65. *The Colour Isomerism and Structure of Copper Co-ordination Compounds. Part VIII.*[1] *The Crystal Structure of a Second Crystalline Form of Bis-salicylaldehydatocopper*(II).

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The crystal structure of a second crystalline modification of bis-salicylaldehydatocopper(II) has been determined by three-dimensional *X*-ray methods. The ligands are distorted from coplanarity by weak polarisation bonds between the copper atom and the chelate ring of adjacent molecules. The dimorphs differ essentially in the nature of such intermolecular interactions.

The crystal structure of bis-salicylaldehydatocopper(II) recently described [1] shows that although the co-ordination is basically planar, weak axial interactions with neighbouring aromatic rings bring about a significant deviation from the overall planarity of the molecule. Another crystalline modification of this chelate has been reported [2] and we have determined its structure with the aim of accounting for the dimorphism.

Experimental

Crystals were obtained by cooling a hot saturated solution in ethanol. They were thin elongated plates with {100} developed and, as previously remarked,[2] were of irregular growth and badly overlaid. The data were: $C_{14}H_{10}CuO_2$, $M = 305{\cdot}7$, monoclinic, $a = 11{\cdot}75 \pm 0{\cdot}03°$, $b = 4{\cdot}00 \pm 0{\cdot}02°$, $c = 12{\cdot}42 \pm 0{\cdot}03$ Å, $\beta = 90{\cdot}3°$, $V = 584$ Å^3, $D_m = 1{\cdot}71$ g. cm.$^{-3}$ by pyknometer,[2] $D_c = 1{\cdot}74$ g. cm.$^{-3}$, $Z = 2$, space group $= P2_1/c$. Intensity data were collected with single-crystal Weissenberg photographs using Cu-K_α radiation. These were from the $h0l$, $h1l$, and $h2l$ reciprocal lattice sections only, giving a 70% coverage of the accessible information.

All crystals were of poor quality and many of the spots (particularly on the $h2l$ photograph) were very diffuse and considerably elongated. Intensities were measured by visual comparison with a standard scale and as far as possible reflexions of the same spot shape were chosen within each layer. The problem of interscaling these data with further low-quality photographs was avoided by leaving the scale factor for each layer as a parameter to be determined. No absorption corrections were made.

[1] Part VII, McKinnon, Waters, and Hall, *J.*, 1964, 3290.
[2] von Stackelberg, *Z. anorg. Chem.*, 1947, **253**, 136.

A direct electron density synthesis was calculated for the (010) projection, planes being phased by the copper atom which was located at a centre of symmetry by the space-group requirements. The light atoms were clearly defined and refinement by difference syntheses proceeded rapidly to an R-factor of 0·15. A preliminary calculation of three-dimensional structure factors using y co-ordinates estimated from the projection, by assuming standard bond lengths and bond angles for the molecule, gave approximate scale factors for the $h1l$ and $h2l$ data. A " heavy atom " three-dimensional electron density synthesis then computed clearly brought

TABLE 1.

Atomic co-ordinates.

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Cu	0	0	0	C(4)	0·2972	0·5681	0·0209
O(1)	0·1234	0·3024	−0·0191	C(5)	0·3831	0·6474	0·0915
O(2)	0·0247	−0·0505	0·1553	C(6)	0·3767	0·5668	0·2010
C(1)	0·1078	0·0829	0·2046	C(7)	0·2843	0·3695	0·2356
C(2)	0·1967	0·2722	0·1620				
C(3)	0·2020	0·3673	0·0547				

TABLE 2.

Observed structure amplitudes and calculated structure factors (×10).

h	l	F_o	F_c	h	l	F_o	F_c	h	l	F_o	F_c	h	l	F_o	F_c
	($h0l$ reflexions)				10	115	−163		12	90	73		4	87	112
0	2	449 *	478		12	141	151		−2	246	260		−2	115	122
	4	699 *	667		14	48	41		−4	220	220		−4	104	111
	6	559 *	575		−2	192	227		−6	144	139		−6	42	66
	8	211	220		−4	29	42		−8	246	174				
	10	161	176		−6	327	317		−10	248	262	15	0	40	57
	12	153	162		−8	295	260		−12	96	59		2	47	105
	14	119	119		−10	113	40						−2	64	85
					−12	236	191	9	0	257	191				
1	2	90	−147		−14	141	116		2	299	251		($h1l$ reflexions)		
	4	498 *	534						4	327	286	0	1	not measured	
	6	426 *	413	5	0	363	437		6	364	339		3	27	19
	8	930 *	845		2	220	211		8	155	162		4	159	197
	10	126	97		4	174	−165		10	141	123		5	201	250
	12	178	183		6	293	253		12	78	64		6	24	−13
	14	121	108		8	43	−100		−2	271	253		7	368 *	382
	16	43	60		12	147	180		−4	129	97		9	153	119
	−2	1247 *	1169		14	31	47		−6	136	146		10	68	64
	−4	200	214		−2	240	293		−8	64	45		11	185	129
	−6	930 *	845		−4	102	−118		−10	96	47		12	97	116
	−8	245	211		−6	228	228						13	143	130
	−10	115	58		−8	260	186	10	0	459	398		14	<38	42
	−12	104	95		−10	124	114		2	184	189		15	100	92
	−14	129	140		−12	189	124		4	256	246				
					−14	153	142		6	246	226	1	0	not measured	
2	0	113	144						10	115	117		1	1091 *	858
	2	328 *	345	6	0	338	325		12	74	115		2	62	−74
	4	273 *	310		2	34	8		−2	200	157		3	53	70
	6	497 *	533		4	144	137		−4	144	145		4	99	−122
	8	219	189		6	346	333		−6	135	73		5	583 *	612
	10	273	312		8	45	65		−8	132	129		6	126	−93
	12	212	246		10	113	141		−10	60	41		7	257	254
	14	222	192		12	129	129						8	93	108
	−2	194	272		14	54	62	11	0	205	195		9	261	217
	−4	157	−189		−2	477	671		2	93	−122		10	136	145
	−6	260	299		−4	189	209		4	174	181		11	170	147
	−8	299	278		−6	254	311		8	54	70		13	158	144
	−10	101	100		−8	313	302		10	93	91		15	66	78
	−12	65	8		−12	147	130		−2	225	220		−1	541 *	448
	−14	74	62		−14	127	91		−4	65	65		−2	187	−145
									−6	149	136		−3	56	−58
3	0	521 *	604	7	0	374	351		−8	119	63		−4	193	193
	2	40	44		2	243	239		−10	78	62		−5	277	250
	4	461 *	525		4	352	337						−6	124	67
	6	324	348		6	277	291	12	0	90	−105		−7	276	236
	8	400	479		8	81	62		4	104	122		−8	93	119
	10	251	271		10	101	93		6	39	56		−9	183	178
	12	135	140		12	146	149		8	43	58		−11	183	150
	14	166	151		−2	341	369		−2	166	152		−13	127	105
	−2	307 *	314		−4	343	440		−6	109	84		−15	96	85
	−4	20	0		−6	212	218		−8	116	109				
	−6	231	155		−8	409	542					2	1	285 *	344
	−8	223	108		−10	200	134	13	2	96	110		3	321 *	353
	−10	121	94		−12	107	83		4	82	100		4	113	−169
	−12	211	164		−14	124	115		6	62	73		5	330 *	390
	−14	88	41						8	33	50		6	94	−92
				8	0	397	369		−2	110	110		7	241	255
4	0	160	165		2	194	141		−4	51	56		8	69	78
	2	262	295		4	293	253		−8	71	91		9	210	184
	4	254	270		6	276	221						10	98	−99
	6	271	262		8	115	112	14	0	57	68		12	83	−69
	8	282	287		10	175	182		2	54	68		13	155	129

TABLE 2. (*Continued.*)

h	*l*	F_o	F_c
	−1	1298 *	1161
	−2	554 *	469
	−3	157	182
	−4	81	35
	−5	556 *	471
	−6	144	121
	−7	367	375
	−9	148	108
	−11	210	183
	−12	68	−60
	−13	167	161
	−15	104	100
3	0	171	139
	1	168	250
	2	45	75
	3	275 *	314
	4	199	−235
	5	137	142
	6	136	−140
	7	256	289
	8	45	−28
	10	164	−139
	11	128	107
	13	151	134
	15	44	50
	−1	539 *	600
	−2	482 *	450
	−3	250	259
	−4	81	95
	−5	292	266
	−6	110	110
	−7	507	458
	−8	77	72
	−9	180	159
	−11	143	94
	−12	74	−61
	−13	154	136
	−15	78	79
4	0	164	161
	1	321 *	379
	3	98	109
	4	192	−214
	5	296	352
	6	40	34
	7	238	251
	8	79	−50
	9	197	187
	10	111	−96
	11	200	212
	13	155	156
	14	48	−40
	15	51	70
	−1	542 *	587
	−2	235	−237
	−3	274	276
	−4	80	−49
	−5	181	145
	−6	225	−208
	−7	381	343
	−9	166	100
	−11	121	119
	−12	65	−49
	−13	107	66
	−14	48	−43
	−15	46	60
5	0	102	56
	1	243	245
	2	87	87
	3	282	340
	4	<37	−67
	5	349	396
	6	60	67
	7	282	374
	8	128	−158
	9	195	188
	11	124	115
	13	147	149
	−1	353	455
	−2	163	−127
	−3	405	422
	−4	156	−148
	−5	193	169
	−6	192	−165
	−7	430	420
	−8	229	−211
	−9	199	140
	−11	102	75
	−13	145	131
	−14	30	−17
6	0	184	184
	1	322	334
	2	65	−40
	3	225	223
	4	91	69
	5	245	262
	7	239	260
	8	49	50
	10	109	103
	11	162	165
	13	70	67
	−1	244	258
	−2	37	1
	−3	181	177
	−4	142	−142
	−5	132	117
	−7	231	206
	−8	110	−76
	−9	268	263
	−10	84	−59
	−11	82	51
	−13	144	152
7	0	49	16
	1	226	191
	2	119	110
	3	91	85
	4	155	155
	5	243	163
	6	82	104
	7	163	169
	8	153	177
	9	69	84
	11	138	151
	13	52	61
	−1	323	326
	−3	159	132
	−4	94	−59
	−5	56	52
	−7	110	99
	−8	70	72
	−9	108	61
	−10	47	−13
	−11	44	61
	−13	84	74
8	0	108	106
	1	245	249
	2	190	182
	3	146	134
	5	257	293
	6	86	91
	7	128	145
	9	58	66
	11	123	117
	13	69	96
	−1	251	221
	−2	78	79
	−3	271	282
	−4	81	78
	−5	108	93
	−7	158	208
	−8	86	84
	−9	119	105
	−13	51	61
9	0	111	84
	1	172	175
	2	124	−133
	3	48	29
	4	60	−70
	5	215	212
	7	49	20
	9	70	68
	11	119	119
	−1	280	278
	−3	161	151
	−4	92	78
	−5	178	204
	−7	131	124
	−8	81	91
	−9	183	229
	−10	72	82
	−11	56	58
10	0	69	−67
	1	70	−51
	2	138	−128
	3	132	105
	5	156	147
	6	59	−40
	7	80	79
	9	98	100
	10	<33	−38
	11	72	70
	−1	207	223
	−3	86	78
	−4	49	75
	−5	121	123
	−7	107	126
	−8	44	−24
	−9	130	103
	−10	61	71
	−11	73	88
11	0	49	−58
	1	137	131
	3	171	178
	5	189	192
	6	44	−46
	7	98	105
	9	73	72
	−1	127	128
	−3	109	132
	−4	<48	56
	−5	46	33
	−7	98	122
	−8	60	−31
	−9	78	88
	−10	37	−47
12	0	57	−71
	1	137	135
	3	119	126
	5	169	162
	9	69	89
	−1	209	228
	−3	120	140
	−5	82	99
	−7	81	80
	−9	58	80
13	0	41	43
	2	56	56
	3	127	133
	5	48	51
	7	48	60
	−1	125	141
	−2	<38	43
	−3	90	116
	−5	58	65
	−7	63	102
14	0	90	96
	1	55	58
	3	74	81
	−1	55	54
	−2	<30	−41
	−3	74	96
		(*h*2*l* reflexions)	
0	2	122	129
	3	27	−37
	4	264	234
	5	36	−52
	6	259	246
	7	55	−47
	8	185	147
	9	109	92
	10	174	154
	11	183	−170
	12	66	57
	13	50	−39
	14	98	101
1	0	290 *	306
	1	99	121
	2	177	185
	3	167	180
	4	100	89
	5	79	−78
	6	94	96
	8	186	160
	9	71	−74
	11	138	−116
	12	66	63
	13	41	41
	14	95	96
	−1	72	59
	−2	182	176
	−3	68	55
	−4	170	150
	−5	94	−72
	−6	374	316
	−7	64	−21
	−8	218	180
	−9	63	37
	−10	216	175
	−12	164	166
	−13	58	−31
	−14	88	84
2	0	390 *	454
	1	131	199
	2	122	148
	3	149	148
	4	<34	58
	5	167	−138
	6	329	286
	7	65	79
	8	161	146
	10	52	36
	11	<49	66
	12	126	115
	14	77	70
	−1	388 *	343
	−2	152	174
	−3	75	−42
	−4	219	199
	−5	167	−132
	−6	350	311
	−7	72	14
	−8	213	163
	−10	121	108
	−12	161	145
	−14	84	104
3	0	521 *	582
	2	152	186
	4	378 *	356
	5	50	−52
	6	349	323
	7	135	155
	8	155	142
	10	90	86
	12	126	125
	14	58	73
	−1	50	64
	−2	434 *	429
	−3	319	−262
	−4	128	135
	−5	99	−68
	−6	420	437
	−7	246	−205
	−8	264	225
	−9	<51	81
	−10	110	99
	−11	49	−23
	−12	125	121
	−13	37	3
	−14	71	80
4	0	291 *	374
	1	148	175
	2	227	281
	3	86	−88
	4	266	291
	6	220	255
	7	49	41
	8	149	148
	10	95	95
	12	129	136
	14	27	30
	−1	308 *	361
	−2	562 *	562
	−3	83	99
	−4	149	172
	−5	76	87
	−6	296	274
	−8	322	317
	−9	112	−65
	−10	89	82
	−12	117	129
	−13	56	−29
	−14	67	95
5	0	206	240
	1	60	42
	2	175	209
	4	208	251
	6	237	270
	7	101	108
	8	140	150
	9	51	63
	10	150	144
	12	111	109
	−1	67	−7
	−2	241	279
	−3	173	210
	−4	170	208
	−6	144	123
	−7	196	208
	−8	229	195

TABLE 2. (*Continued.*)

h	*l*	F_o	F_c	*h*	*l*	F_o	F_c	*h*	*l*	F_o	F_c	*h*	*l*	F_o	F_c
	−9	52	56		8	89	110	9	0	150	117		2	77	93
	−10	79	83		10	70	72		3	117	104		4	136	142
	−12	57	44		12	123	120		4	161	154		6	40	52
	−13	45	−31		−2	178	174		6	87	88		8	54	54
					−3	48	46		7	83	78		−2	149	141
6	0	211	235		−4	140	143		10	87	89		−3	47	−13
	1	97	84		−6	117	108		−2	200	182		−4	118	115
	2	209	259		−7	52	−12		−3	52	64		−6	111	126
	4	205	248		−8	139	133		−4	52	30		−7	45	−35
	6	190	231		−10	55	49		−5	72	−51		−8	84	92
	7	63	67		−12	70	75		−6	80	75		−9	40	74
	8	185	204						−7	83	−68				
	9	109	−110	8	0	209	190		−8	136	135	12	0	102	101
	10	109	121		1	150	−135		−9	57	−46		1	53	43
	12	117	130		2	50	−22		−10	59	56		2	94	102
	13	36	−22		3	109	−119		−11	42	−16		4	78	90
	−2	206	211		4	97	109						6	71	81
	−4	110	103		6	167	168	10	0	159	124		−1	68	−39
	−5	78	−39		7	50	−24		1	97	75		−2	123	128
	−6	122	121		9	79	68		2	89	92		−4	48	72
	−8	127	109		10	86	76		4	141	151		−6	75	75
	−9	71	68		11	54	−42		6	99	106				
	−10	58	63		12	60	74		8	<38	49	13	0	114	112
	−12	45	48		−1	70	−57		10	81	85		2	47	74
					−2	114	92		−1	109	−78		4	91	115
7	0	229	233		−3	<49	68		−2	194	185		−2	104	110
	1	132	130		−4	72	62		−4	181	158		−3	45	−17
	2	168	182		−5	104	−93		−6	81	84		−4	40	69
	3	183	−235		−6	117	127		−7	43	−27				
	4	70	83		−8	135	121		−8	128	135				
	6	206	251		−10	70	64		−10	80	99				
	7	141	−156		−12	42	50	11	0	127	123				

* Corrected for secondary extinction.

out two symmetry-related molecules and the atomic co-ordinates of one of these were determined. Three cycles of refinement involving the least-squares adjustment of positional parameters and temperature factors (an overall isotropic factor for the light atoms and a separate isotropic factor for copper) and a determination of scale factors by setting $k\Sigma \mid F_o \mid = \Sigma \mid F_c \mid$ for observed

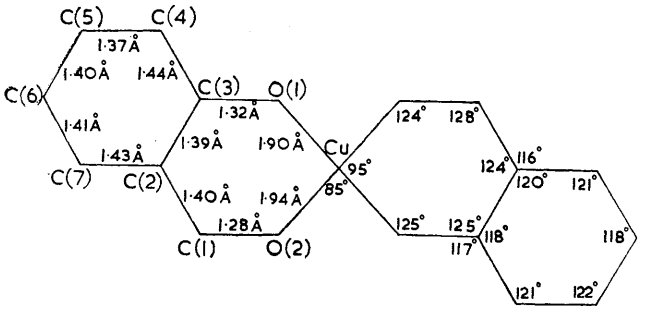

FIG. 1. Molecular bond lengths and angles.

planes reduced the R factor to 0·136 (observed planes only, with 38 corrected for secondary extinction [3]). This may be broken down into $R_{h0l} = 0{\cdot}141$, $R_{h1l} = 0{\cdot}131$, $R_{h2l} = 0{\cdot}137$, there being, respectively, 178, 272, and 239 observed planes.

Atomic co-ordinates are listed in Table 1. The numbering system is shown in Fig. 1 together with the observed bond lengths and angles. The maximum standard deviations in atomic positions for the light atoms are $\sigma_x = 0{\cdot}020$ Å, $\sigma_y = 0{\cdot}025$ Å, $\sigma_z = 0{\cdot}019$ Å. Final isotropic temperature factors of 2·90 for the light atoms and 2·50 for the copper atom were obtained. Observed structure amplitudes and calculated structure factors are listed in Table 2.

DISCUSSION

The molecular bond lengths and bond angles are normal and in reasonable agreement with those derived from the other dimorph.

The inclination of the molecules to the (010) plane (Fig. 2) is such that neighbours make a number of close contacts and the 3·15 Å separations between a copper atom and the hydroxy-oxygen atoms of adjacent molecules seem particularly significant. These complete a very distorted octahedron about the copper. They are shown to be genuine interactions by the distortion of the molecules from the overall planarity seen in the similar

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

complexes bis-(*N*-methylsalicylaldiminato)copper(II) [4] and bis-salicylaldiminatonickel(II).[5] The mean plane through the whole molecule was calculated by the method of Schomaker *et al.*,[6] as $x - 0{\cdot}51921y - 0{\cdot}37101z = 0$ and the mean plane through one benzene ring as $x - 0{\cdot}56908y - 0{\cdot}44641z + 0{\cdot}03172 = 0$ (co-ordinates in Å). The individual atomic deviations of the copper atom and one ligand from these planes are listed in Table 3. Each ligand is essentially planar but their two planes are separated within the complex by 0·37 Å. This deviation from overall planarity occurs within the co-ordinating sphere and introduces a " step " into this region of the molecule (Fig. 2).

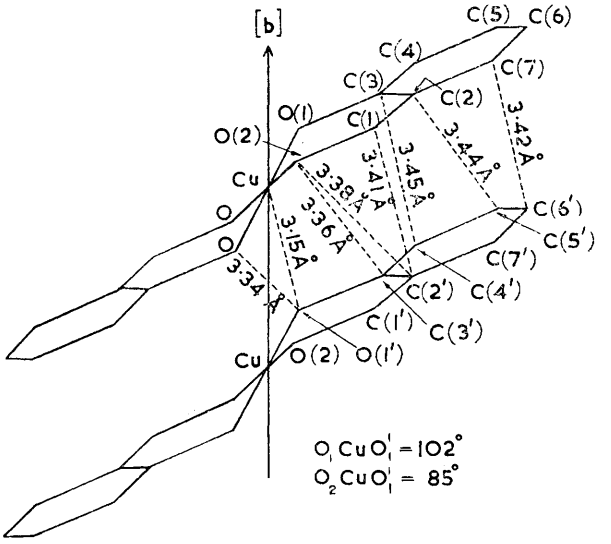

FIG. 2. Intermolecular approaches. The molecular distortion is exaggerated for clarity.

The perpendicular distance from a copper atom to the plane of a neighbouring chelate ring is 3·13 Å, slightly shorter than the distance to the oxygen, so the interaction may be with a delocalised system rather than with a specific atom. Interactions with such

TABLE 3.

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

Atom	Deviation in Å (i)	(ii)	Atom	Deviation in Å (i)	(ii)
Cu	0	−0·187	C(3)	+0·057	−0·002
O(1)	+0·168	+0·050	C(4)	+0·035	+0·022
O(2)	+0·038	−0·098	C(5)	−0·082	−0·033
C(1)	+0·071	−0·006	C(6)	−0·050	+0·023
C(2)	+0·030	−0·007	C(7)	−0·032	−0·003

systems are also found in bis(acetylacetonato)copper(II),[7] *NN'*-ethylenebis(acetylacetoneiminato)copper(II),[8,9] and the other crystalline form of bis-salicylaldehydatocopper(II).[1] Attention has been drawn to their similarity with the polarisation bonds of organic chemistry.[8]

The two dimorphs of this complex may now be compared. In both, chains of molecules exist parallel to *b* such that successive members make numerous close contacts. The angle of tilt differs in the two forms such that the copper atom makes its closest contact with a different delocalised system in each. The molecules are in each case distorted, but not in

[4] Lingafelter, Simmons, and Morosin, *Acta Cryst.*, 1961, **14**, 1222.
[5] Stewart and Lingafelter, *Acta Cryst.*, 1959, **12**, 842.
[6] Schomaker, Waser, Marsh, and Bergman, *Acta Cryst.*, 1959, **12**, 600.
[7] Dahl, personal communication to Piper and Belford, *Mol. Phys.*, 1962, **5**, 169.
[8] Hall, Rae, and Waters, *Proc. Chem. Soc.*, 1962, 143.
[9] Hall, Rae, and Waters, *J.*, 1963, 5897.

the same way. In the present form the two planar ligands are displaced in a sense which increases the angle of tilt in the region of the copper atom (Fig. 2). This seems clearly a consequence of the intermolecular interactions, the molecules being " stepped " in such a way as to allow the 3·15 Å approach to the chelate rings in the vicinity of O(1) without imposing excessively close contacts elsewhere. Where the polarisation bond involves the outer reaches of the molecules [near C(6) in the other modification] the distortions will, of necessity, be reversed.

The interactions, though weak, are thus seen to have structural significance and through the choice of alternative bond sites stabilise the molecular arrangement in one or other of the dimorphic forms.

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