530. *The Colour Isomerism and Structure of Some Copper Co-ordination Compounds. Part IV.* The Structure of* NN′*-Disalicylidene-ethylenediaminecopper.*

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A two-dimensional *X*-ray analysis has shown that *NN*′-disalicylidene-ethylenediaminecopper is dimeric, with two copper–oxygen bonds of length 2·41 Å binding the two units of the dimer in a manner similar to that recently found in copper dimethylglyoxime. There is some distortion of the molecule to allow formation of the dimer while maintaining van der Waals contact distances between non-bonding atoms.

The configuration about the quinquecovalent copper atoms is pyramidal in accordance with previous observations on the colour and spectra of similar copper complexes.

As a further check on the explanation put forward[1] for the colour isomerism of some copper complexes the co-ordination arrangement of *NN*′-disalicylidene-ethylenediamine-copper has been ascertained by *X*-ray methods.

EXPERIMENTAL

Crystals previously prepared[1] were recrystallised from nitrobenzene, giving dark green plates. The crystal data were: $C_{16}H_{14}O_2N_2Cu$, $M = 329·9$, monoclinic, $a = 26·55 \pm 0·1$, $b = 6·93 \pm 0·02$, $c = 14·60 \pm 0·05$ Å, $\beta = 97·5° \pm 0·5°$ (values previously reported[2] are $a = 26·50 \pm 0·1$, $b = 7·05 \pm 0·1$, $c = 14·80 \pm 0·15$ Å, $\beta = 82·1°$), $U = 2663$ Å^3, $D_m = 1·61$ g./c.c. by flotation, $Z = 8$, $D_c = 1·644$ g./c.c., $F(000) = 1352$. Space group, $C_c^2(C_{2h}^6$, No. 15). Cu-K_α radiation, single-crystal oscillation, and rotation photographs. The space group C_c^2 was chosen after the statistical test due to Howells, Phillips, and Rogers[3] showed the (010) projection to be centrosymmetric. Intensity data were collected for the $hk0$, $h0l$, and $h1l$ zones, the multiple-film method being used. Relative intensities were estimated by visual comparison against a standard scale. Absorption corrections were not applied as small sections of crystals were used.

Although a postulated structure, derived from consideration of the packing of the molecules, was available,[2] an independent analysis was made. The co-ordinates of the copper atom were first determined from two-dimensional Patterson functions, sharpened according to the method of Donohue and Trueblood,[4] and the heavy-atom method was then applied. It was assumed that the heavy-atom co-ordinates obtained from the Patterson functions were accurate and that the signs of the structure factors were those of the copper contributions in most instances. The first electron-density map was computed for the (001) projection and as in the previous analysis[5] initial atomic positions were tentatively established by means of a model (shown in Fig. 1 with the numbering of the atoms) and by computing a number of difference cycles. An approximate scaling factor was used together with the atomic scattering and temperature factors determined for *NN*′-disalicylidenepropane-1,2-diaminecopper monohydrate.[5] The co-ordinates were then refined by means of four difference-cycles, the same scattering and temperature factors being used and with $F_{\text{obs.}}$ brought to the absolute scale by successive least-squares adjustments. At this stage the reliability factor was 0·20 for all observed planes, and the refinement was stopped. The final electron-density map is shown in Fig. 3.

The (010) projection was analysed similarly. For the first electron-density map, based on the heavy-atom contribution, 193 of 215 observed planes were used. The model was then placed on this map and the z-co-ordinates of the atoms estimated. With the x-co-ordinates from the previous projection these atomic positions gave a reliability factor of 0·28 for all

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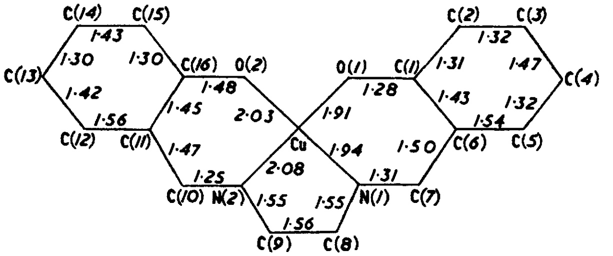
* Part III, preceding paper.

[1] Part I, *J.*, 1959, 1200; Part II, *J.*, 1959, 1203.
[2] von Stackelberg, *Z. anorg. Chem.*, 1947, **253**, 136.
[3] Howells, Phillips, and Rogers, *Acta Cryst.*, 1950, **3**, 210.
[4] Donohue and Trueblood, *Acta Cryst.*, 1952, **5**, 414.
[5] Part III, preceding paper.

observed planes. Two difference cycles were computed by using the same atomic scattering factors and temperature factors as before. The reliability factor was then 0·18 for observed planes and the refinement was stopped, the final electron-density map being shown in Fig. 4.

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

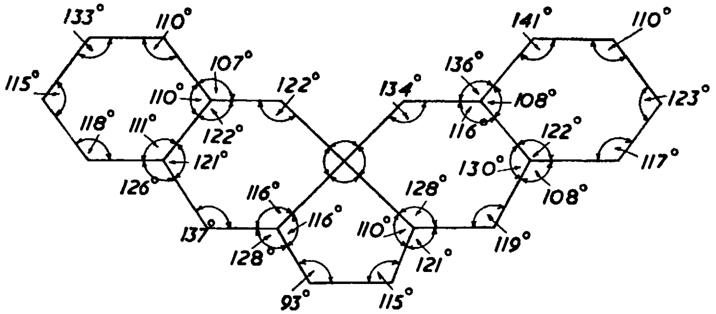


In order to determine whether the (010) projection had been referred to an origin at a centre of symmetry or at a two-fold axis, $h11$ structure factors were calculated for both these possibilities. A comparison with the observed amplitudes, brought to the absolute scale through common reflections, showed:

(i) reliability factor for origin at a centre of symmetry = 0·13,

and (ii) reliability factor for origin at a two-fold axis = 0·83.

FIG. 2. *Calculated bond lengths.*



Additional angles

O(2)-Cu-O(1)	89°
O(1)-Cu-N(1)	90°
N(1)-Cu-N(2)	82°
N(2)-Cu-O(2)	95°

Observed structure amplitudes and calculated structure factors are listed in Table 2. The atomic co-ordinates referred to an origin at a centre of symmetry are given in Table 1 as fractions of the unit translations.

Where the x-co-ordinates disagreed between projections those of the (010) projection were taken because of the better resolution. The greatest disagreements were 0·011 for C(8), 0·007 for C(10), 0·006 for N(1), and 0·004 for C(12) and C(15) (numbered as in Fig. 1).

TABLE 1.

Atom	x	y	z	Atom	x	y	z
Cu	0·233	0·202	0·098	C(7)	0·142	0·062	0·172
O(1)	0·184	0·405	0·088	C(8)	0·219	−0·146	0·198
O(2)	0·285	0·392	0·062	C(9)	0·260	−0·225	0·140
N(1)	0·189	0·032	0·157	C(10)	0·330	0·023	0·146
N(2)	0·284	−0·023	0·130	C(11)	0·362	0·186	0·125
C(1)	0·137	0·414	0·100	C(12)	0·420	0·208	0·159
C(2)	0·100	0·539	0·082	C(13)	0·445	0·378	0·135
C(3)	0·051	0·558	0·087	C(14)	0·415	0·519	0·106
C(4)	0·032	0·385	0·129	C(15)	0·362	0·528	0·073
C(5)	0·060	0·231	0·151	C(16)	0·340	0·369	0·093
C(6)	0·117	0·250	0·143				

The standard deviation in atomic positions has not been assessed but the poor resolution attained and the discrepancies between the x-co-ordinates suggest that the derived parameters cannot be very accurate. This view is reflected in the calculated bond lengths and angles shown in Figs. 1 and 2, respectively.

TABLE 2. *Observed structure amplitudes and calculated structure factors* (×10).

$h0l$ and $\bar{h}0l$ zones

Plane	$h0l$		$\bar{h}0l$	
	$\lvert F_{\text{obs.}} \rvert$	$F_{\text{calc.}}$	$\lvert F_{\text{obs.}} \rvert$	$F_{\text{calc.}}$
000	not	13520		
2	obs.	−3612		
4	496	644		
6	2072	−1760		
8	356	340		
10	1208	−1348		
12	392	−280		
14	532	476		
16	332	−268		
18	640	348		
20	768	−652		
22	1112	1156		
24	688	−820		
26	212	372		
28	272	−492		
30	496	432		
32	416	−484		
34	416	404		
002	852	1072		
2	1492	−1272	188	−144
4	604	608	<84	−12
6	1716	−1372	1052	788
8	1136	944	<108	−120
10	2024	−1572	1844	1356
12	<132	140	472	−64
14	308	−264	680	124
16	1372	1248	1516	−1704
18	1052	−1040	1408	1360
20	864	980	1372	−1164
22	852	−748	1420	1436
24	688	284	700	−720
26	436	276	<212	−56
28	308	−228	<208	−196
30	224	412	<176	24
32	368	−364	<148	32
34			<56	−28
004	3832	−6344		
2	1844	1760	1584	1404
4	1160	−932	368	68
6	752	516	1740	1732
8	272	236	1256	−916
10	828	1008	1880	1160
12	272	68	688	−328
14	828	−692	1268	916
16	1052	1072	1572	−1324
18	888	−948	948	752
20	1100	1140	392	−340
22	1208	−1220	<212	−160
24	744	820	496	276
26	472	−684	<212	−44
28	392	600	188	376
30	284	−440	604	−376
32	164	284	436	536
34			472	−588
006	1844	−1596		
2	1680	1300	1572	1496
4	1244	−924	1016	−720
6	1220	1028	436	404
8	1112	−1020	888	−712
10	1324	1152	640	−428
12	356	−280	<156	−136
14	248	236	<172	−40
16	392	−108	992	992
18	<212	240	1112	−868
20	<212	−172	1112	708
22	416	−372	992	−1148
24	<212	112	688	1004
26	472	−384	356	−372
28	448	452	696	588
30	416	−520	436	−464
			392	296
008	472	536		
2	616	464	520	−252
4	530	−232	888	860
6	780	740	1552	−1504
8	744	−864	1584	1384
10	580	484	1868	−1448
12	768	−836	1868	1204
14	768	772	1584	−1452
16	828	−972	1552	1404
18	580	828	992	−924
20	640	−876	640	660
22	532	452	720	−512
24	248	−144	<212	96
26	368	348	<192	−72
28	284	−332	<172	−76
30			248	60
00,10	852	812		
2	768	−584	1300	−1440
4	688	568	1268	972
6	436	−444	1052	−908
8	520	580	1016	1016
10	496	−476	604	−428
12	<212	140	640	596
14	<212	−44	<212	16
16	356	−528	<212	−120
18	332	260	<212	32
20	532	−468	276	−116
22	804	920	284	336
24	248	−292	472	−844
26	268	456	700	600
28			744	−568
30			392	512
00,12	852	700		
2	804	−712	<192	−40
4	852	640	804	−784
6	768	−792	720	556
8	688	636	720	−672
10	948	−1020	864	828
12	1112	1300	948	−744
14	1112	−804	664	648
16	580	680	284	−468
18	448	−520	496	588
20	284	472	520	−592
22	<120	−8	664	688
24			284	−388
26			<148	392
28			496	−480
00,14	<212	−112		
2	<212	4	852	868
4	<212	16	948	−764
6	<200	−120	864	816
8	<196	44	864	−936
10	368	−260	804	784
12	448	248	828	−880
14	308	−208	<196	24
16	416	548	<188	−344
18	284	−316	532	596
20			284	−260
22			212	232
24			188	372
26			392	−408
00,16	616	−732		
2	496	536	308	492
4	520	−616	188	−20
6	332	472	248	348
8	<152	−132	308	−168
10	616	504	<172	−24
12	700	−764	<168	28
14	368	380	<160	−12
16			332	16
18			272	−408
20			496	464
22			368	−552
00,18	308	−184		
2	332	212	556	−256
4	284	−316	448	328
6	212	324	448	−412
8			436	524
10			496	−556
12			448	684
14			<88	−64

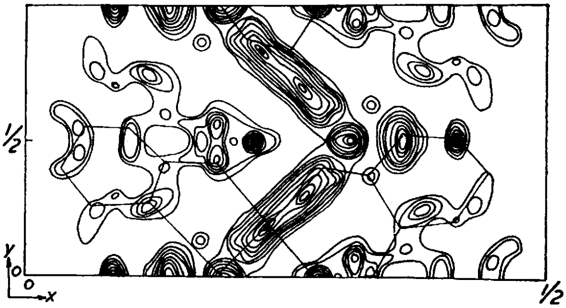
$hk0$ zone

Plane	$\lvert F_{\text{obs.}} \rvert$	$F_{\text{calc.}}$
110	237	−205
3	638	−620
5	154	213
7	556	−488
9	504	538
11	597	−667
13	875	902
15	381	171
17	<95	8
19	391	−201
21	<108	240
23	<113	−232
25	196	158
020	350	−99
2	823	839
4	1369	−1769
6	1615	2012
8	1296	−1464
10	875	996
12	535	−458
14	154	99
16	<95	−228
18	504	−425
20	340	488
22	<113	−2
24	525	419
26	535	−704
28	545	560
30	453	−408
32	268	327
130	72	8
3	391	354
5	1224	−1137
7	1420	1363
9	875	−917
11	957	1120
13	916	−937
15	978	1173
17	916	−1007
19	422	−330
21	463	−1
23	196	224
25	<108	−51
27	165	222
29	<84	57
31	144	−129
040	576	633
2	391	−335
4	<89	−47
6	731	−814
8	432	427
10	<98	5
12	350	420
14	185	−115
16	216	235
18	<113	−20
20	154	−126
22	268	150
24	247	−129
26	360	191
28	319	−219
150	350	138
3	309	−132
5	370	423
7	473	−389
9	514	456
11	556	−516
13	381	360
15	504	−614
17	710	679
19	782	−886
21	556	667
23	484	−402
25	268	172
060	196	− 29
2	422	−262
4	340	168
6	226	−129
8	<113	95
10	<113	61
12	196	212
14	196	112
16	257	−265
18	<100	30
20	<90	−122
22	<78	98
24	216	17
170	196	144
3	<111	48
5	268	−305
7	257	219
9	453	−409
11	535	413
13	422	−337
15	484	405
17	453	−362
19	370	244
21	206	−159
080	185	−188
2	185	303
4	206	−197
6	298	236
8	370	−308
10	257	199
12	211	−103
14	175	−38

DISCUSSION

The complexity of the atomic arrangement in the (001) projection where there are four overlapping molecules can be seen from Fig. 3. The disposition in the (010) projection is displayed in Fig. 4 which also gives calculated values for some of the intermolecular distances. The asymmetry of the benzene rings as they appear in Fig. 3 arises from errors in the refinement, but the regularity of the rings in Fig. 4 indicates that more reliance can be placed on the atomic positions in this projection. From this it would appear that the non-planarity of the central co-ordinated group is probably real. Equally evident from Fig. 4 is the twist in the ethylene bridge and the bending of the ends of the molecule away from its neighbour across the centre of symmetry.

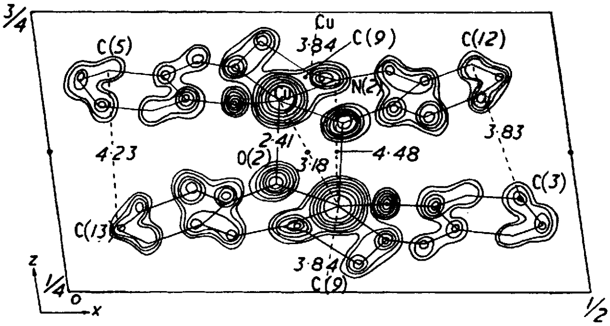
FIG. 3. *Electron density along the* [*c*] *axis.*



Copper contours are at arbitrary intervals; other contours are at 1 e$Å^{-2}$ *intervals, the lowest at* 7 e$Å^{-2}$.

The explanation for these distortions can be deduced from the intermolecular distances shown in Fig. 4. The close approach, to within 2·41 Å, of an oxygen atom, O(2), of one molecule and the copper atom of another indicates covalent bonding between them. The geometry of the arrangement (Fig. 5) shows that the bond is towards one of the octahedral co-ordinating positions of the copper atom. The other octahedral position is close to a carbon, C(9), of a neighbouring ethylene bridge which has been distorted to maintain the copper–carbon distance at 3·84 Å. Calculation shows that the bridge atom, C(8), is +0·1 Å from the plane through N(1), Cu, and N(2), and that C(9) is −0·6 Å from this plane. (Positive distances are measured away from the origin which is not in the plane.) Even after allowance for the low accuracy of the analysis these figures suggest some distortion. Thus deviations from overall planarity seen in the (010) projection are undoubtedly

FIG. 4. *Electron density along the* [*b*] *axis and intermolecular distances. Contours as in Fig.* 3 *but lowest at* 5 e$Å^{-2}$.



due to the close intermolecular approach and the twisting of the ethylene bridge. In particular the molecules must be bent to allow the almost parallel benzene rings of the close neighbours to be kept a van der Waals contact distance apart. The centres of the molecules approach to a distance of 2·41 Å but this increases to more than 4·0 Å at the extremities, which illustrates the strength of the intermolecular bond.

The compound can best be described as dimeric with two long copper–oxygen bonds between the two halves of the dimer. This situation is similar to that found in copper dimethylglyoxime where dimers are formed by two long copper–oxygen bonds[6] of 2·43 Å. Each copper atom is five co-ordinated with a pyramidal arrangement of ligands in agreement with the earlier suggestion[1] that green salicylaldehyde complexes of copper have a covalency greater than four. The bond hybridisation of the copper is presumably dsp^3 with the promotion of one electron to a higher level, and the bond geometry of the unusually bound oxygen suggests normal sp^2 hybridisation (to give two normal intramolecular bonds and a lone pair) with the unhydridised p orbital taking part in the third long bond.

The close stacking in the crystal of this essentially planar molecule contrasts with that of its propane-1,2-diamine analogue[5] where the projecting methyl group introduces voids into the structure. This difference accounts for the higher density of crystals of the ethylenediamine complex and is the probable explanation of the fact that this compound, in contrast to its analogue, does not form a hydrate.

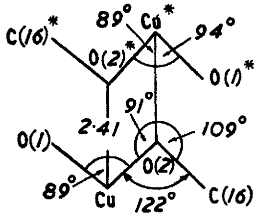


FIG. 5. *The geometry of the copper–oxygen bonds.*

The structure found differs in detail only from that proposed by von Stackelberg[2] on packing considerations. The present analysis has, however, disclosed the dimeric nature of the compound. The main orientations of the molecules proposed by von Stackelberg have been verified.

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[6] Frasson, Bardi, and Bezzi, *Acta Cryst.*, 1959, **12**, 201.