

623. *The Colour Isomerism and Structure of Copper Co-ordination Compounds. Part VII.* The Crystal Structure of Bissalicylaldehydatocopper(II).*

By A. J. MCKINNON, T. N. WATERS, and D. HALL.

The crystal structure of bisalicylaldehydatocopper(II) has been determined by two-dimensional projection methods. The two salicyldehyde ligands are individually planar, but the molecule is slightly distorted such that they are not coplanar.

THE crystal structure of bisalicylaldehydatocopper(II)¹ shows the co-ordination of the metal to be strictly square planar, there being no axial approach of less than 3.85 Å. This is an interesting contrast to the situation in the structure of bis-(*N*-methylsalicylaldehydato)copper(II)² where the molecules all lie parallel, the copper atoms forming a chain with Cu-Cu separations of 3.33 Å. As part of a study of the factors which cause the presence or absence of such axial bonds we have determined the structure of the closely related complex bisalicylaldehydatocopper(II).

* Part VI, *J.*, 1964, 2489.

¹ Stewart and Lingafelter, *Acta Cryst.*, 1959, **12**, 842.

² Lingafelter, Simmons, Morosin, Scheringer, and Freiburg, *Acta Cryst.*, 1961, **14**, 1222.

EXPERIMENTAL

Crystals were obtained by evaporation of a cold chloroform solution as small prisms with $\{101\}$, $\{10\bar{1}\}$, and $\{111\}$ equally developed. The crystal data were: $C_{14}H_{10}CuO_4$, $M = 305.7$, monoclinic, $a = 8.72 \pm 0.02$, $b = 6.19 \pm 0.02$, $c = 11.26 \pm 0.03$ Å, $\beta = 104.8^\circ$, $U = 587.6$ Å³, $D_m = 1.71$ by flotation, $Z = 2$, $D_c = 1.725$. Space group $P2_1/n$. Cu- K_α radiation, single-crystal Weissenberg photographs. Data were collected for the $hk0$, $h0l$, and $0kl$ zones by the multiple-film method, and intensities estimated by visual comparison with a standard scale. Small equant crystals were used and no absorption corrections made.

Symmetry considerations demand that the copper atom be at a centre of symmetry, and a direct electron-density synthesis could therefore be calculated for the (010) projection. The light-atom positions were clearly defined, and refinement proceeded by difference syntheses

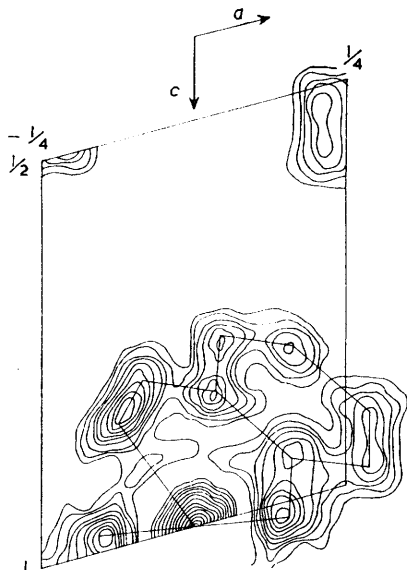


FIG. 1. Electron density projection on (010). Contours are at intervals of $1e \cdot \text{Å}^{-2}$, the lowest being the zero contour.

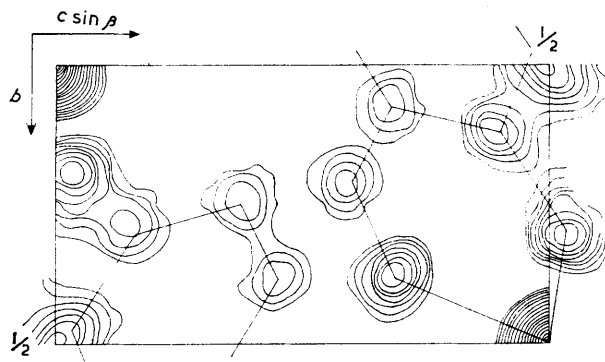


FIG. 2. Electron density projection on (100). Contours are at intervals of $1e \cdot \text{Å}^{-2}$, the lowest being the zero contour.

together with a least-squares procedure for determining the scale constant, the copper temperature factor, and an overall light-atom temperature factor. Seven reflections, of a total of 123, were corrected for secondary extinction.³ When the reliability factor was 0.13 the outstanding features of the difference map suggested distinct anisotropy in the thermal motion of the copper atom, which was corrected accordingly. The final reliability factor, including unobserved reflections, was 0.099. The electron density map is shown in Fig. 1.

For the (100) projection only planes of the type $h + l$ even are phase-determined by the copper atom. The false mirror plane thereby introduced into a direct electron-density synthesis was partially removed by the inclusion of an arbitrarily phased, high index, high intensity reflection of the type $h + l$ odd and interpretation was not difficult. Subsequent refinement was as above, except that only isotropic temperature factors were used. With 4 out of 86 reflections corrected for extinction the final R factor was 0.103. The electron-density map is shown in Fig. 2. Co-ordinates for the (001) projection were taken from the previous work and were refined as above to an R factor of 0.093.

Atomic co-ordinates are listed in Table 1. The numbering system, the bond lengths and the bond angles are shown in Fig. 3. Observed structure amplitudes and calculated structure factors are listed in Table 2. All atoms were clearly resolved in at least one projection and the

³ Pinnock, Taylor, and Lipson, *Acta Cryst.*, 1956, **9**, 175.

3292 McKinnon et al.: *The Colour Isomerism and Structure of*

standard deviations in atomic positions calculated by Cruickshank's⁴ procedure are thus appropriate. These are 0.022 Å for carbon atoms and 0.016 Å for oxygen. In no case did the co-ordinates obtained from different projections differ by more than 2σ.

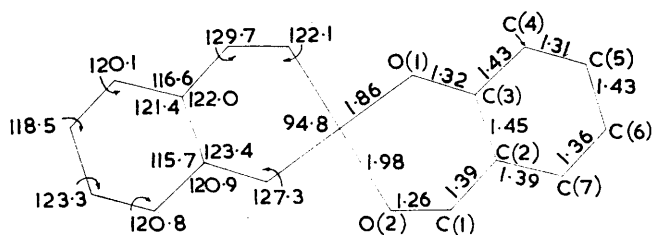


FIG. 3. Bond lengths and bond angles.

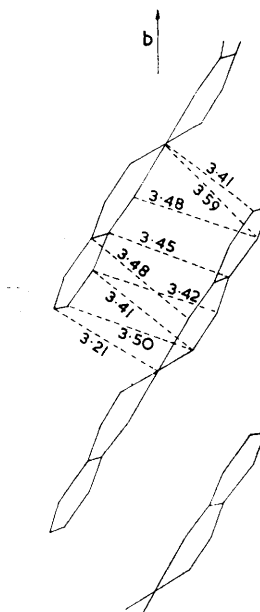


FIG. 4. Intermolecular approaches between successive molecules along (010).

TABLE 1.
Atomic co-ordinates.

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Cu.....	0.5000	0.5000	0.5000	C(3).....	0.3390	0.8787	0.5488
O(1).....	0.3393	0.7035	0.4819	C(4).....	0.2150	1.0346	0.5146
O(2).....	0.6280	0.6184	0.6572	C(5).....	0.2135	1.2064	0.5825
C(1).....	0.5950	0.7960	0.6995	C(6).....	0.3380	1.2580	0.6887
C(2).....	0.4630	0.9284	0.6586	C(7).....	0.4573	1.1140	0.7270

DISCUSSION

The molecules are steeply inclined to the (010) plane with the result that successive molecules along b make a large number of close van der Waals's contacts, as shown in Fig. 4. The axial separation from the copper atom (perpendicular to the co-ordination square) to the aromatic ring of the next molecule is 3.21 Å. The mean plane through the molecule was calculated by the method of Schomaker *et al.*⁵ as $x + 0.5662y - 1.332z = 0$ (co-ordinates expressed in Å), and individual atomic displacements from this plane are listed in Table 3. Several of these, *viz.*, for atoms O(1), O(2), C(3), and C(6), are highly significant in terms of the standard deviations, and the molecule must be distorted from the expected overall planarity. The mean plane through the benzene ring alone is $x + 0.5121y - 1.3522z + 0.3275 = 0$, and displacements from this are also listed in Table 3. None of these is significant for the light atoms, and it appears that the individual ligands are effectively planar, but that a bend in the molecule occurs at the points of co-ordination. The planes of the two benzene rings are separated by 0.39 Å. Chemically similar molecules, *e.g.*, bis-(*N*-methylsalicylaldiminato)copper(II), are perfectly planar, and the distortion of the molecule in the present structure may indicate a weak attraction between the copper atom and the adjacent aromatic ring. It has similarly been observed that in

⁴ Cruickshank, *Acta Cryst.*, 1949, **2**, 65.

⁵ Schomaker, Waser, Marsh, and Bergman, *Acta Cryst.*, 1959, **12**, 600.

TABLE 2.

Observed structure amplitudes and calculated structure factors ($\times 10$).

Planes $h0l$			Plane	F_o	F_c	Plane	F_o	F_c	Plane	F_o	F_c	Plane	F_o	F_c
Plane	F_o	F_c	501	354	321	110 $\bar{1}$	96	127	046	204	208	260	103	108
002	561 *	552	1	93	58	3	117	119	7	69	71	7	59	-61
4	587 *	606	3	381	349	5	86	77	8	147	124			
6	598 *	640	5	316	330				9	24	30			
8	240	214	7	202	224				10	187	209	310	40	44
10	211	213	9	513	290				11	64	88	4	182	138
12	187	207	11	259	209	002	533 *	536	12	63	74	3	375	392
14	150	46	13	243	218	4	618 *	600				4	119	92
			15	0	41	6	602 *	612	051	209	204	5	140	136
101	1210 *	1150	17	0	119	8	180	131	2	79	-55	6	13	7
3	206	161	19	58	124	10	155	147	3	246	259	7	140	137
5	206	-187	21	134	129	12	132	136	4	71	-20			
7	833 *	833	23	0	49	14	72	88	5	188	190	400	94	96
9	467 *	501	25	0	0				6	48	-44	1	250	255
11	341	302	27	382	383	011	138	149	7	139	132	2	452	466
13	329	346	29	442	420	2	31	41	8	63	-36	3	17	-20
15	155	124	31	273	269	3	246	310	9	94	105	4	248	249
17	281	274	33	137	140	4	200	-200	10	0	8	5	61	-49
19	114	155	35	466	502	5	252	223	11	24	28	6	119	138
21	174	170	37	232	229	6	138	-118				7	29	33
23	134	173	39	309	297	7	324	332	060	73	82			
25	173	162	41	224	210	8	78	85	1	102	-99	510	272	288
			43	119	100	9	186	149	2	207	148	2	140	-132
200	203	248	45	90	96	10	61	-45	3	84	89	3	211	197
2	242	-268	47	190	173	11	153	150	4	153	152	4	13	-24
4	64	-1	49	0	0	12	72	-55	5	68	67	5	279	273
6	277	274	51	503	547	13	77	75	6	86	77	6	92	80
8	240	256	53	211	213	14	23	-36	7	41	-29	7	37	43
10	352	331	55	3	263				8	106	109			
12	256	256	57	332	312	020	75	84	9	26	-15	600	362	372
14	175	189	59	166	179	1	105	134	1			1	114	-108
16	333	352	61	291	282	2	371 *	422	071	89	92	2	156	137
18	133	138	63	7	249	3	308	-102	2	35	-23	3	48	-31
20	204	181	65	7	154	4	233	254	3	0	8	4	142	137
22	81	134	67	9	139	5	128	-89	4	51	-63	5	40	-59
24	195	184	69	194	182	6	257	266	5	50	54	6	85	75
26	155	174	71	106	131	7	113	-111	6	0	8			
			73	0	0	8	258	282				710	189	172
301	41	27	75	180	153	9	15	-3				2	29	-33
1	252	275	77	283	272	10	64	42	080	72	88	3	105	103
3	240	183	79	0	38	11	36	-41	1	12	11	4	48	28
5	415 *	495	81	50	97	12	114	105				5	99	88
7	238	203	83	195	160	13	0	11				6	39	26
9	137	107	85	218	222				Planes $hk0$					
11	151	160	87	65	103	031	167	192	020	85	71			
13	263	276	89	170	166	2	282	307	4	246	209	800	138	135
15	279	292	91	125	116	3	187	191	6	75	87	1	85	-19
17	265	258	93	102	102	4	17	5	8	75	101	2	153	157
19	133	164	95	0	0	5	155	131				3	0	-11
21	226	211	97	97	97	6	56	-7	110	290	289	4	77	72
23	196	212	99	38	12	7	29	-31	2	62	-12	5	22	17
			101	32	72	8	160	142	3	358	340			
400	123	132	103	130	135	9	127	140	4	184	169	910	180	196
2	377	407	105	85	110	10	82	-79	5	281	255	2	70	56
4	264	310	107	77	76	11	75	76	6	169	-172	3	97	106
6	370	391	109	130	125	12	20	-3	7	119	120	4	0	9
8	214	224	111	115	110	13	26	55	8	9	6			
10	169	132	113	68	65									
12	190	120												
14	299	276	1000	78	92	040	209	199	200	228	233	1	18	-1
16	261	243	2	64	111	1	35	22	1	103	82	2	79	91
18	232	237	4	151	164	2	306	326	2	489	521	3	28	26
20	135	134	6	123	116	3	87	-79	3	37	-15			
22	195	193	8	96	82	4	278	282	4	112	97			
24	54	27	10	96	101	5	70	65	5	0	-6			

* denotes corrected for extinction.

TABLE 3.

Deviations from the mean planes through (i) the molecule and (ii) the benzene ring.

Atom	Deviation (Å)		Atom	Deviation (Å)	
	(i)	(ii)		(i)	(ii)
Cu	0	+0.193	C(3)	-0.067	-0.002
O(1)	-0.129	+0.005	C(4)	-0.010	+0.011
O(2)	-0.084	+0.052	C(5)	+0.020	-0.021
C(1)	-0.019	+0.056	C(6)	+0.090	+0.022
C(2)	-0.034	+0.004	C(7)	+0.013	-0.015

the crystal structure of bisacetylacetonatocopper(II),⁶ the copper atom makes an axial approach of 3.09 Å to a neighbouring conjugated ring, and this approach is associated

⁶ Dahl, Personal communication quoted by Piper and Belford, *Mol. Physics*, 1962, 5, 169.

with a distortion from the expected planarity of the molecule. It has been suggested⁷ that such weak attractions may be examples of polarisation bonds, the copper atom acting as acceptor and the π -bond system as donor.

While this Paper was being prepared a preliminary Note appeared⁸ describing an independent investigation of the same structure. The results appear to be in agreement but no mention is made of the above molecular distortion.

Calculations involved in this work were performed on SILLIAC, University of Sydney, and the IBM 1620 at the University of Canterbury.

We thank Dr. H. Freeman and Dr. D. van der Helm for the programmes used, and Dr. J. G. Sime, Dr. B. R. Penfold, and Mr. W. T. Robinson for assistance with the computations; also Professor D. R. Llewellyn for his interest, and the Research Committee of the New Zealand University Grants Committee for financial assistance.

UNIVERSITY OF AUCKLAND, NEW ZEALAND.

[Received, September 16th, 1963.]

⁷ Hall, Rae and Waters, *J.*, 1963, 5897.

⁸ Bevan, McConnell, and Graddon, *Nature*, 1963, **199**, 373.
