through the sulfur S(2) atom. The optically excited electron is assumed to be spread over both the copper atoms and the intervening bridging sulfur atom, in agreement with McConnell and Davidson.[15] This fact might also explain the particularly low B factor of sulfur S(2).

The effect of these different functions of the thiocyanate groups on the interatomic distances and on the valence angles is shown in Table V.

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(15) H. McConnell and N. Davidson, *J. Am. Chem. Soc.*, **72**, 3168 (1950).

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The Crystal and Molecular Structure of the Yellow Form of Dichlorobis(2,6-lutidine N-oxide)copper(II)

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The crystal and molecular structure of dichlorobis(2,6-lutidine N-oxide)copper(II), $(C_7H_9NO)_2CuCl_2$, has been determined by single-crystal X-ray diffraction techniques. The crystals belong to the orthorhombic space group $Pna2_1$ with unit cell dimensions a = 13.88 (1), b = 7.677 (5), and c = 16.23 (1) Å. There are four molecules per unit cell, and the observed and calculated densities are 1.49 and 1.48 g/cm^3, respectively. The equiinclination Weissenberg technique was used to record the intensities of 981 nonzero reflections. Positional and isotropic thermal parameters were refined by least-squares methods to a conventional R factor of 8.3%. The molecules are monomeric, and the coordination around the central Cu ion is intermediate between tetrahedral and *cis* square planar. The Cu–Cl distances are 2.221 (4) and 2.247 (4) Å while the Cu–O distances are 1.97 (1) and 1.93 (1) Å.

Introduction

Complexes of Cu(II) compounds and various N-oxide ligands have been the subject of a number of studies. Most of the ligands form complexes in both a 1:1 and a 2:1 ligand-to-metal ratio;[1–7] however, complexes with other ligand-to-metal ratios also occur. Most 1:1 complexes have low magnetic moments at room temperature, and an oxygen-bridged dimeric structure was proposed.[8,9] A single-crystal study of dichloro(pyridine N-oxide)copper(II) showed the structure to be composed basically of oxygen-bridged dimeric units.[10,11] The dimeric units are chlorine bridged to adjacent dimers to form infinite chains, and the geometry around the Cu(II) ion is square pyramidal[12] with the apical chloride bond elongated to 2.836 Å. The two bridging oxygen atoms form an edge of the square base, and the apical chlorides are *trans* with respect to the joined basal planes. The low magnetic moments of the 1:1 complexes are rationalized in terms of a superexchange mechanism.

The structure and properties of the 2:1 complexes have not been studied as extensively as the 1:1 complexes. The 2:1 complexes in general are monomeric and have normal magnetic moments although both low-moment and normal-moment dimeric structures are known. The low-moment dimers are similar to the 1:1 complexes with the extra pyridine N-oxide ligands in the fifth coordination site rather than a bridging chloride ion. The normal-moment dimers are similar except one bridging oxygen is apical and the other basal. If the magnetic electrons are restricted to orbitals of approximately $d_{x^2-y^2}$ symmetry, superexchange does not occur because the orbitals of the magnetic electrons do not overlap significantly at the shared oxygen atoms.

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

(2) Y. Muto and H. B. Jonassen, *Bull. Chem. Soc. Japan*, **39**, 58 (1966).

(3) W. E. Hatfield and J. C. Morrison, *Inorg. Chem.*, **5**, 1390 (1966).

(4) M. R. Kidd, R. S. Sager, and W. H. Watson, *ibid.*, **6**, 946 (1967).

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

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

(7) R. Whyman, D. B. Copley, and W. E. Hatfield, *J. Am. Chem. Soc.*, **89**, 3135 (1967).

(8) C. M. Harris, E. Kokot, S. L. Lenzer, and T. N. Lockyer, *Chem. Ind.* (London), 651 (1962).

(9) M. Kubo, Y. Kuroda, M. Kishita, and Y. Muto, *Australian J. Chem.*, **16**, 7 (1963).

(10) H. L. Schäfer, J. C. Morrow, and H. M. Smith, *J. Chem. Phys.*, **42**, 504 (1965).

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

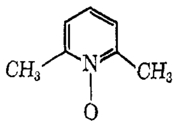
(12) R. S. Sager, R. J. Williams, and W. H. Watson, submitted for publication.

The green form of dichlorobis(4-picoline N-oxide)-copper(II) belongs to space group $P2_1/c$ with two molecules per unit cell.[4] The complexes must therefore be centrosymmetric and like ligands are required to be *trans*. A recent refinement of the structure in this laboratory confirms the *trans*-square-planar molecular conformation and the absence of any intermolecular coordination between Cu(II) ions which are separated by 6.29 Å.

The structure of the yellow form of the 2:1 complexes must be determined before the chemistry of these systems can be understood. We have completed a three-dimensional X-ray structural analysis of the yellow form of dichlorobis(2,6-lutidine N-oxide)copper(II), and we wish to report the details of the structure.

Experimental Section

The 2,6-lutidine N-oxide (I), obtained from Reilly Tar &



I

Chemical Corp., was purified by vacuum distillation. Copper(II) chloride obtained from Allied Chemical Corp. was used without further purification. Ethanol solutions of the ligand and copper(II) chloride were prepared in which the molar ratio of N-oxide ligand to copper was 2:1. The solutions were mixed, and the complex precipitated within a few minutes. The complex was recrystallized from an ethanol solution, and a mixture of the yellow and green crystalline modifications were obtained. A crystal of the yellow form with dimensions 0.63 × 0.17 × 0.16 mm was selected for all intensity measurements. The systematic absences observed on precession and Weissenberg photographs ($0kl$ absent for $k + l$ odd and $h0l$ absent for h odd) are consistent with both the centric space group Pnma, k and l interchanged, and the acentric space group $Pna2_1$. A positive pyroelectric test and Rogers' $N(z)$ test[13] indicated the crystal belonged to the acentric space group. This choice was justified by the successful refinement of the structure.

The unit cell dimensions were determined using an a-axis layer line and the $0kl$ Weissenberg photographs which were calibrated with superimposed NaCl powder lines, a = 5.6402 Å. The cell dimensions are a = 13.89 (1), b = 7.677 (5), and c = 16.23 (1) Å. The errors are standard deviations obtained from a manual calculation of the cell edges from a number of reflections. The density of 1.49 (3) g/cm^3 was determined by the flotation method using a mixture of $CHCl_3$ and CCl_4. The calculated density for four molecules per unit cell is 1.48 g/cm^3. Three-dimensional intensity data were collected at room temperature around the a axis for levels 0 through 8 using the multiple-film (three films) equiinclination Weissenberg technique. Nickel-filtered copper radiation [λ(Cu Kα) 1.54178 Å] was used. The intensities of 981 nonzero reflections were estimated visually by comparison with a calibration strip. Lorentz-polarization corrections were applied to the observed intensities, and the data were corrected for absorption using Bond's values[14] for a cylinder with μ = 48.6 cm^{-1} and μR = 0.428. The maximum error in any structure factor due to the absorption approximation is less than 2%.

The computer programs used for the structure determination are listed in ref 15.

Structure Determination

Scale factors obtained from Wilson plots were used initially to scale the nine levels together. The x and y coordinates of the copper(II) ions were determined from a three-dimensional Patterson map. The z coordinate of one copper atom was chosen arbitrarily to be 0.2500. Peaks tentatively identified as copper–chloride vectors appeared to have approximately the same x coordinate as the copper ion. Structure factors were calculated with these coordinates using the atomic scattering factors of Cromer and Waber.[16] Those for Cu^{2+} and Cl^- were corrected only for the real part of the anomalous dispersion.[17] An R factor of 46% was obtained where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. Because of the large R factor, an $h0l$ Fourier map was calculated using only the phases of the copper positions. Peaks identified as chloride ions were found to lie at ±0.053 Å in the x direction with respect to the copper positions. Structure factor calculations gave an R value of 30%, and the phases were used to calculate a three-dimensional Fourier map. The coordinates of two oxygen atoms and one carbon atom were assigned from this Fourier map. A three-dimensional Fourier map was calculated using the phases from the additional atoms, and approximate positions were obtained for all atoms except hydrogen. The contributions of the hydrogen atoms have been ignored. A structure factor calculation indicated an R value of 20% at this stage.

A preliminary full-matrix, least-squares refinement of three cycles was carried out on scale, positional, and isotropic thermal parameters. A version of the Busing and Levy program which had been modified for the IBM 7094 was used, and the quantity $\Sigma w(|F_o| - |F_c|)^2$ was minimized. The weighting factors in the initial calculation were given the value of unity. This is satisfactory only for preliminary refinement and scaling and is not acceptable for a final set of parameters. The R factor dropped to 9.9%. Three additional refinement cycles were carried out on positional and thermal parameters using the IBM 360 Model 50. This program also minimized the quantity $\Sigma w(|F_o| - |F_c|)^2$, but a modified Hughes[18,19] weighting scheme was used where w = 1.00 for $F_o < 4F_{\min}$ and $w = 4F_{\min}/F_o$

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(13) D. Rogers, *Acta Cryst.*, **3**, 455 (1950).

(14) "International Tables for X-Ray Crystallography," Vol. II, The Kynoch Press, Birmingham, England, 1959, p 295.

(15) W. H. Watson and R. J. Williams, Data Reduction Program (IBM 1620); D. Hall and R. Shiono, General Three-Dimensional Fourier Synthesis Program (IBM 1620, 8.4.006); D. Hall and R. Shiono, Alphabetic Plotting Program for Output of Fourier Synthesis Program (IBM 1620, 8.4.007); R. Shiono, Structure Factor Calculations in X-Ray Crystallography (IBM 1620, 8.4.004); W. R. Busing and H. A. Levy, Full-Matrix Least Squares (Modified for IBM 7094); Y. Okaya, Full-Matrix Least-Squares Refinement (Modified for IBM 360/50); Y. Okaya, Standard Deviation Program for Least-Squares Matrix (IBM 360/50); Y. Okaya, Bonds and Angles Program (IBM 360/50); H. G. Norment, Least-Squares Line and Plane Fitter (IBM (1620).

(16) D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

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

(18) E. W. Hughes, *J. Am. Chem. Soc.*, **63**, 1737 (1941).

(19) C. N. Caughlan, H. M. Smith, and K. Watenpaugh, *Inorg. Chem.*, **5**, 2131 (1966).

Table I

Observed and Calculated Structure Factors for $(C_7H_9NO)_2CuCl_2$

l	k	|10Fo|	|10Fc|
h = 0			
4	0	372	244
6	0	424	430
8	0	664	719
10	0	953	972
12	0	764	754
14	0	197	185
18	0	248	211
20	0	288	236
1	1	89	110
3	1	613	479
5	1	1187	1206
7	1	297	287
9	1	845	845
11	1	437	409
15	1	203	193
17	1	126	101
19	1	253	181
0	2	395	296
2	2	1288	1016
4	2	1414	1440
6	2	795	786
8	2	342	319
10	2	157	173
12	2	239	268
14	2	601	547
16	2	339	306
20	2	75	75
1	3	591	547
3	3	674	610
5	3	1181	1221
7	3	849	835
9	3	121	124
11	3	128	101
13	3	402	341
15	3	451	427
17	3	226	225
19	3	96	107
0	4	610	601
2	4	419	370
4	4	418	380
6	4	132	110
8	4	204	197
10	4	447	431
12	4	275	264
14	4	114	108
16	4	108	102
1	5	992	977
3	5	597	566
5	5	258	243
7	5	350	344
9	5	549	548
11	5	412	397
13	5	242	219
17	5	92	96
0	6	125	133
2	6	164	162
4	6	190	198
6	6	206	167
8	6	173	164
10	6	267	221
12	6	173	133
14	6	106	125
16	6	79	61
1	7	183	188
3	7	356	308
5	7	357	332
7	7	259	232
9	7	181	182
11	7	114	107
0	8	132	84
2	8	160	160
4	8	190	189
6	8	226	228
8	8	165	169
3	9	106	129
h = 1			
0	1	386	399
1	1	1415	1448
2	1	1116	1179
3	1	1080	1072
4	1	398	343
5	1	633	717
6	1	247	265
7	1	588	608
8	1	534	528
9	1	559	535
10	1	251	254
11	1	443	416
12	1	182	213
13	1	242	236
14	1	125	173
15	1	223	196
17	1	187	161
18	1	89	54
19	1	120	130
20	1	65	61
0	2	80	90
1	2	1015	974
2	2	130	122
3	2	269	283
4	2	61	49
5	2	440	389
6	2	225	221
7	2	297	259
8	2	439	416
9	2	86	65
10	2	406	372
11	2	99	76
12	2	196	222
13	2	128	126
14	2	114	99
15	2	155	179
16	2	155	169
18	2	147	148
20	2	80	86
1	3	301	285
2	3	100	135
3	3	592	602
4	3	71	71
5	3	488	473
6	3	311	317
7	3	242	277
8	3	169	184
9	3	139	147
10	3	160	161
11	3	185	188
12	3	109	60
13	3	285	212
14	3	130	162
15	3	231	218
16	3	102	70
17	3	106	116
0	4	474	431
1	4	194	212
2	4	471	479
3	4	273	272
4	4	725	728
5	4	313	308
6	4	657	674
7	4	199	209
8	4	264	347
9	4	160	47
10	4	130	132
11	4	106	89
12	4	292	285
14	4	319	293
16	4	150	181
1	5	179	196
2	5	42	75
3	5	216	209
4	5	111	90
5	5	142	170
6	5	152	148
7	5	168	189
9	5	219	191
11	5	131	155
13	5	117	96
17	5	74	76
0	6	722	736
1	6	200	210
2	6	455	493
3	6	147	162
4	6	174	212
5	6	127	128
6	6	174	202
7	6	149	152
8	6	342	317
9	6	115	101
10	6	308	320
11	6	100	66
12	6	153	184
1	7	147	148
3	7	111	96
5	7	115	105
7	7	143	140
9	7	175	189
11	7	120	125
1	8	108	97
2	8	130	144
4	8	174	187
6	8	120	131
3	9	102	125
4	9	86	66
5	9	137	188
7	9	103	138
h = 2			
3	0	657	808
4	0	287	306
5	0	173	184
6	0	656	647
7	0	332	280
8	0	1005	837
9	0	461	473
10	0	846	845
11	0	506	548
12	0	352	311
13	0	268	274
14	0	104	76
15	0	127	137
16	0	161	157
17	0	95	59
18	0	203	216
19	0	104	110
20	0	140	155
0	1	624	715
1	1	879	943
2	1	521	453
3	1	217	265
4	1	349	342
5	1	749	737
6	1	499	468
7	1	205	199
8	1	569	544
9	1	632	590
10	1	224	247
11	1	338	328
12	1	134	145
13	1	104	104
14	1	110	101
15	1	194	193
16	1	94	95
18	1	85	72
19	1	118	112
20	1	76	73
0	2	1473	1283
1	2	962	855
2	2	199	207
3	2	614	611
4	2	1055	1108
5	2	503	515
6	2	821	813
7	2	397	414
8	2	385	376
9	2	227	206
10	2	145	135
11	2	88	82
12	2	187	164
13	2	218	191
14	2	416	373
15	2	233	215
16	2	272	266
17	2	97	107
1	3	332	328
2	3	383	384
3	3	251	271
4	3	768	774
5	3	891	895
6	3	391	411
7	3	455	430
8	3	176	197
11	3	161	157
12	3	164	164
13	3	241	253
14	3	215	222
15	3	218	197
16	3	178	194
17	3	124	114
18	3	89	94
0	4	488	577
1	4	242	259
2	4	94	95
3	4	113	101
4	4	190	230
5	4	208	221
6	4	83	73
7	4	263	274
8	4	202	192
9	4	220	229
10	4	340	343
11	4	179	211
12	4	163	140
13	4	129	123
14	4	137	181
16	4	61	77
0	5	448	422
1	5	671	678
2	5	436	451
3	5	464	471
4	5	190	198
5	5	103	100
7	5	274	302
8	5	209	204
9	5	427	446
10	5	211	228
11	5	278	276
12	5	140	158
13	5	155	150
14	5	91	98
0	6	256	273
1	6	229	257
2	6	110	83
3	6	205	217
4	6	100	111
5	6	119	130
6	6	101	74
7	6	137	146
9	6	150	178
10	6	107	86
11	6	107	101
12	6	106	79
0	7	109	67
1	7	146	156
2	7	118	107
3	7	175	209
4	7	143	171
5	7	205	280
6	7	175	210
7	7	167	196
8	7	115	124
0	8	57	88
1	8	88	76
2	8	103	110
3	8	58	120
4	8	97	103
5	8	101	136
6	8	69	78
7	8	80	65
8	8	89	110
2	9	73	74
3	9	79	80
5	9	71	34
h = 3			
0	1	586	527
1	1	573	513
2	1	590	609
3	1	567	555
4	1	488	463
5	1	560	496
6	1	680	661
7	1	655	616
8	1	326	325
9	1	543	574
10	1	287	273
11	1	355	381
12	1	193	179
13	1	299	347
14	1	153	160
15	1	164	176
16	1	136	133
17	1	145	146
18	1	109	97
19	1	102	95
0	2	1206	1155
1	2	628	561
2	2	484	490
3	2	449	440
4	2	91	65
5	2	111	110
6	2	195	196
7	2	308	294
8	2	309	264
9	2	343	324
10	2	254	257
11	2	142	157
12	2	148	145
13	2	211	225
14	2	121	107
15	2	104	96
17	2	104	80
19	2	73	60
0	3	612	654
1	3	530	495
2	3	468	460
3	3	189	205
4	3	417	409
5	3	472	496
6	3	241	271
7	3	228	246
8	3	241	300
9	3	142	144
10	3	101	69
11	3	281	265
12	3	218	191
13	3	318	329
14	3	185	162
15	3	109	132
16	3	95	100
17	3	82	80
1	4	259	254
2	4	646	631
3	4	381	363
4	4	575	641
5	4	276	231
6	4	461	440
7	4	142	163
8	4	267	289
9	4	218	253
10	4	158	167
11	4	230	210
12	4	189	186
13	4	151	138
14	4	185	206
15	4	134	138
16	4	102	127
17	4	74	97
0	5	140	144
1	5	358	363
2	5	97	89
3	5	104	139
4	5	102	96
5	5	234	232
6	5	105	115
7	5	111	141
9	5	206	223
11	5	113	138
0	6	260	288
1	6	183	177
2	6	340	389
3	6	208	213
4	6	164	188
5	6	178	203
6	6	197	215
7	6	191	146
8	6	268	373
9	6	162	170
10	6	218	282
11	6	96	131
12	6	142	174
0	7	124	137
1	7	186	213
2	7	104	101
4	7	101	94
5	7	98	99
6	7	45	81
7	7	96	148
8	7	117	128
9	7	117	130
4	8	157	195
5	8	107	117
6	8	147	184
3	9	115	149
5	9	39	114
h = 4			
2	0	814	852
3	0	867	870
4	0	231	238
5	0	403	436
6	0	107	119
7	0	334	300
8	0	509	493
9	0	687	640
10	0	534	594
11	0	478	474
12	0	525	484
13	0	294	308
14	0	117	102
15	0	223	230
16	0	191	168
17	0	149	126
18	0	166	149
19	0	171	153
0	1	1035	1058
1	1	591	668
2	1	695	734
3	1	601	573
4	1	398	352
5	1	257	232
6	1	189	154
7	1	734	722
8	1	507	512
9	1	248	212
10	1	379	365
12	1	307	298
13	1	112	89
14	1	110	88
17	1	117	113
18	1	120	119
19	1	92	84
0	2	215	238
1	2	546	564
2	2	668	594
3	2	925	887
4	2	517	503
5	2	937	1008
6	2	307	338
7	2	693	620
8	2	356	354
9	2	233	272
11	2	193	183
12	2	356	337
13	2	354	330
14	2	240	214
15	2	280	276
16	2	129	118
17	2	176	198
19	2	68	61
0	3	255	247
1	3	270	290
2	3	480	475
3	3	525	516
4	3	584	609
5	3	303	164
6	3	695	664
7	3	211	196
10	3	127	129
11	3	245	231
12	3	191	189
13	3	211	210
14	3	245	222
15	3	111	173
16	3	165	186
17	3	97	90
18	3	100	112
0	4	443	421
1	4	919	921
2	4	527	486
3	4	473	443
4	4	107	91
6	4	201	220
7	4	215	210
8	4	265	228
9	4	362	406
10	4	119	85
11	4	217	265
13	4	179	169
15	4	92	82
0	5	399	415
2	5	379	380
3	5	289	274
4	5	354	340
5	5	221	182
6	5	188	166
7	5	391	192
8	5	263	254
9	5	273	278
10	5	379	406
11	5	171	182
12	5	248	258
13	5	129	102
14	5	141	159
15	5	78	80
16	5	89	93
0	6	105	33
1	6	208	218
2	6	109	100
6	6	136	150
7	6	107	68
8	6	104	59
9	6	136	142
11	6	97	102
13	6	87	76
1	7	110	105
2	7	196	192
4	7	249	321
5	7	105	72
6	7	320	341
7	7	139	118
8	7	193	205
9	7	107	114
11	7	78	95
12	7	85	91
0	8	119	121
1	8	102	75
2	8	110	122
3	8	174	202
5	8	141	171
7	8	119	130
9	8	89	79
0	9	94	128
2	9	87	111
3	9	70	63
5	9	68	68
h = 5			
0	1	317	366
1	1	133	114
2	1	624	617
3	1	287	223
4	1	546	555
5	1	111	82
6	1	293	272
7	1	93	74
8	1	500	441
9	1	193	197
10	1	402	393
11	1	226	230
12	1	328	318
13	1	99	108
14	1	299	288
16	1	224	232
18	1	133	147
0	2	175	182
1	2	677	672
2	2	457	425
3	2	582	514
4	2	171	166
5	2	562	567
6	2	395	297
7	2	466	441
8	2	168	161
9	2	280	259
10	2	108	104
11	2	248	242
14	2	102	88
17	2	84	57
0	3	375	430
1	3	91	91
2	3	637	650
3	3	357	345
4	3	531	541
5	3	206	211
6	3	551	452
7	3	133	147
8	3	240	255
9	3	155	222
10	3	286	107
11	3	233	202
12	3	177	149
13	3	49	57
14	3	109	83
15	3	104	104
1	4	393	380
2	4	273	253
3	4	328	333
4	4	244	262
5	4	449	400
6	4	173	155
7	4	311	344
9	4	255	268
10	4	126	131
11	4	213	196
12	4	115	98
13	4	235	211
14	4	102	113
15	4	146	149
16	4	91	86
17	4	79	106
18	4	46	[illegible]
0	5	95	94
1	5	140	155
3	5	228	229
4	5	175	148
6	5	47	87
7	5	219	237
8	5	117	67
11	5	120	117
13	5	108	131
0	6	233	250
1	6	242	251
2	6	104	124
3	6	213	227
4	6	164	148
5	6	177	191
6	6	142	175
7	6	173	180
8	6	111	114
9	6	197	195
10	6	135	169
11	6	122	160
12	6	93	107
13	6	108	156
15	6	87	116
0	7	168	175
1	7	155	158
2	7	160	168
3	7	124	134
4	7	106	109
5	7	120	135
6	7	131	145
7	7	120	125
8	7	99	91
9	7	91	93
1	8	117	148
2	8	111	171
3	8	124	143
4	8	111	85
5	8	133	163
7	8	95	117
0	9	66	70
2	9	75	86
4	9	68	91
5	9	75	95
h = 6			
1	0	510	541
2	0	439	473
3	0	284	297
4	0	280	329
5	0	126	156
6	0	390	392
7	0	466	391
8	0	546	519
9	0	451	401
11	0	463	475
12	0	288	334
13	0	468	447
14	0	124	115
15	0	217	181
16	0	126	115
17	0	123	165
18	0	124	122
19	0	145	171
0	1	451	391
1	1	436	437
2	1	375	388
3	1	737	767
4	1	444	471
6	1	268	276
7	1	461	484
8	1	148	147
9	1	227	205
10	1	268	256
11	1	244	252
12	1	109	141
13	1	275	259
14	1	178	164
0	2	161	175
1	2	468	420
2	2	783	759
3	2	397	401
4	2	256	249
5	2	529	546
6	2	236	276
7	2	402	434
8	2	358	372
9	2	317	306
11	2	324	286
12	2	270	241
13	2	245	211
14	2	134	121
15	2	190	179
16	2	104	126
17	2	117	129
18	2	95	105
0	3	300	281
1	3	143	156
2	3	454	423
3	3	429	431
4	3	607	641
5	3	107	69
6	3	495	519
7	3	405	412
8	3	353	328
9	3	148	167
10	3	185	179
11	3	170	170
12	3	148	174
13	3	161	158
14	3	158	156
16	3	107	113
17	3	97	100
18	3	65	57
0	4	124	104
1	4	188	224
2	4	405	421
3	4	205	209
4	4	229	207
5	4	270	286
6	4	183	177
7	4	268	246
8	4	246	223
9	4	192	189
11	4	117	133
12	4	241	241
14	4	124	112
16	4	95	96
0	5	366	332
1	5	136	150
2	5	283	289
3	5	163	180
4	5	234	198
5	5	107	107
6	5	141	119
7	5	280	290
8	5	309	286
9	5	158	136
10	5	185	137
12	5	217	211
14	5	131	142
16	5	104	89
0	6	153	132
1	6	185	195
2	6	226	218
3	6	178	173
4	6	141	118
11	6	102	96
12	6	102	89
14	6	75	55
0	7	205	188
1	7	114	114
2	7	226	219
3	7	149	131
4	7	200	204
5	7	153	136
6	7	112	118
7	7	100	115
8	7	95	123
9	7	87	88
10	7	114	129
12	7	87	94
1	8	92	109
3	8	95	104
5	8	148	170
7	8	114	127
0	9	87	117
2	9	78	99
h = 7			
0	1	466	473
1	1	175	168
2	1	115	121
3	1	239	216
4	1	308	365
5	1	329	290
6	1	441	444
7	1	251	272
8	1	421	421
9	1	205	177
10	1	390	352
11	1	191	142
12	1	352	347
14	1	331	232
16	1	221	143
18	1	196	138
0	2	100	39
1	2	271	318
2	2	178	172
3	2	523	536
4	2	105	122
5	2	411	446
6	2	212	206
7	2	301	308
8	2	143	114
9	2	343	288
10	2	260	192
11	2	185	192
12	2	205	174
13	2	164	119
15	2	148	95
0	3	299	287
1	3	242	233
2	3	349	327
3	3	130	134
4	3	528	511
6	3	406	338
7	3	356	332
8	3	313	332
10	3	262	245
12	3	201	154
14	3	150	103
0	4	285	261
1	4	347	351
2	4	267	239
3	4	299	320
5	4	315	351
6	4	148	116
7	4	322	352
8	4	169	160
9	4	194	176
10	4	171	159
11	4	219	193
12	4	176	130
13	4	201	171
15	4	166	137
1	5	166	148
3	5	194	181
5	5	212	201
6	5	162	142
9	5	180	149
1	6	237	273
2	6	173	153
3	6	219	244
4	6	178	170
5	6	113	153
6	6	166	147
7	6	176	173
8	6	164	151
9	6	167	170
11	6	178	162
12	6	112	98
h = 8			
2	0	716	820
3	0	549	590
4	0	470	513
5	0	560	559
6	0	565	494
7	0	408	502
8	0	455	476
9	0	278	287
10	0	365	376
11	0	148	153
12	0	312	305
13	0	125	122
14	0	161	151
15	0	217	216
16	0	179	134
17	0	166	137
18	0	107	89
0	1	92	69
1	1	166	184
2	1	253	269
3	1	360	440
4	1	263	281
5	1	140	136
6	1	212	204
7	1	255	283
8	1	106	159
9	1	115	101
10	1	84	40
11	1	312	289
12	1	127	146
13	1	245	247
14	1	102	104
15	1	112	87
17	1	107	84
16	1	51	49
0	2	432	432
1	2	542	525
2	2	537	547
3	2	540	507
4	2	279	249
5	2	244	267
6	2	345	304
7	2	309	307
8	2	352	343
9	2	312	350
10	2	135	129
11	2	296	275
12	2	227	207
13	2	150	146
15	2	81	71
16	2	104	123
17	2	61	82
0	3	474	398
1	3	327	298
2	3	340	364
3	3	442	427
4	3	155	185
5	3	245	219
6	3	150	122
7	3	450	467
8	3	304	313
9	3	243	221
10	3	255	249
11	3	143	71
12	3	235	224
13	3	148	114
14	3	125	111
15	3	83	103
17	3	184	154
0	4	241	245
2	4	317	309
3	4	340	302
4	4	150	159
5	4	199	159
6	4	86	14
7	4	168	140
8	4	130	100
9	4	135	142
10	4	89	70
11	4	97	80
12	4	207	184
13	4	79	93
14	4	81	87
15	4	79	77
0	5	209	205
1	5	207	209
2	5	191	186
3	5	299	295
4	5	232	223
5	5	140	138
6	5	341	367
7	5	240	211
8	5	174	192
9	5	202	203
11	5	189	204
12	5	102	106
13	5	104	103
14	5	117	115
0	6	97	100
2	6	135	132
3	6	176	183
4	6	115	113
5	6	112	107
8	6	135	123
12	6	120	114
0	7	168	162
2	7	153	165
4	7	107	115
5	7	107	132
6	7	84	77
7	7	107	131
8	7	122	115
9	7	43	53
10	7	117	118
1	8	106	129
2	8	69	62
4	8	127	147

for $F_o > 4F_{\min}$. No unobserved reflections were included. This lowered R to 8.2%.

Three more isotropic least-squares refinement cycles were carried out using a different weighting scheme, where $w = 1.0$ for $F_o < 4F_{\min}$ and $w = (4F_{\min}/F_o)^2$ for $F_o > 4F_{\min}$. The R value after this refinement increased slightly to 8.3%. Essentially the same bond lengths and angles were obtained as with the other weighting scheme. The average esd's for the two refinements were about the same. This also was found to be the case in the structure determination of $(DMSO)_2PdCl_2$,[20] where different weighting schemes gave essentially the same parameters.

An attempt was made to differentiate between the *hkl* and $hk\bar{l}$ reflections in order to determine the polarity. No observable differences were found on close examination of the photographs. This is not surprising owing to the small values of the complex part of the anomalous dispersion correction (0.75 e^- for Cu and 0.72 e^- for Cl).[12] Thus it was not possible to determine the polarity, and the complex part of the anomalous dispersion term was ignored. We feel that any errors in atomic positions due to this term should be less than the estimated standard deviations.

After the last refinement cycle, the final shifts in all parameters were well below their estimated standard deviations. The largest shift is less than one-seventh the esd for that parameter. The observed and calculated structure factors are listed in Table I while Table II gives the final positional and thermal parameters with their esd's. The estimated standard deviations are obtained from the normal equations matrix of the last least-squares cycle. A final three-dimensional difference Fourier was calculated. No peaks larger than 0.60 e/Å^3 were found. Most of the large peaks were located where one would expect to find hydrogen atoms.

Results and Discussion

Table III gives the molecular dimensions and shortest nonbonding distances while Figure 1 shows a projection of the structure down the *b* axis. The arrangement of ligands around the copper ions can be described as intermediate between tetrahedral and *cis*-square-planar configurations. The angles around the copper ion are Cl–Cu–Cl = 100.8°, O–Cu–O = 86.7°, Cl_1–Cu–O_1 = 99.1°, and O_2–Cu–Cl_2 = 99.0°. The Cu–O bond lengths of 1.93 and 1.97 Å are slightly smaller than the Cu–O distances in $(C_5H_5NOCuCl_2)_2$, 1.98 and 2.04 Å, while the Cu–Cl distances of 2.221 and 2.247 Å are slightly larger than the 2.206 and 2.217 Å found in the pyridine N-oxide complex. The angle between the copper–oxygen and copper–

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[20] M. J. Bennett, F. A. Cotton, D. L. Weaver, R. J. Williams, and W. H. Watson, *Acta Cryst.*, **23**, 788 (1967).

TABLE II

ATOMIC PARAMETERS WITH STANDARD DEVIATIONS[a]

Atom	*x*	*y*	*z*	*B*, Å²	Atom	*x*	*y*	*z*	*B*, Å²
Cu	0.2071 (2)	0.0459 (2)	0.2500	3.06 (6)	C_5	0.370 (2)	0.829 (2)	0.102 (1)	3.9 (3)
Cl_1	0.2473 (5)	0.2141 (5)	0.1441 (3)	3.81 (8)	C_6	0.441 (2)	0.001 (3)	0.309 (1)	5.2 (4)
Cl_2	0.1741 (4)	0.2481 (5)	0.3460 (3)	3.86 (8)	C_7	0.282 (2)	0.740 (3)	0.076 (1)	5.8 (5)
O_1	0.2974 (9)	0.852 (1)	0.2310 (6)	3.1 (2)	C_8	0.084 (2)	0.840 (3)	0.421 (1)	4.8 (4)
O_2	0.114 (1)	0.871 (2)	0.2823 (7)	4.1 (2)	C_9	0.025 (2)	0.858 (3)	0.489 (1)	5.4 (5)
N_1	0.374 (1)	0.880 (2)	0.1852 (9)	3.8 (3)	C_{10}	−0.065 (3)	0.935 (4)	0.480 (2)	7.1 (7)
N_2	0.054 (1)	0.895 (1)	0.3476 (7)	2.5 (2)	C_{11}	−0.092 (3)	0.990 (4)	0.406 (2)	6.9 (7)
C_1	0.453 (2)	0.957 (2)	0.221 (1)	4.3 (4)	C_{12}	−0.034 (2)	0.977 (3)	0.335 (2)	5.8 (5)
C_2	0.534 (2)	0.991 (3)	0.170 (1)	5.6 (5)	C_{13}	0.186 (2)	0.748 (3)	0.425 (1)	5.4 (5)
C_3	0.530 (3)	0.942 (4)	0.085 (2)	7.5 (7)	C_{14}	−0.054 (2)	0.038 (2)	0.253 (1)	4.7 (4)
C_4	0.453 (2)	0.863 (3)	0.054 (1)	4.7 (4)					

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

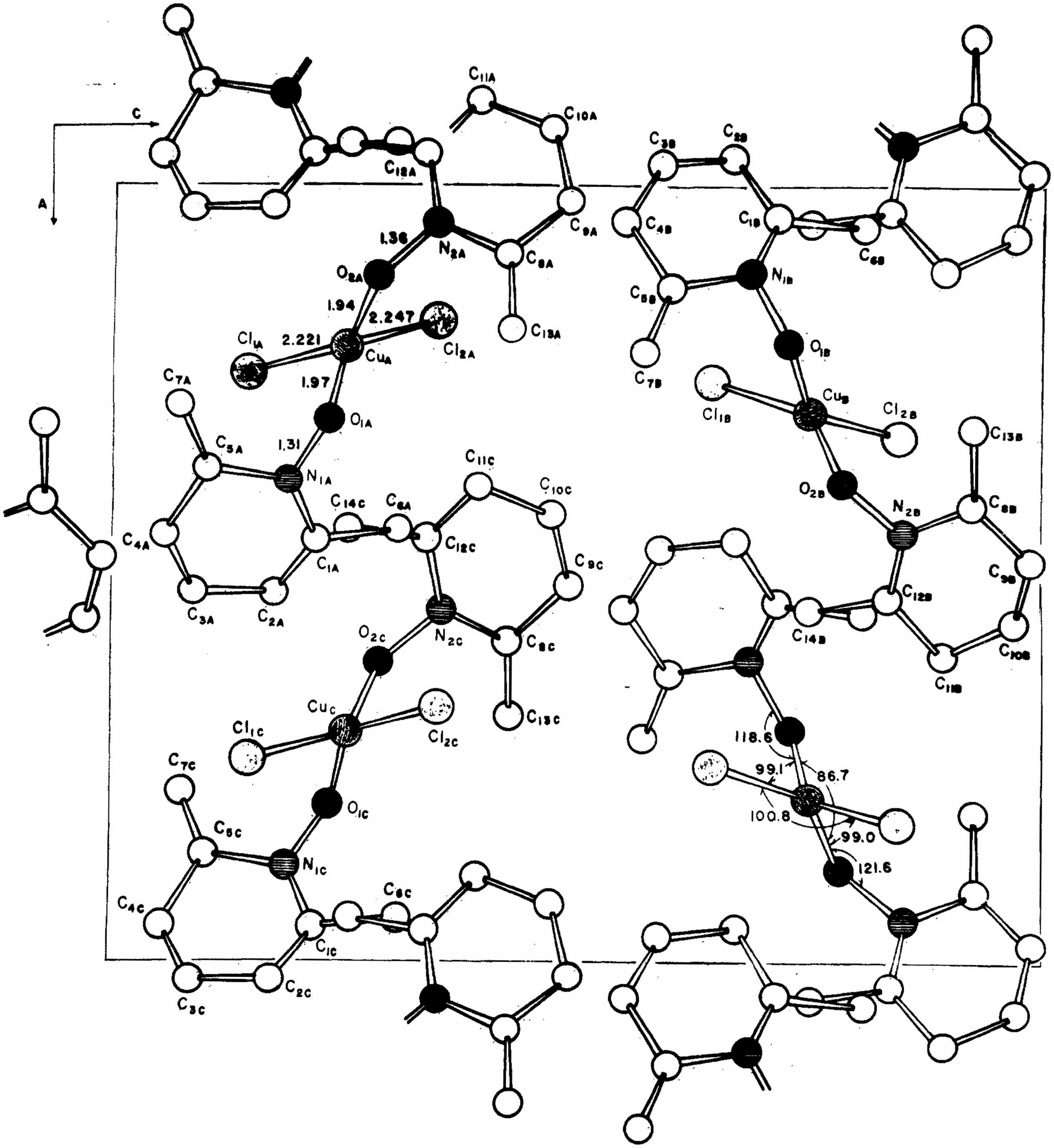

Figure 1.—A projection of the yellow form of $(C_7H_9NO)_2CuCl_2$ down the *b* axis.

chlorine planes is 54.6°. The N–O bond lengths, 1.31 and 1.36 Å, are comparable with that of 1.35 Å in $(C_5H_5NOCuCl_2)_2$, and they show the expected increase in length over those in the free aromatic amine N-oxides (1.24–1.28 Å) where considerable π bonding occurs.[21–23]

TABLE III

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

Bond lengths		Shortest nonbonding distances		Bond angles	
				O_1–N_1–C_5	118 (1)
Cu–Cl_1	2.221 (4)	Cl_1–Cl_2	3.442 (4)	N_1–C_1–C_2	118 (2)
Cu–Cl_2	2.247 (4)	O_1–O_2	2.68 (1)	C_1–C_2–C_3	119 (2)
Cu–O_1	1.97 (1)	Cl_2–C_{13}	4.05 (3)	C_2–C_3–C_4	121 (2)
Cu–O_2	1.93 (1)	Cl_1–C_7	3.84 (3)	C_3–C_4–C_5	123 (2)
O_1–N_1	1.31 (1)	Cl_{2a}–C_{11c}	3.87 (3)	C_4–C_5–N_1	117 (2)
O_2–N_2	1.36 (1)	Cl_{2a}–C_{7b}	3.78 (2)	C_1–N_1–C_5	123 (2)
N_1–C_1	1.39 (2)	Cl_{1b}–C_{13a}	3.68 (2)	N_1–C_1–C_6	114 (2)
C_1–C_2	1.41 (3)	Cl_{1a}–C_{14c}	3.79 (2)	C_2–C_1–C_6	128 (2)
C_2–C_3	1.44 (3)	C_{1a}–C_{14c}	3.83 (3)	N_1–C_5–C_7	116 (2)
C_3–C_4	1.32 (4)	C_{13a}–C_{11c}	3.68 (4)	C_4–C_5–C_7	127 (2)
C_4–C_5	1.41 (2)	C_{9a}–C_{4b}	3.95 (4)	O_2–N_2–C_8	117 (1)
C_5–N_1	1.41 (2)	C_{14c}–N_{1a}	3.53 (3)	O_2–N_2–C_{12}	119 (1)
C_1–C_6	1.48 (2)	C_{9a}–C_{3b}	3.62 (4)	N_2–C_8–C_9	120 (2)
C_5–C_7	1.47 (3)	C_{3a}–C_{7c}	3.77 (4)	C_8–C_9–C_{10}	119 (2)
N_2–C_8	1.33 (2)	Bond angles		C_9–C_{10}–C_{11}	118 (2)
C_8–C_9	1.39 (2)	Cl_1–Cu–Cl_2	100.8 (2)	C_{10}–C_{11}–C_{12}	124 (3)
C_9–C_{10}	1.39 (4)	O_1–Cu–O_2	86.7 (5)	C_{11}–C_{12}–N_2	114 (2)
C_{10}–C_{11}	1.33 (3)	O_1–Cu–Cl_1	99.1 (3)	C_8–N_2–C_{12}	124 (2)
C_{11}–C_{12}	1.41 (3)	O_2–Cu–Cl_2	99.0 (4)	N_2–C_8–C_{13}	118 (2)
C_{12}–N_2	1.38 (3)	Cu–O_1–N_1	118.6 (9)	C_9–C_8–C_{13}	122 (2)
C_8–C_{13}	1.59 (3)	Cu–O_2–N_2	121.6 (9)	C_{11}–C_{12}–C_{14}	129 (2)
C_{12}–C_{14}	1.43 (3)	O_1–N_1–C_1	119 (1)	N_2–C_{12}–C_{14}	117 (2)

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

The bond lengths around the ring are too inaccurate for any conclusions to be drawn concerning the effects of complex formation on the aromatic π system. The atoms of each ring were least-squares-fitted to a plane with all atoms weighted equally. The average deviation of the atoms from the planes is 0.008 Å. The largest deviation is 0.015 Å, which is less than the estimated standard deviations of the atoms.

The yellow form of $(4\text{-}CH_3C_5H_4NO)_2CuCl_2$ is irreversibly converted to the green *trans*-square-planar form on heating. The green form is also formed predominantly when the complex is prepared by heating an ethanol solution with a large excess of ligand. The *trans* isomer probably is stabilized by π back-bonding of the appropriate copper(II) d orbitals with the low-lying antibonding π orbitals of the aromatic N-oxide. There is little steric interaction in the *trans* configuration which would hinder the ligands from obtaining a configuration compatible with maximum π bonding.

In contrast, the yellow form of $[2,6\text{-}(CH_3)_2C_5H_3NO]_2CuCl_2$ does not convert to the green form when the solid is warmed. The reason for this is not known, but it seems likely that the steric effects of the methyl groups could hinder the conversion. The energy of transformation would then be too high and the complex would melt before converting to the green form.

There is considerable steric and electrostatic interaction in a *cis*-square-planar structure, and it probably cannot be stabilized by π-bond formation. A tetrahedral structure is the most stable from electrostatic considerations. This is demonstrated by the structure of $[2,6\text{-}(CH_3)_2C_5H_3NO]_2ZnCl_2$[24] where no crystal field stabilization is present. The structure is tetrahedral with a small expansion of the Cl–Zn–Cl angle due to electrostatic repulsion. The tetrahedral Cu(II) structure would be unstable due to a Jahn–Teller distortion. The E-symmetry vibration of a tetrahedral molecule is Jahn–Teller active and in the extreme would lead to either a *cis*- or *trans*-square-planar configuration. The distorted configuration of the yellow form of $[2,6\text{-}(CH_3)_2C_5H_3NO]_2CuCl_2$ is probably a compromise between the sterically unstable *cis* and the Jahn–Teller unstable tetrahedral configurations.

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(21) E. L. Eichhorn, *Acta Cryst.*, **9**, 787 (1956).
(22) R. Curti, V. Riganti, and S. Locchi, *ibid.*, **14**, 133 (1961).
(23) E. L. Eichhorn, *ibid.*, **12**, 746 (1959).
(24) R. S. Sager and W. H. Watson, *Inorg. Chem.*, **7**, 1358 (1968).