529. *The Colour Isomerism and Structure of Some Copper Co-ordination Compounds. Part III.*[1] *The Structure of* NN′-*Disalicylidenepropane-*1,2-*diaminecopper Monohydrate.*

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A two-dimensional *X*-ray analysis of *NN′*-disalicylidenepropane-1,2-diaminecopper monohydrate has shown that the copper atom is quinquecovalent. The ligands are arranged in pyramidal configuration with four "normal" planar bonds and a fifth copper–water bond, of length 2·53 Å, perpendicular to this plane.

The quinquecovalency is in accord with previous observations on the colour and spectra of a number of similar copper complexes.

A recent investigation[1] of some salicylaldehyde and 2-hydroxy-1-naphthaldehyde complexes of copper indicated that the metal had a co-ordination number greater than four in the green compounds. An *X*-ray examination of the green, *NN′*-disalicylidenepropane-1,2-diamine copper monohydrate has supported this observation. This compound was chosen for study as likely to throw light on the connection between colour and co-ordination number because the presence of a water molecule and the difference in colour from the violet anhydrous complex suggested a copper covalency of five or six (cf. tetramminecupric sulphate monohydrate[2]).

Experimental

The preparation and characterisation of the complex have been described.[1] The crystals employed were dark green needles elongated along the [*a*] axis and showing well developed {001} and {011} faces. The crystal data were: $C_{17}H_{18}O_3N_2Cu$, $M = 361{\cdot}5$, orthorhombic, $a = 5{\cdot}15 \pm 0{\cdot}02$, $b = 13{\cdot}22 \pm 0{\cdot}05$, $c = 22{\cdot}66 \pm 0{\cdot}08$ Å, $U = 1543$ Å^3, $D_m = 1{\cdot}51$ g./c.c. by flotation, $Z = 4$, $D_c = 1{\cdot}556$ g./c.c., $F(000) = 748$. Space group, $P2_12_12_1$ (D_2^4, No. 19). Cu-K_α radiation, single-crystal rotation, and oscillation photographs. Intensities were recorded for the *h*0*l* and 0*kl* zones by using the multiple-film technique, the relative intensities being measured by visual comparison with a standard scale and converted into structure amplitudes. Small sections of crystal were used and no absorption corrections were made.

As all the atoms are in general positions the copper co-ordinates were determined from two-dimensional Patterson functions sharpened with a factor similar to that applied by Donohue and Trueblood.[3] The (100) and (010) projections were then analysed by application of the heavy-atom method. As an aid, a model with accepted ideas of bond lengths and angles was used. This model is shown in Fig. 1 (in which the bond lengths determined are given), but the position of the water molecule, O(3), was not known in the initial stages. The structure-factor machine designed by Llewellyn[4] was used and the syntheses were computed at 6° intervals with Robertson's stencils.[5] All the two-dimensional co-ordinates were referred to a screw

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[1] Part I, *J.*, 1959, 1200; Part II, *J.*, 1959, 1203.
[2] Mazzi, *Acta Cryst.*, 1955, **8**, 137.
[3] Donohue and Trueblood, *Acta Cryst.*, 1952, **5**, 414.
[4] Llewellyn, *J. Sci. Instr.*, 1951, **28**, 229.
[5] Robertson, *J. Sci. Instr.*, 1948, **25**, 28.

axis as the effective centre of symmetry. Extensive use was made of difference syntheses at an early stage and before all the atomic positions were known. These syntheses usually gave a clear indication of the positions of atoms not yet found and almost always showed where atoms had been incorrectly placed. At the same time an improvement in the known atomic parameters and the temperature factors was brought about. Although the aim, as in the refinement of a structure, was to produce zero electron density everywhere in the cell, this was not done in detail at this stage. The difference map was altered by adding or withdrawing atoms at points of large positive or negative density and by making large adjustments in the known

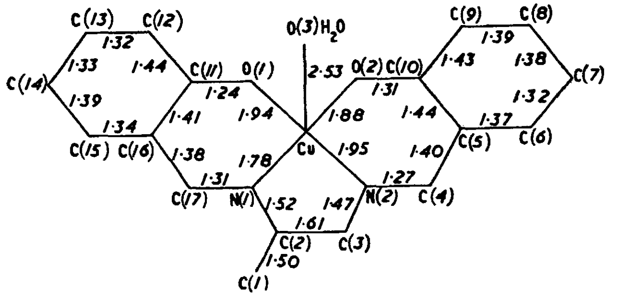

FIG. 1. *The model used as a guide, showing the numbering of the atoms and the calculated bond lengths.*

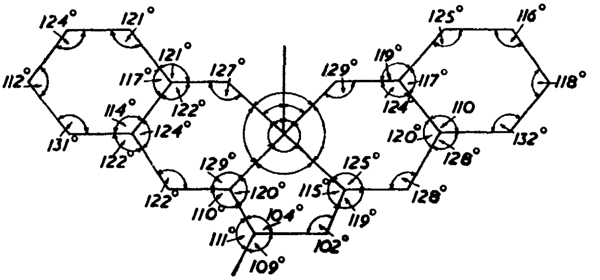

FIG. 2. *Calculated bond angles.*

Additional angles

O(1)–Cu–O(2)	93°	O(1)–Cu–O(3)	89°
O(2)–Cu–N(2)	93°	O(2)–Cu–O(3)	99°
N(2)–Cu–N(1)	83°	N(2)–Cu–O(3)	102°
N(1)–Cu–O(1)	90°	N(1)–Cu–O(3)	93°

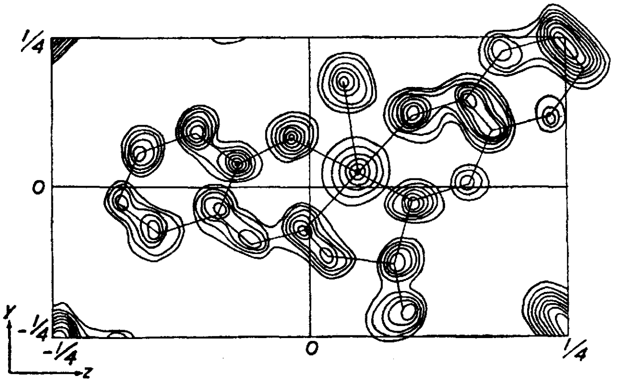

FIG. 3. *Electron density along the* [*a*] *axis; the axis of projection is away from the reader. Copper contours are at arbitrary intervals; other contours are at* 1 eÅ^{-2} *intervals, the lowest at* 3 eÅ^{-2}.

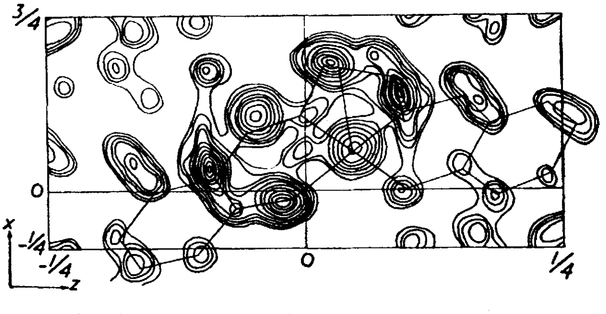

FIG. 4. *Electron density along the* [*b*] *axis. Contours as in Fig.* 3.

atomic co-ordinates. A particular value of this approach was that it incorporated planes whose observed structure amplitudes were zero and which would not otherwise have been used to give useful information in the initial stages. Eventually the signs of nearly all the observed reflections were found. The atomic scattering factors due to Berghius *et al.*[6] were used for the light atoms and Thomas–Fermi [7] values for copper, with initial temperature factors of $B = 3$ Å^2 and 1 Å^2, respectively.

After the observed amplitudes had been scaled to the absolute value by applying Wilson's [8] method between cycles, an average temperature factor of $B = 2{\cdot}8$ Å^2, calculated by the least-squares method for well-resolved carbon atoms, was applied to all the light atoms. A value of $B = 1{\cdot}4$ Å^2 was similarly found by the least-squares method for the copper atom.

Refinement of the projection was continued by successive difference cycles until the reliability factor of the observed planes was 0·16 (omitting the 020 reflection which appeared to have suffered extinction). No attempt was made to introduce individual or anisotropic temperature factors. The electron density map finally resulting is shown in Fig. 3.

The electron density in the (010) projection was determined in a similar manner by using the z co-ordinates found in the early stages. Here again difference syntheses were used before all the atomic positions were known. They proved particularly valuable in placing atoms in the region near the copper atom where considerable overlapping occurs (Fig. 4). With the initial aid of the previous z co-ordinates it was possible to locate all the atomic positions in this projection without use of a model. Several difference cycles were then computed with the atomic-scattering curves and temperature factors given above. The scaling factor was obtained by comparing the 00l structure amplitudes with those of the (100) projection. The reliability factor of the observed planes was brought to 0·18. Again individual or anisotropic temperature factors were not employed. The resulting electron density map is shown in Fig. 4. The (001) projection was not analysed because poor resolution was expected. Observed structure amplitudes and calculated structure factors for the two analysed projections are listed in Table 2.

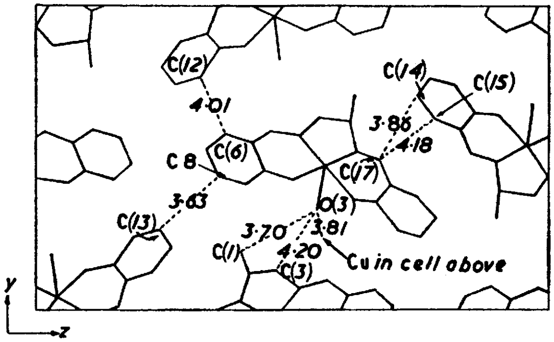

FIG. 5. *Intermolecular distances. Structure viewed along the [a] axis.*

TABLE 1.

Atom	x	y	z	Atom	x	y	z
Cu	0·178	0·039	0·044	C(7)	−0·204	−0·027	−0·182
O(1)	0·008	0·122	0·103	C(8)	−0·334	0·058	−0·163
O(2)	−0·048	0·083	−0·016	C(9)	−0·276	0·089	−0·106
O(3)	0·525	0·173	0·034	C(10)	−0·089	0·043	−0·068
N(1)	0·349	−0·026	0·101	C(11)	0·090	0·143	0·153
N(2)	0·318	−0·069	−0·005	C(12)	−0·015	0·227	0·186
C(1)	0·290	−0·213	0·097	C(13)	0·073	0·250	0·239
C(2)	0·477	−0·127	0·088	C(14)	0·278	0·207	0·264
C(3)	0·548	0·120	0·019	C(15)	0·359	0·122	0·233
C(4)	0·252	−0·087	−0·058	C(16)	0·296	0·089	0·179
C(5)	0·046	−0·045	−0·090	C(17)	0·411	0·005	0·154
C(6)	−0·033	−0·069	−0·146				

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[6] Berghius, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

[7] Thomas and Fermi: as compiled in *Internationale Tabellen*, Vol. II, 1935, 572.

[8] Wilson, *Nature*, 1942, **150**, 152.

TABLE 2. *Observed structure amplitudes and calculated structure factors for the* 0*kl and h*0*l zones.* (×10.) *The atomic co-ordinates have been referred to an effective centre for the computations.*

0*kl zone*

Plane	$\|F_{obs.}\|$	$F_{calc.}$
000		7480
2	1238	−1409
4	227	196
6	204	85
8	381	−227
10	525	420
12	321	77
14	807	805
16	426	−410
18	188	−153
20	414	472
22	287	−434
011	525	508
2	464	−483
3	569	−518
4	392	−289
5	895	867
6	580	−545
7	453	−387
8	580	501
9	641	536
10	<72	−48
11	271	−227
12	227	−143
13	216	−68
14	238	246
15	547	481
16	359	−278
17	663	−722
18	188	113
19	525	552
20	260	−208
21	298	−256
22	<119	−7
020	1249	1908
1	619	−654
2	1116	−1425
3	177	−169
4	381	−329
5	332	−308
6	497	−410
7	<59	0
8	597	−572
9	414	363
10	403	404
11	381	−412
12	381	−282
13	497	467
14	298	170
15	497	−437
16	260	−157
17	<108	−59
18	321	−264
19	144	127
20	332	330
21	<119	−50
22	204	−265
031	740	−716
2	569	−576
3	177	−192
4	426	349
5	249	234
6	525	−382
7	453	−381
8	321	267
9	426	308
10	<83	−35
11	155	−26
12	392	−336
13	567	−491
14	381	326
15	442	387
16	464	−453
17	442	−386
18	381	402
19	216	231
20	309	−303
21	<119	−17
22	<119	−16
040	260	160
1	547	−459
2	321	220
3	403	303
4	94	87
5	94	−29
6	94	129
7	414	−360
8	525	−478
9	403	351
10	486	450
11	525	−455
12	321	−246
13	392	319
14	271	245
15	381	−347
16	122	58
17	155	−136
18	166	−15
19	166	157
20	166	185
21	<119	−128
22	188	−233
051	359	299
2	216	−217
3	619	−511
4	414	366
5	381	365
6	829	−799
7	403	−284
8	558	469
9	497	431
10	155	−37
11	133	−76
12	144	−84
13	177	−68
14	426	411
15	105	70
16	392	−284
17	227	−229
18	238	224
19	122	173
20	359	−422
21	216	111
22	111	51
060	475	−492
1	525	−490
2	72	11
3	840	842
4	271	−198
5	426	−412
6	227	82
7	287	−184
8	238	−186
9	962	927
10	309	234
11	713	−637
12	271	−253
13	536	507
14	<106	69
15	<106	16
16	249	−242
17	166	60
18	<119	89
19	122	105
20	<119	15
21	<119	−51
22	<119	−2
071	232	264
2	260	−230
3	497	−469
4	807	715
5	133	−124
6	740	−677
7	<95	44
8	785	755
9	332	239
10	381	−321
11	<106	36
12	188	155
13	122	106
14	298	247
15	392	−381
16	166	−170
17	<119	−34
18	414	451
19	<119	−59
20	249	−269
21	260	245
22	144	175
080	332	−222
1	558	−520
2	558	478
3	580	564
4	321	−222
5	94	−66
6	260	211
7	287	−175
8	177	189
9	641	548
10	216	−229
11	796	−817
12	227	209
13	155	158
14	<119	−14
15	122	−133
16	<119	−21
17	<119	60
18	<119	69
19	166	234
20	<106	−69
21	177	−218
091	370	340
2	271	−286
3	177	102
4	309	189
5	414	−383
6	403	−362
7	359	398
8	271	228
9	298	−277
10	298	−273
11	188	127
12	<119	−18
13	309	316
14	<119	43
15	309	−318
16	332	−384
17	249	209
18	227	228
19	188	−168
20	204	−207
21	133	132
22	133	−44
0,10,0	426	−370
1	188	−134
2	392	300
3	188	100
4	188	−134
5	155	−56
6	<106	−26
7	122	−86
8	271	250
9	381	276
10	426	−382
11	392	−425
12	204	229
13	<119	84
14	<119	−117
15	<119	74
16	<106	83
17	105	−102
18	<97	13
19	144	184
20	133	−157
0,11,1	188	−170
2	<106	−17
3	426	352
4	<119	34
5	475	−438
6	204	−163
7	260	205
8	166	160
9	260	−222
10	<119	34
11	204	164
12	<119	12
13	<106	79
14	188	185
15	188	−243
16	177	−174
17	177	267
18	166	94
19	83	−200
20	133	−16
21	72	6
0,12,0	426	−455
1	<55	−94
2	332	283
3	204	176
4	<119	−54
5	<119	27
6	332	−296
7	<119	8
8	238	235
9	<119	−45
10	188	−179
11	122	−112
12	188	221
13	<106	22
14	177	−243
15	<106	−8
16	133	151
17	<106	33
18	<83	40
19	<83	38
20	94	−153
0,13,1	<119	−98
2	<119	−35
3	287	324
4	<119	−29
5	381	−472
6	149	−143
7	188	201
8	<106	47
9	249	−320
10	105	69
11	177	158
12	<106	−41
13	<95	67
14	<95	−28
15	<83	−173
16	<83	−52
17	133	259
18	<59	−71
19	72	−156
0,14,0	238	−264
1	<106	16
2	249	288
3	<106	−18
4	155	−189
5	105	−62
6	155	−169
7	105	98
8	177	235
9	94	−111
10	166	−223

h0*l zone*

Plane	$\|F_{obs.}\|$	$F_{calc.}$
101	1038	1304
2	449	354
3	641	669
4	397	418
5	210	−77
6	66	−26
7	391	−357
8	105	22
9	630	−391
10	92	58
11	630	−481
12	257	149
13	432	−337
14	496	462
15	327	−273
16	484	517
17	<105	−9
18	356	194
19	367	338
20	181	75
21	432	490
22	<131	−16
23	303	382
200	233	73
1	210	103
2	105	5
3	496	−404
4	251	216
5	840	−802
6	146	−150
7	915	−906
8	367	−382
9	618	−622
10	397	−337
11	181	−107
12	432	−314
13	420	321
14	262	−286
15	315	281
16	251	163
17	128	102
18	338	358
19	181	190
20	181	188
301	303	312
2	315	−238
3	513	549
4	735	−731
5	303	233
6	685	−684
7	<105	31
8	758	−825
9	303	−239
10	432	−377
11	169	−74
12	303	204
13	303	−231
14	181	139
15	286	189
16	181	166
17	<131	21
18	432	403
400	<118	165
1	<118	91
2	<118	47
3	379	−300
4	<118	−71
5	379	−353
6	<118	−28
7	356	−427
8	<131	14
9	<131	−38
10	222	239
11	<131	−19
12	<131	44
13	257	286
14	<131	−93
15	274	327
16	<118	35
17	262	294
18	<118	−71
19	233	310
501	315	−334
2	257	−168
3	286	−276
4	262	−307
5	181	−195
6	163	−257

The final atomic co-ordinates, referred to an origin midway between the three non-intersecting screw axes, are set out in Table 1. Where there was disagreement between the z co-ordinates in the two projections, the value for the (100) projection was taken as correct because of the better resolution available. The greatest discrepancies were 0·005 for C(4) and 0·004 for C(12) and C(16) (expressed in fractional co-ordinates).

The numbering of the atoms is shown in Fig. 1.

It is obvious that a two-dimensional analysis of this molecule which is poorly resolved in one projection will not give accurate atomic positions. As an indication of the errors involved, the standard deviations of a few resolved atoms were obtained by Cruickshank's method,[9] but these somewhat over-estimate the accuracy of the analysis. The R.M.S. deviations are:

Atomic co-ordinates σ_r = 0·029 Å for light atoms and = 0·0049 Å for the copper atom.

Bond lengths σ_d = 0·041 Å for light atom–light atom bonds, and 0·029 Å for light atom–copper atom bonds.

Bond angles σ_θ = 1·7° for light atom–copper–light atom angles and 2·3° for other angles.

The measured bond lengths and angles are shown in Figs. 1 and 2, respectively. Application of the test for significant differences in bond lengths and angles [9] shows that the calculated deviations are a reasonable guide.

DISCUSSION

The ligands are arranged about the quinquecovalent copper atom in a pyramidal configuration. The length of the copper–water bond, 2·53 Å, suggests that it is appreciably covalent and this is reflected in the fact that the copper atom is 0·2 Å above the plane through the co-ordinating atoms O(1), O(2), N(1), N(2) (themselves co-planar to within 0·03 Å) in the direction of the water molecule. The other copper–ligand bonds are of normal length so that, in accord with the Jahn–Teller effect,[10] the fifth out-of-plane bond is longer than the four planar ones. The copper–ethylenedi-imine ring system is non-planar. The carbon atom C(4) is −0·2 Å from the plane through N(1), Cu, and N(2), and C(3) is +0·4 Å from this plane. Distances measured away from the origin, not itself in the plane, are positive. The ethylenedi-imine bridge is thus in the *gauche* form already observed in co-ordination compounds.[11,12] Buckling of the bridge may also occur to avoid a too close approach of the methyl carbon atom C(1) to a neighbouring water molecule, see Fig. 5. Both benzene rings are planar within 0·1 Å but the whole molecule does not lie in one plane. This condition may arise from the distorting effect of the *gauche* N–C–C–N bridge which tends to prevent the nitrogen atoms being co-planar with the molecule, and to the methyl group which, projecting from the molecule plane, prevents efficient packing.

This structure is in accord with the previous suggestion [1] that green compounds of this type should exhibit a co-ordination number greater than four. Five co-ordination is unusual for copper but not unknown.[13] It is probably accounted for here by the constraint exercised on the packing of the molecules by the methyl groups. Small voids thereby left in the structure facilitate the attachment of a solvent molecule at one of the octahedral co-ordinating positions of the metal atom.

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[11] Scouloudi, *Acta Cryst.*, 1953, **6**, 651.
[12] Nakahara, Saito, and Kuroya, *Bull. Chem. Soc. Japan*, 1952, **25**, 331.
[13] Corbridge and Cox, *J.*, 1956, 594.