	**	19
3	−4	438	452
3	−3	117	107
3	−2	194	−174
3	−1	238	−246
3	0	213	−205
3	1	**	31
3	2	337	−310
3	3	99	−117
3	4	**	27
3	5	**	18
4	−11	151	−158
4	−10	206	175
4	−9	**	49
4	−8	115	89
4	−7	459	492
4	−6	86	89
4	−5	537	552
4	−4	84	80
4	−3	325	310
4	−2	326	−309
4	−1	**	18
4	0	109	−116
4	1	412	−397
4	2	**	9
4	3	**	18
4	4	**	83
4	5	**	77
5	−11	**	69
5	−10	**	110
5	−9	151	153
5	−8	226	253
5	−7	134	146
5	−6	223	213
5	−5	**	41
5	−4	748	757
5	−3	**	73
5	−2	185	−169
5	−1	89	−64
5	0	75	−49
5	1	**	56
5	2	370	−352
5	3	217	220
5	4	**	30
5	5	**	44
6	−10	**	128
6	−9	142	−163
6	−8	229	213
6	−7	**	74
6	−6	75	37
6	−5	106	72
6	−4	150	155
6	−3	**	16
6	−2	188	−186
6	−1	**	11
6	0	**	70
6	1	209	−189
6	2	240	227
6	3	**	18
6	4	**	67
7	−9	302	297
7	−8	141	−145
7	−7	141	107
7	−6	278	−261
7	−5	145	150
7	−4	88	71
7	−3	350	−341
7	−2	197	−189
7	−1	131	−86
7	0	125	138
7	1	125	−137
7	2	**	57
7	3	236	219
7	4	130	111
8	−8	337	330
8	−7	195	−218
8	−5	147	−186
8	−4	263	−260
8	−3	**	40
8	−2	192	−173
8	−1	**	62
8	0	227	−194
8	1	194	181
8	2	**	56
8	3	117	85
8	4	**	19
9	−10	**	116
9	−9	207	195
9	−8	175	197
9	−6	144	−178
9	−5	**	25
9	−4	221	−243
9	−3	246	−253
9	−2	125	105
9	−1	**	19
9	0	265	258
9	1	157	−101
9	2	141	102
9	3	**	10
9	4	**	28
10	−10	**	25
10	−8	**	52
10	−7	190	−204
10	−6	**	15
10	−5	244	−226
10	−4	**	47
10	−3	**	59
10	−2	**	20
10	−1	**	111
10	0	**	8
10	1	301	281
10	2	**	7
10	3	**	93
11	−9	108	−107
11	−7	107	−8
11	−8	**	57
11	−5	**	26
11	−4	173	−179
11	−3	141	130
11	−2	217	189
11	−1	260	259
11	0	180	171
11	1	**	2
11	2	179	155
11	3	**	34
12	−8	223	−217
12	−7	165	−159
12	−6	**	70
12	−5	114	−135
12	−4	171	165
12	−3	114	−99
12	−2	337	305
12	−1	152	127
12	0	213	194
12	1	173	137
12	2	**	12
13	−8	**	83
13	−7	211	−213
13	−6	165	−145
13	−5	**	8
13	−4	240	−216
13	−3	243	216
13	−2	**	39
13	−1	203	149
13	0	**	45
13	1	**	33
13	2	179	143
H = 7			
0	−9	445	−471
0	−8	**	0
0	−7	96	−128
0	−6	**	0
0	−5	**	386
0	−2	**	0
0	−1	564	521
0	0	**	0
0	1	**	96
0	2	**	0
0	3	**	55
0	4	**	0
1	−11	**	90
1	−10	244	−296
1	−9	**	24
1	−8	84	−132
1	−7	**	66
1	−6	**	97
1	−5	**	10
1	−2	124	−113
1	−1	86	−72
1	0	174	160
1	1	**	104
1	2	**	98
1	3	**	18
1	4	**	78
2	−11	**	30
2	−10	132	−142
2	−9	105	−129
2	−8	**	62
2	−7	**	12
2	−6	63	117
2	−5	135	215
2	−2	104	109
2	−1	115	103
2	0	220	−186
2	1	183	−147
2	2	92	−37
2	3	**	49
3	−10	**	8
3	−9	**	54
3	−8	**	22
3	−7	106	167
3	−6	**	8
3	−5	160	265
3	−4	**	12
3	−3	**	131
3	−2	**	28
3	−1	**	61
3	0	**	16
3	1	299	−259
3	2	130	−109
3	3	**	53
4	−10	**	49
4	−9	102	139
4	−8	112	156
4	−7	**	33
4	−6	211	271
4	−5	**	74
4	−4	286	261
4	−3	**	38
4	−2	**	3
4	−1	137	−130
4	0	223	−177
4	1	**	6
4	2	155	−127
4	3	**	39
5	−10	**	137
5	−9	94	25
5	−8	101	160
5	−7	129	193
5	−6	77	54
5	−5	240	244
5	−4	182	−181
5	−3	111	85
5	−2	**	50
5	−1	**	51
5	0	**	24
5	1	243	−197
5	2	**	66
5	3	**	6
6	−9	169	202
6	−8	**	9
6	−7	99	89
6	−6	**	10
6	−5	167	−172
6	−4	171	165
6	−3	165	−142
6	−2	**	14
6	−1	**	61
6	0	95	−62
6	1	161	108
6	2	**	52
6	3	**	119
7	−10	167	210
7	−8	139	138
7	−7	193	−250
7	−6	**	41
7	−5	86	−53
7	−4	282	−280
7	−3	145	−156
7	−2	98	−95
7	−1	**	39
7	0	**	82
7	1	**	12
7	2	200	160
7	3	**	41
8	−9	226	247
8	−8	115	−169
8	−6	210	−239
8	−5	107	−113
8	−4	185	−174
8	−3	259	−227
8	−2	**	6
8	−1	243	−227
8	0	**	34
8	1	**	57
8	2	189	156
9	−9	**	10
9	−8	**	30
9	−7	166	−196
9	−6	143	127
9	−5	142	−96
9	−4	245	−226
9	−3	**	19
9	−2	151	−126
9	−1	129	−73
9	0	174	152
9	1	219	182
9	2	**	54
10	−9	**	10
10	−7	**	41
10	−6	102	−107
10	−5	**	25
10	−4	103	−83
10	−3	**	25
10	−2	143	104
10	−1	**	65
10	0	195	169
10	1	123	85
10	2	**	36

TABLE II

ATOMIC AND THERMAL PARAMETERS FOR DICHLOROBIS(4-METHYLPYRIDINE 1-OXIDE)COPPER(II), YELLOW MODIFICATION[a]

Atom	x	y	z	B or B_{11}[b]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	0.0274 (2)	0.07510 (6)	0.0752 (1)	3.71 (2)	3.4 (2)	3.77 (4)	−0.1 (1)	4.7 (1)	−0.5 (1)
Cl(1)	0.3026 (3)	0.0568 (1)	0.2700 (3)	3.2 (1)	5.5 (2)	5.0 (2)	−0.2 (2)	1.6 (2)	−0.8 (2)
Cl(2)	0.0010 (4)	0.1716 (1)	−0.0409 (3)	4.8 (1)	4.2 (1)	6.4 (2)	0.9 (2)	6.8 (3)	1.9 (2)
O(1)	0.1182 (9)	0.0209 (3)	−0.0423 (7)	6.1 (4)	3.2 (3)	5.2 (4)	−2.1 (5)	9.3 (8)	−1.2 (6)
O(2)	−0.1552 (9)	0.0999 (3)	0.1575 (7)	3.3 (3)	4.9 (3)	4.3 (4)	−2.2 (5)	4.5 (6)	−3.1 (6)
N(1)	0.2113 (12)	0.0469 (4)	−0.1185 (8)	4.5 (4)	3.2 (3)	3.7 (4)	−0.2 (7)	6.0 (9)	−0.2 (6)
N(2)	−0.1083 (10)	0.1375 (4)	0.2692 (8)	2.4 (3)	3.3 (5)	3.6 (4)	−0.1 (6)	0.3 (7)	−0.4 (6)
C(2)	0.1218 (14)	0.0445 (5)	−0.2521 (11)	4.0 (5)	3.8 (5)	4.4 (6)	0.3 (9)	4.3 (1.1)	0.7 (9)
C(3)	0.2184 (14)	0.0689 (5)	−0.3312 (10)	3.9 (5)	4.8 (6)	5.0 (6)	0.4 (9)	5.0 (1.1)	2.6 (1.0)
C(4)	0.4049 (14)	0.0959 (5)	−0.2729 (10)	3.7 (5)	4.6 (6)	3.4 (5)	0.7 (8)	4.3 (1.0)	2.4 (8)
C(5)	0.4901 (14)	0.0983 (5)	−0.1332 (11)	3.4 (5)	3.5 (5)	5.2 (6)	−0.2 (8)	5.3 (1.1)	0.5 (9)
C(6)	0.3915 (13)	0.0718 (5)	−0.0543 (10)	3.1 (4)	2.8 (5)	5.3 (6)	−1.5 (8)	4.5 (1.0)	−1.2 (9)
C(M1)	0.5166 (16)	0.1228 (6)	−0.3557 (12)	6.2 (6)	6.8 (8)	5.9 (6)	−1.8 (1.1)	8.0 (1.3)	2.9 (1.1)
C(8)	0.0367 (13)	0.1827 (5)	0.3048 (10)	2.8 (5)	3.0 (5)	5.1 (6)	−0.5 (8)	3.1 (1.0)	0.2 (9)
C(9)	0.0744 (15)	0.2204 (5)	0.4198 (10)	3.9 (5)	4.1 (6)	3.5 (6)	0.6 (9)	1.4 (1.1)	−1.5 (9)
C(10)	−0.0402 (15)	0.2131 (5)	0.4945 (10)	4.1 (5)	3.6 (5)	3.1 (5)	0.7 (9)	2.5 (1.1)	−0.2 (8)
C(11)	−0.1908 (14)	0.1668 (5)	0.4542 (10)	4.4 (5)	3.9 (5)	2.8 (5)	−1.1 (9)	2.0 (1.1)	−0.1 (8)
C(12)	−0.2215 (13)	0.1289 (5)	0.3417 (9)	3.6 (5)	4.3 (5)	2.6 (5)	1.4 (8)	3.3 (1.0)	1.1 (8)
C(M2)	0.0043 (16)	0.2536 (6)	0.6233 (11)	6.4 (7)	6.1 (8)	5.0 (6)	0.9 (1.0)	3.6 (1.3)	3.8 (1.1)
H(2)[c]	−0.023	0.024	−0.297	2.0					
H(3)	0.149	0.067	−0.438	2.0					
H(5)	0.632	0.121	−0.086	2.0					
H(6)	0.458	0.071	0.053	2.0					
H(8)	0.124	0.190	0.244	2.0					
H(9)	0.194	0.256	0.451	2.0					
H(11)	−0.284	0.160	0.511	2.0					
H(12)	−0.337	0.092	0.311	2.0					

[a] Numbers in parentheses are estimated standard deviations of the last significant digit. [b] Anisotropic thermal parameters have the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [c] Hydrogen atom parameters were used to calculate structure factors but they were not refined.

$0.456x - 0.270y + 0.848z - 4.710 = 0$. The chlorine atom Cl(2) is 32° out of the plane, which leaves the atom 1.19 Å below the basal plane. The Cl(1)–Cu–Cl(2) angle is 119.8°. This angle is greater than would be expected from Cl–Cl repulsion. The copper ion is displaced above the basal plane toward the apical Cl(1) position by 0.44 Å.

The geometrical distortion about the copper ion

TABLE III

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (DEG) FOR DICHLOROBIS(4-METHYLPRYIDINE 1-OXIDE)COPPER(II), YELLOW MODIFICATION[a]

Cu–Cl(1)	2.354 (3)	N(2)–C(8)	1.340 (10)
Cu–Cl(2)	2.258 (3)	N(2)–C(12)	1.346 (9)
Cu–O(1)	1.957 (6)	C(8)–C(9)	1.386 (14)
Cu–O(1′)	2.153 (6)	C(9)–C(10)	1.371 (11)
Cu–O(2)	1.925 (5)	C(10)–C(11)	1.384 (12)
O(1)–N(1)	1.349 (9)	C(11)–C(12)	1.374 (13)
N(1)–C(2)	1.348 (14)	C(12)–C(M2)	1.532 (15)
Cu–Cu	3.348 (2)	O(2)–C(2)	3.02 (1)
O(1)–O(1)	2.391 (7)	O(2)–N(1)	2.95 (1)
O(1)–O(2)	2.760 (9)	Cu–H(2)	3.10
Cl(1)–Cl(2)	3.990 (4)	Cu–H(8)	2.84
Cl(1)–O(1)	3.216 (7)	Cl(1)–H(8)	2.89
Cl(1)–O(2)	3.255 (5)	Cl(1)–H(2)	2.71
Cl(2)–O(1)	3.116 (6)	Cl(1)–H(6)	2.97
Cl(2)–O(2)	3.117 (6)	Cl(1)–H(26)	2.62
N(1)–C(6)	1.347 (10)	Cl(2)–H(8)	2.89
C(2)–C(3)	1.382 (12)	Cl(22)–H(9)	2.66
C(3)–C(4)	1.393 (11)	O(24)–H(5)	2.55
C(4)–C(5)	1.404 (15)	O(24)–H(6)	2.72
C(5)–C(6)	1.407 (12)	Cl(24)–H(5)	2.77
C(4)–C(M1)	1.514 (13)	Cl(24)–H(43)	2.66
O(2)–N(2)	1.349 (10)	C(M2)–C(46)	3.41
Cl(1)CuCl(2)	119.8 (1)	N(1)C(2)C(3)	119.0 (7)
Cl(1)CuO(1)	96.1 (2)	C(2)C(3)C(4)	120.2 (9)
Cl(1)CuO(1)	103.0 (2)	C(3)C(4)C(5)	118.6 (8)
Cl(1)CuO(2)	98.5 (2)	C(3)C(4)C(M1)	121.9 (8)
Cl(2)CuO(1)	95.1 (2)	C(4)C(5)C(6)	120.5 (7)
Cl(2)CuO(1′)	136.3 (3)	C(5)C(6)N(1)	117.2 (9)
Cl(2)CuO(2)	96.0 (2)	CuO(2)N(2)	123.9 (4)
O(1)CuO(1)	71.0 (2)	O(2)N(2)C(8)	123.0 (7)
O(1)CuO(2)	154.1 (5)	C(12)N(2)C(8)	121.1 (8)
O(2)CuO(1)	85.0 (2)	N(2)C(8)C(9)	119.8 (7)
CuO(1)Cu	109.0 (2)	C(8)C(9)C(10)	120.2 (8)
CuO(1)N(1)	123.6 (5)	C(9)C(10)C(11)	118.8 (9)
O(1)N(1)C(2)	118.5 (6)	C(9)C(10)C(M2)	120.2 (9)
O(1)N(1)C(6)	117.0 (7)	C(10)C(11)C(12)	119.7 (7)
C(6)N(1)C(2)	124.5 (7)	C(11)C(12)N(2)	120.4 (7)

[a] Figures in parentheses are estimated standard deviation of the last significant digit.

arises as a consequence of several factors. These include the compressed O(1)–Cu–O(1′) bond angle of 71°, due to oxygen bridging, and the expanded Cl(2)–Cu–O bond angles of 95 and 96° which arise from the interaction of Cl(2) with each of the ring systems. The Cl(2) atom is distorted from the basal plane by an interaction with the ortho ring hydrogen attached to C(8). The interaction distance is 2.89 Å. The two chlorine atoms achieve positions of minimum steric interaction consistent with the fivefold geometry.

The approximate square-based pyramidal geometry about the copper ion has been observed for the 1:1 pyridine *N*-oxide complex[15] and the 2:3 2-methylpyridine 1-oxide complex.[17] Both complexes have chloride ions occupying the apical site of the pyramid. The Cu–Cl bond lengths of 2.836 and 2.635 Å may be compared to the 2.354-Å distance in this complex. This is a significant structural difference and indicates a much stronger coordination.

The one Cu–O bond length of 2.153 Å in the bridging system is significantly longer than Cu–O bond lengths observed in the bridged complexes of pyridine 1-oxide (1.98 and 2.04 Å)[15] and 2-methylpyridine 1-oxide (1.98 and 2.01 Å).[17] In the bridging system the Cu–O(1)–Cu angle is 109.0° and the O(1)–Cu–O(1′) angle is 71.0°. The oxygen atoms are compressed to within 2.39 Å of each other and the Cu–Cu distance is 3.348 Å. These angles and distances are comparable to those observed in the 1:1 pyridine 1-oxide complex[15] where the Cu–O–Cu angle is 107.3°, the O–Cu–O angle is 72.2°, and the O–O and Cu–Cu distances are 2.37 and 3.245 Å, respectively. The greater Cu–Cu separation for the complex reported here is due to the elongated Cu–O bond.

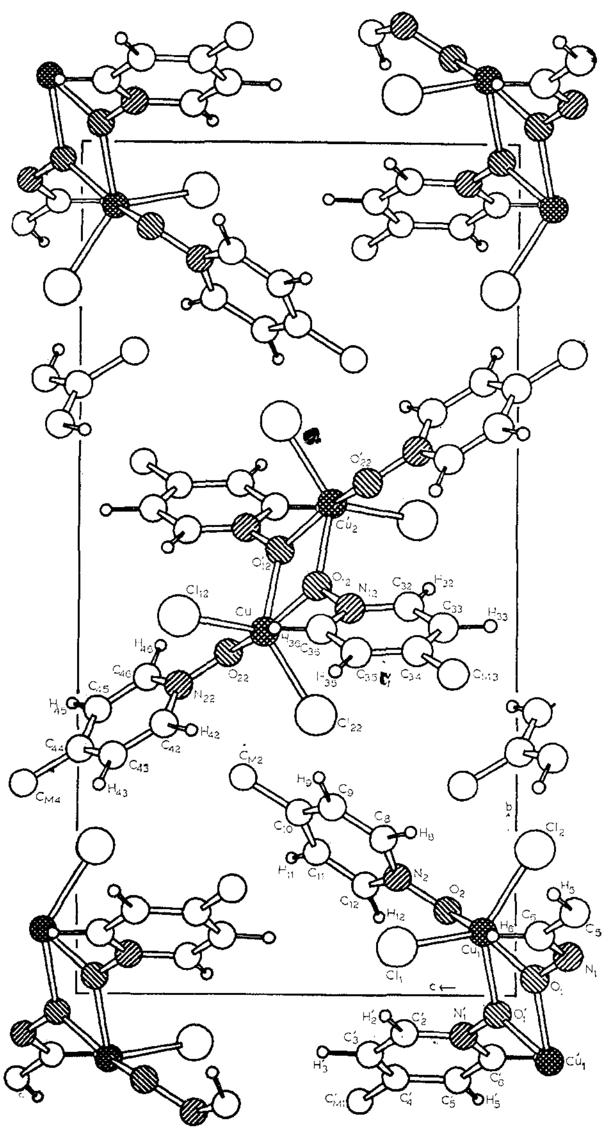

Figure 1.—Projection of the structure of dichlorobis(4-methylpyridine 1-oxide)copper(II) onto the *bc* plane.

The distorted copper–oxygen bridging system is consistent with a reduction in the efficiency of the superexchange mechanism. The elongation of the Cu–O bond reduces the overlap of the magnetic orbitals and leads to a reduction in the magnitude of the exchange interaction. An insufficient quantity of sample has prevented an accurate determination of the magnetic moment; however, the magnetic moment of the corresponding bromide complex is reported to be 1.33 BM.[8] A recent communication has described the structure of the complex dibromobis(pyridine 1-oxide)copper(II)[20] which has a magnetic moment of 1.4 BM at room temperature.[7] The bridging system in this complex is similar to the one reported here. The Cu–O bond lengths in the bridging system are 1.975

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[20] A. D. Mighell, C. W. Reimann, and A. Santoro, *Chem. Commun.*, 204 (1970).

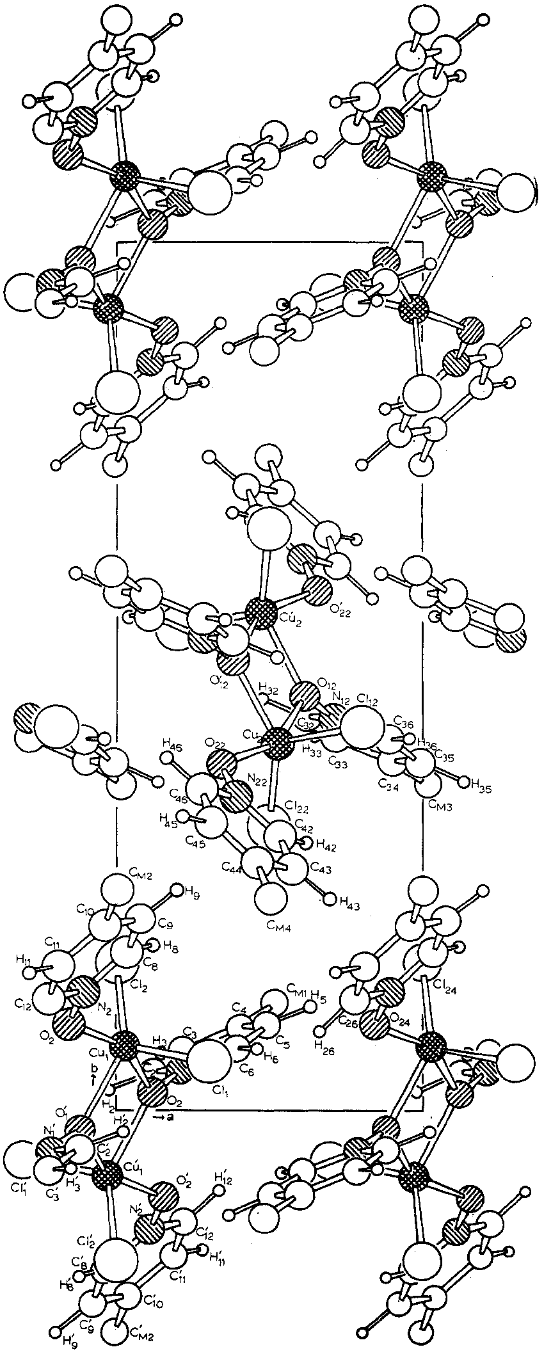

Figure 2.—Projection of the structure of dichlorobis(4-methylpyridine 1-oxide)copper(II) onto the *ab* plane.

and 2.162 Å. On the basis of the similarities of the two bridging systems, the yellow modification should have an intermediate moment. The increase in magnetic moment, the elongation of the Cu–O bond, and the short Cu–Cl(1) distance are all intimately related.

A unit weighted least-squares plane fitted to the bridging *N*-oxide ligand gives the equation $0.429x + 0.903y - 0.007z - 0.032 = 0$. The average deviation of the six ring atoms from the plane is 0.006 Å, and all atoms lie within one standard deviation of the plane. The ring is planar within experimental error. The oxygen atom is 0.04 Å from the ring plane and the N–O bond makes an angle of 1.7° with the plane. This distortion is consistent with that observed in the 1:1 pyridine 1-oxide complex, where the angle is 1.4°. The methyl carbon atom lies within the plane of the ring. All of the C–C bond distances, which average 1.396 Å, are within one standard deviation of the expected value of 1.395 Å. The N–C distances of 1.347 and 1.348 Å are normal.

The dihedral angle between the normal to the copper–oxygen bridging plane and the normal to the bridging pyridine ring plane is 57.6°. This is smaller than the 70.0° angle or the 89° angle observed in the 1:1 pyridine 1-oxide and the 2:3 2-methylpyridine 1-oxide complexes. The orientation of the ring is determined by nonbonding interactions with the apical chlorine atom Cl(1), the oxygen atom of the second *N*-oxide ligand O(2), the oxygen atom O(24), and chlorine atom Cl(24). The two ortho hydrogens on the ring are pointing toward the apical chloride ions, but the ring does not achieve perpendicular orientation due to interactions with the adjacent dimer. The N–O bond makes an angle of 14.1° with the bridging plane.

A unit weighted least-squares plane fitted to the nonbridging *N*-oxide ligand yields the equation $-0.457x + 0.704y - 0.544z - 1.304 = 0$. The average deviation for the six ring atoms from the plane is 0.006 Å, and the ring is planar within experimental error. The oxygen atom is 0.038 Å out of the plane and the N–O bond makes an angle of 1.6° with the ring plane. The methyl carbon is 2.1° out of the ring plane. The average C–C bond length of 1.379 Å is within experimental error of the expected value, and the average N–C bond length of 1.343 Å also is normal.

Figures 1 and 2 show the dimer units are not associated by intermolecular interactions between chlorine and copper atoms. The short nonbonding distances given in Table III indicate the packing restrictions imposed by interactions between the atoms. The dimer units are held in the crystal lattice by van der Waals forces.

The method of preparing the 2:1 trans square-planar complex from the 1:1 4-methylpyridine 1-oxide complex, together with the structure of the yellow modification, indicate the yellow modification may be an intermediate in the formation of the thermodynamically stable trans square-planar form. Although the structure of the 1:1 complex has not been determined, magnetic studies indicate the structure is similar to that of the 1:1 pyridine 1-oxide complex.[21] In solution, each copper ion in the 1:1 dimer can be considered to have a cis square-planar geometry. Additional ligand initially adds to the bridged square-planar structure in the trans configuration. The geometry about each copper ion can be thought of as a square-based pyramid with the extra *N*-oxide ligand in the apical site. The *N*-oxide ligand is a stronger ligand than the chloride ion, and the complex tends to rearrange with a chloride ion ending up in the apical site. Whether this is a concerted or a two-step process is not known. The Cu–O bond cis to the added *N*-oxide ligand elongates and breaks. This probably is assisted by steric interactions. The resulting product is the 2:1 trans square-planar complex. When the *N*-oxide ligand contains methyl groups in the ortho positions, the ligand may remain at the apical site due to steric interactions. When either bridge bond breaks, a

[21] M. R. Kidd and W. H. Watson, *Inorg. Chem.*, **8**, 1886 (1969).

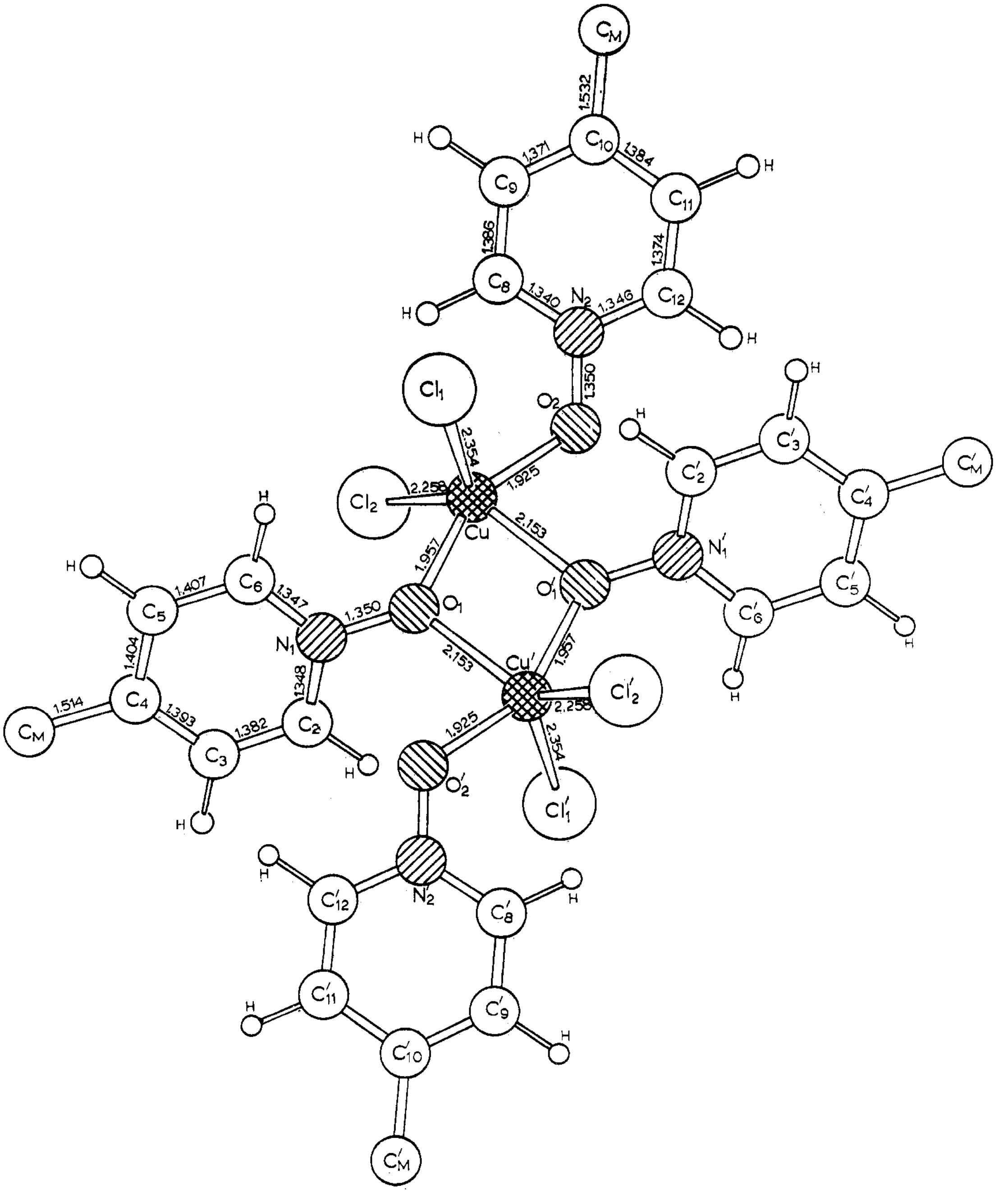

Figure 3.—Projection of the structure of dichlorobis(4-methylpyridine 1-oxide)copper(II) onto the plane of the copper–oxygen bridge.

structure intermediate between tetrahedral and cis square-planar is obtained. If this material crystallizes rapidly enough, the yellow 2:1 monomer is obtained. In solution the complex rearranges to the more stable trans configuration. We postulate the yellow 2:1 dimer molecule and the yellow 2:1 monomer molecule are both intermediates in the formation of the trans isomer. The two forms may be identified by the magnitudes of their magnetic moments.

Acknowledgment.—We wish to express our appreciation to the National Science Foundation (GP-9537) for their finanical support and Texas Christian University Research Foundation for the equipment.