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The Crystal Structure of Bis-(2-hydroxyacetophenone)-trimethylenediiminocopper(II)

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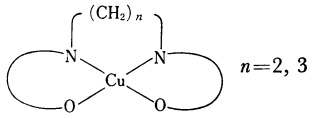
The crystal structure of bis-(2-hydroxyacetophenone)trimethylenediiminocopper(II), [Cu-(hapt)], has been determined on the basis of the X-ray diffraction data. The crystals are monoclinic. The cell dimensions are: $a=17.746$, $b=9.467$, $c=10.646$ Å, and $\beta=114.06°$. The space group is *Cc*, with four formula units in the unit cell. The structure has been refined from three-dimensional data by the least-squares method with anisotropic temperature factors to an *R*-value of 0.093. The copper atom is four-covalent, with the two planar 2-hydroxyacetophenone groups oriented so as to give a flattened tetrahedral co-ordination geometry. The six-membered copper-trimethylenediamine ring takes a "twisted boat" configuration. The Cu–O bonds are 1.88 and 1.89 Å in length, while the Cu–N bonds are 1.94 and 1.97 Å. The angle between the mean planes of the 2-hydroxyacetophenone moieties is 46.2°.

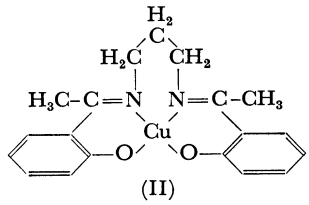
An extensive study has recently been made of the copper(II) complexes with tetradentate Schiff bases derived from several aldehydes or ketones and diamines by Nakahara and his collaborators.[1] These complexes possess three chelate rings, and their structures can be represented as follows:



$n=2, 3$

(I)

An investigation of the relative stabilities of the complexes has revealed that those complexes which have a five-membered central chelate ring ($n=2$) are generally more stable than those with a six-membered central chelate ring ($n=3$). It seemed that it would be of interest to clarify this point by determining the structure of a complex with a six-membered central chelate ring. For this purpose crystals of bis-(2-hydroxyacetophenone)trimethylenediiminocopper(II) were chosen. The complex has a 6-6-6*3 fused chelate ring structure, (II). The molecular structures of the complexes with a 6-5-6 (*N,N'*-disalicylidene-ethylenediaminecopper) and a 6-7-6 (*N,N'*-(2,2'-biphenyl)bis(salicylaldiminato)copper(II)) fused chelate ring structure have already been determined by Waters and his collaborators.[2,3] The former has a pyramidal-square coordination, while the latter has a distorted flattened-tetrahedral coordination, around the copper atom.



(II)

[Cu(hapt)]

The crystal and molecular structure of the complex, [Cu(hapt)], will be reported in this paper.

Experimental

The crystals of [Cu(hapt)] were prepared according to the method described by Tsumaki *et al.*[4] They are dark green in color and very stable in the air. The unit-cell dimensions were determined from higher-order reflections recorded on Weissenberg photographs (Cu$K\alpha$, $\lambda=1.5418$ Å). The possible space group was found to be $C2/c$ or Cc from the following systematic absences: hkl when $h+k$ is odd and $h0l$ when l is odd. Cc was shown to be consistent with the structure.

The specimens with dimensions of $0.05\times0.20\times0.80$ mm were used for the collection of the intensity data around the *c*-axis. Equi-inclination Weissenberg photographs were taken around the *c*-axis up to the eighth

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*3 The abbreviation "6-6-6" indicates the fused-chelate ring structure containing six-, six-, and six-membered rings, in a clockwise direction.

1) Y. Nakao, N. Nonagase and A. Nakahara, This Bulletin, **42**, 452 (1969).

2) D. Hall and T. N. Waters, *J. Chem. Soc.*, **1960**, 2644.

3) T. P. Cheeseman, D. Hall and T. N. Waters, *ibid.*, **1966**, 1396.

4) P. Pfeiffer, E. Breith, E. Lübbe and T. Tsumaki, *Ann.*, **503**, 84 (1933).

layer, while the zero layer photograph was taken around the b-axis with Cu$K\alpha$ radiation. A multiple film technique was used. Of the 1454 independent reflections within the effective copper sphere ($\sin\theta \leqq 0.98$), 1220 non-zero reflections were observed. The intensities were estimated visually with a standard film strip. The usual Lorentz, polarization, and spot-shape corrections were applied, but the absorption correction was neglected. The crystal data are shown in Table 1.

TABLE 1. CRYSTALLOGRAPHIC DATA

Monoclinic
$a=17.746\pm0.006$Å
b= 9.467 ± 0.002Å
$c=10.646\pm0.004$Å
$\beta=114.06\pm0.02°$
$Dm=1.500$ g/cm^3
$Dx=1.511$ g/cm^3
$Z=4$
Space group C_s^4-Cc
Linear absorption coefficient for Cu$K\alpha$, $\mu=19.0$ cm^{-1}

Structure Analysis

The positions of the copper atom and the four-coordinating atoms around the copper atom could be easily deduced from the three-dimensional Patterson maps. The structure factors were calculated from the parameter values of these atoms. The discrepancy factor, R (defined as $\sum||F_o|-|F_c||/\sum|F_o|$), was 0.32. Preliminary Fourier projections of the electron density upon (010) and (001) were then synthesized, using phases determined by the parameters of these five atoms. The approximate orientation of two 2-hydroxyacetophenone moieties could be deduced from these projections, but the trimethylenediamine ring could not be fixed. The atomic parameters of the trimethylenediamine ring were, therefore, assigned by constructing a scale model of the molecule. Considerable improvement was achieved in the agreement between the observed and calculated structure factors. The structure thus obtained was refined by the three-dimensional difference synthesis to $R=0.20$, and later by a block-diagonal least-squares method using a HBLS-4 program written by T. Ashida. After six cycles of this refinement, anisotropic temperature factors were introduced. The weighting scheme for the least-squares procedure was:

$$w=0.2, \quad \text{if } F_o \leqq F_{\min} \ (4.0)$$
$$w=1.0, \quad \text{if } F_{\min} < F_o < F_{\max} \ (25.0)$$
$$w=F_{\max}/F_o, \quad \text{if } F_o \geqq F_{\max}.$$

The effect of secondary extinction was corrected for five reflections which showed a marked extinction effect ($F_o > 45$). The final R-value became

TABLE 2(a). FINAL ATOMIC COORDINATES AND THEIR E.S.D.'S ($\times10^4$)

Atom	x/a	y/b	z/c
Cu	− 3(5)	392(2)	12(10)
O(1)	− 635(7)	−1001(13)	397(14)
O(2)	643(6)	−1002(9)	− 357(11)
N(1)	− 231(6)	1803(13)	1115(15)
N(2)	234(8)	1812(11)	−1128(13)
C(1)	−1230(10)	− 757(16)	777(16)
C(2)	−1792(12)	−1895(23)	549(22)
C(3)	−2416(13)	−1770(18)	1041(19)
C(4)	−2496(12)	− 555(19)	1742(22)
C(5)	−1941(10)	545(14)	1949(18)
C(6)	−1299(9)	518(16)	1460(16)
C(7)	− 770(8)	1772(15)	1710(15)
C(8)	− 873(13)	2981(17)	2532(20)
C(9)	321(7)	3043(13)	1327(18)
C(10)	4(23)	3943(14)	6(44)
C(11)	− 312(15)	3040(19)	−1305(18)
C(12)	769(10)	1745(14)	−1652(18)
C(13)	831(14)	2951(17)	−2608(23)
C(14)	1309(9)	512(14)	−1478(18)
C(15)	1940(11)	601(23)	−1970(23)
C(16)	2490(11)	− 473(21)	−1724(20)
C(17)	2441(8)	−1705(21)	−1053(23)
C(18)	1824(9)	−1844(13)	− 579(16)
C(19)	1233(8)	− 723(13)	− 794(16)

TABLE 2(b). THE TEMPERATURE FACTORS ($\times10^4$)
(The expression of the temperature factor is $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	37	85	88	7	68	6
O(1)	44	109	119	− 2	105	15
O(2)	36	39	72	12	73	37
N(1)	14	92	125	28	35	105
N(2)	48	53	49	65	85	106
C(1)	44	91	32	− 5	50	−4
C(2)	41	116	121	−58	42	67
C(3)	67	97	60	−55	98	−10
C(4)	46	122	110	−73	68	−36
C(5)	39	71	73	− 1	84	−13
C(6)	34	109	29	−19	52	19
C(7)	22	91	43	−42	42	−28
C(8)	60	83	95	−33	105	−67
C(9)	15	46	131	4	45	19
C(10)	37	77	74	−25	42	66
C(11)	92	127	20	133	104	79
C(12)	39	53	84	−52	34	21
C(13)	75	80	141	−58	160	−38
C(14)	28	54	104	−29	51	−21
C(15)	39	173	144	−39	92	−138
C(16)	38	168	103	−49	102	−81
C(17)	10	162	177	19	17	−82
C(18)	34	56	52	− 3	59	38
C(19)	28	63	56	− 4	43	−27

TABLE 3. OBSERVED AND CALCULATED STRUCTURE FACTORS

Columns are h, F_o, F_c

H FO FC	H FO FC	H FO FC	H FO FC	H FO FC	H FO FC	H FO FC	H FO FC
K,L= 0 0	-12 13 13	-6 106 94	3 117 149	-20 48 48	-6 72 72	15 37 41	8 23 26
2 478 478	-10 95 100	-4 60 54	5 66 49	-18 58 60	-4 80 107	K,L= 4 4	10 36 39
4 404 431	-8 48 50	-2 113 115	7 48 65	-16 30 35	-2 72 79	-20 28 28	K,L= 3 5
6 100 107	-6 105 124	0 179 181	9 79 91	-14 100 93	0 94 95	-18 27 28	-19 47 50
8 206 223	-4 46 51	2 206 212	11 59 64	-12 12 19	2 94 98	-16 18 27	-17 55 57
10 126 118	-2 97 117	4 96 94	K,L= 4 2	-10 47 44	4 94 98	-12 64 66	-15 79 78
12 178 155	0 179 170	6 82 67	-18 32 31	-8 164 169	6 32 40	-10 80 95	-13 61 61
14 75 60	2 174 209	8 25 32	-14 34 30	-6 93 79	8 56 65	-8 135 123	-11 127 129
16 162 144	4 61 82	10 55 44	-12 33 40	-4 114 135	10 40 42	-6 117 106	-9 151 158
K,L= 1 0	6 239 226	12 26 25	-10 70 75	-2 36 59	12 33 44	-4 124 125	-7 177 174
1 617 688	8 124 135	14 54 52	-8 96 115	0 149 134	K,L= 9 3	-2 98 109	-5 185 201
3 22 33	10 134 129	K,L= 9 1	-6 195 200	2 151 119	-15 32 39	0 57 67	-3 318 308
5 184 200	12 54 53	-13 51 47	-4 180 182	4 252 226	-13 27 29	4 63 55	-1 269 244
7 160 154	14 55 50	-11 26 28	-2 105 106	6 65 66	-11 54 51	6 35 42	1 134 125
9 170 155	K,L= 3 1	-9 23 23	0 25 30	8 154 163	-9 36 38	8 56 56	3 48 39
11 98 93	-19 44 37	-7 32 31	2= 8 8	10 48 45	-7 51 50	10 39 36	5 121 105
13 77 67	-17 32 35	-5 66 59	4 13 22	12 61 54	-5 63 68	12 45 38	7 128 96
15 138 126	-15 55 51	-3 26 27	6 77 80	14 14 15	-3 52 53	14 23 23	9 67 63
17 84 74	-13 114 105	-1 94 66	8 80 77	K,L= 3 3	-1 50 58	K,L= 5 4	11 17 27
K,L= 2 0	-11 89 85	1 91 72	10 64 64	-21 29 36	1 164 145	-19 47 49	13 42 36
0 113 184	-9 191 182	3 14 20	12 37 42	-19 59 61	3 82 96	-17 29 37	15 15 27
4 122 119	-7 135 121	7 54 48	K,L= 5 2	-17 55 49	5 37 44	-15 33 33	K,L= 4 5
6 210 207	-5 371 399	9 76 60	-15 44 38	-15 21 23	7 11 18	-13 68 71	-20 39 44
8 254 259	-3 135 152	11 61 45	-13 52 47	-13 46 46	11 14 23	-9 56 49	-18 60 61
10 104 121	-1 48 53	13 16 19	-11 137 149	K,L= 10 3	-7 107 109	-16 40 40	-16 145 147
12 43 46	1 41 43	K,L= 10 1	-9 59 48	-9 134 154	-12 27 33	-5 186 171	-12 63 66
14 118 105	3 31 46	-12 17 25	-7 15 22	-7 207 231	-10 44 45	-3 205 179	-10 250 261
16 123 111	5 139 155	-8 54 44	-5 53 49	-5 213 239	-8 34 32	3 59 58	-8 117 120
18 70 53	7 272 268	-6 59 50	-3 43 41	-3 370 344	-6 47 51	5 32 34	-6 157 154
20 38 43	9 111 129	-4 62 50	1 95 108	-1 138 146	-4 47 48	7 107 108	-4 49 58
K,L= 3 0	11 142 156	-2 20 17	3 43 38	1 95 75	-2 22 26	9 50 46	-2 165 153
1 166 149	13 31 40	0 55 51	5 196 191	3 192 174	0 61 67	11 22 24	0 93 107
3 161 151	15 25 31	8 31 36	7 139 135	5 183 160	2 57 72	13 14 22	2 152 142
5 80 108	17 16 26	10 21 27	9 88 90	7 136 123	K,L= 11 3	K,L= 6 4	4 83 83
7 224 213	K,L= 4 1	K,L= 11 1	11 77 76	9 76 82	-9 19 22	-18 32 30	6 200 209
9 180 167	-20 45 51	-9 28 31	13 64 60	11 56 58	-7 34 42	-12 72 79	8 68 66
11 72 60	-18 21 22	-7 66 63	K,L= 6 2	13 62 69	-5 36 39	-6 14 17	10 49 41
13 30 31	-16 82 60	-5 17 26	-14 87 90	K,L= 4 3	-3 21 27	-4 40 30	12 20 21
15 82 67	-14 85 61	-3 25 28	-10 59 46	-20 40 38	-1 16 21	0 81 79	14 43 50
17 54 49	-12 97 87	-1 23 25	-8 31 25	-18 30 31	1 19 24	2 84 82	K,L= 5 5
K,L= 4 0	-10 174 150	1 15 24	-4 47 36	-16 75 76	K,L= 0 4	4 130 134	-19 44 46
0 10 17	-8 207 191	3 15 23	-2 74 62	-14 58 62	-22 45 54	6 43 34	-17 47 45
2 12 33	-6 292 290	5 16 20	0 50 35	-12 236 230	-20 64 65	8 37 33	-15 77 76
4 61 79	-4 329 354	K,L= 0 2	2 73 89	-10 160 166	-18 98 102	K,L= 7 4	-13 24 19
6 103 128	-2 69 30	-20 38 42	4 58 56	-8 174 165	-16 146 157	-5 66 78	-11 155 157
8 101 106	0 105 144	-18 28 24	6 99 105	-6 120 143	-14 208 210	-1 21 17	-9 171 186
10 90 77	2 38 53	-16 94 87	K,L= 7 2	-4 396 390	-12 240 244	3 79 71	-7 148 141
12 34 30	6 152 164	-14 183 145	-15 26 26	-2 276 274	-10 270 278	5 21 27	-5 114 110
14 23 17	8 40 45	-12 157 132	-13 43 37	0 118 130	-8 134 131	K,L= 8 4	-3 165 152
K,L= 5 0	10 64 65	-10 120 115	-5 31 31	2 34 45	-6 154 167	-16 29 37	-1 173 162
1 12 3	12 57 58	-8 258 251	1 134 130	4 56 47	-4 40 62	-14 17 21	1 141 147
3 69 65	16 22 27	-6 411 393	3 69 59	6 41 42	0 70 63	-12 22 21	3 86 77
5 197 190	18 13 21	-4 353 368	5 32 33	8 59 58	2 303 291	-10 20 27	5 158 165
7 113 114	K,L= 5 1	2 816 798	9 34 39	10 25 32	4 176 156	-8 30 44	7 97 103
9 79 75	-19 46 39	4 236 273	11 33 38	12 65 78	6 175 152	-6 18 29	9 43 39
11 86 82	-17 60 46	6 250 290	K,L= 8 2	14 29 33	8 54 55	-4 18 22	11 18 18
13 65 51	-15 99 80	8 138 142	-8 75 58	K,L= 5 3	10 138 144	0 51 54	13 21 26
15 12 16	-13 105 91	10 108 121	-6 85 82	-19 46 48	12 98 94	10 40 45	K,L= 6 5
K,L= 6 0	-11 77 64	12 81 85	-4 60 58	-17 35 38	14 65 69	K,L= 9 4	-18 51 58
0 29 34	-9 123 125	14 34 52	-2 71 56	-15 49 58	K,L= 1 4	-15 13 17	-16 82 86
2 21 26	-7 91 102	16 80 93	2 91 86	-13 92 112	-21 42 43	-13 16 14	-14 121 117
4 109 104	-5 286 267	18 76 108	4 12 12	-11 179 194	-19 24 34	-11 41 41	-12 121 117
6 42 28	-3 121 143	K,L= 1 2	6 51 47	-9 87 105	-17 94 98	-9 23 25	-10 166 160
12 59 52	-1 105 113	-21 19 23	8 28 29	-7 144 146	-15 92 97	-7 42 41	-8 97 87
16 28 32	1 146 175	-19 59 48	10 30 29	-5 142 134	-13 157 159	-5 81 87	-6 132 121
K,L= 7 0	3 69 78	-15 120 127	K,L= 9 2	-3 316 307	-11 209 181	-3 71 70	-4 125 115
1 48 39	5 99 105	-13 115 128	-11 15 20	-1 184 168	-9 82 85	-1 43 35	-2 198 206
3 55 59	7 116 135	-11 111 115	-9 33 35	1 188 176	-7 72 69	3 14 20	0 158 160
7 56 43	9 84 75	-9 18 29	-7 100 114	3 179 164	-5 289 283	5 20 24	2 44 44
9 33 29	11 100 100	-7 225 223	-5 84 78	5 128 128	-3 114 133	7 18 25	4 71 77
15 35 35	13 33 32	-5 23 26	-3 78 62	7 60 61	-1 163 214	9 28 37	6 82 80
K,L= 8 0	15 37 33	-3 212 231	-1 47 43	9 67 63	1 80 104	K,L= 10 4	8 25 27
0 219 240	17 53 41	-1 60 42	1 86 79	11 49 48	3 294 307	-10 25 17	10 37 40
2 53 38	K,L= 6 1	1 741 756	3 57 49	13 58 66	5 175 164	-8 37 33	12 15 14
4 54 42	-18 34 32	3 381 353	5 77 67	K,L= 6 3	7 73 79	-6 76 90	K,L= 7 5
6 39 31	-16 47 41	5 185 188	7 61 53	-18 51 63	9 61 51	-4 71 74	-17 65 78
8 66 50	-14 136 127	7 90 99	9 66 70	-16 22 32	11 92 82	-2 79 86	-15 74 78
10 23 24	-12 82 71	9 181 163	11 22 32	-14 34 39	13 44 57	4 50 52	-13 83 90
K,L= 9 0	-10 84 76	11 85 85	K,L= 10 2	-12 116 124	15 17 18	6 27 27	-11 95 113
1 123 117	-8 73 60	13 82 74	-12 19 20	-10 67 58	K,L= 2 4	K,L= 11 4	-9 49 48
5 80 61	-6 87 94	15 31 20	-10 20 17	-8 133 128	-22 21 24	-9 34 51	-7 39 40
7 74 59	-4 142 147	17 73 89	-8 46 46	-6 69 73	-18 53 47	-7 40 44	-3 38 36
9 74 67	-2 192 207	19 13 22	-6 63 49	-4 127 116	-16 44 47	-5 48 53	-1 93 91
11 56 42	0 195 204	K,L= 2 2	-4 46 41	-2 133 147	-14 74 70	-3 47 51	1 52 50
K,L= 10 0	2 237 261	-20 27 32	-2 45 35	0 142 144	-12 211 182	3 35 53	3 24 31
2 12 22	4 123 135	-18 84 74	2 72 59	2 206 197	-10 137 140	K,L= 9 5	5 82 77
4 35 27	6 145 156	-16 69 53	4 15 23	4 271 272	-8 182 177	-21 23 32	9 32 37
6 65 57	8 122 136	-14 215 212	6 51 47	6 84 89	-6 356 330	-19 55 60	11 23 27
8 77 80	10 111 125	-12 149 145	K,L= 11 2	8 98 103	-4 315 341	-17 94 101	K,L= 8 5
10 36 36	12 93 70	-10 90 109	-9 42 47	10 50 49	-2 352 341	-15 38 42	-16 53 65
K,L= 11 0	14 79 67	-8 172 153	-7 66 73	12 58 59	0 281 249	-11 45 45	-14 62 70
3 37 31	16 64 59	-6 202 187	-5 69 73	14 30 34	2 210 205	-9 39 36	-12 83 95
5 57 44	K,L= 7 1	-4 118 140	-3 76 81	K,L= 7 3	4 378 357	-7 106 83	-10 79 85
7 73 68	-15 26 31	-2 392 382	-1 37 38	-17 48 56	6 113 99	-5 39 36	-8 60 57
K,L= 12 0	-13 95 79	0 224 255	1 13 18	-15 18 25	8 50 51	-1 71 69	-6 49 52
0 36 33	-11 26 29	2 475 515	3 36 31	-13 80 102	10 64 56	1 63 52	-4 52 51
2 27 32	-9 108 102	4 96 114	K,L= 1 3	-11 48 44	12 35 34	3 100 87	-2 60 57
K,L= 1 1	-7 79 64	8 121 132	-21 20 28	-9 38 36	14 26 26	5 32 38	0 79 83
-17 82 59	-5 92 80	10 138 149	-19 42 46	-7 65 58	K,L= 3 4	7 24 16	2 81 81
-15 69 53	-3 95 90	12 83 73	-17 56 54	-5 50 57	-21 37 38	9 66 60	4 88 96
-13 28 21	-1 219 213	14 34 34	-15 27 42	-3 61 64	-17 78 65	11 32 35	6 40 46
-11 31 17	1 223 242	16 25 29	-13 62 65	-1 83 81	-13 164 175	13 27 34	8 22 24
-9 234 212	3 259 264	18 20 25	-11 43 35	1 14 21	-11 164 172	15 19 20	10 19 25
-7 155 161	5 76 72	K,L= 3 2	-9 42 52	3 160 152	-9 204 212	K,L= 9 5	K,L= 9 6
-5 178 150	7 93 84	-19 65 44	-7 93 91	5 75 69	-7 171 192	-18 59 60	-15 25 35
-3 91 90	9 15 25	-17 75 61	-5 150 137	7 53 59	-5 169 181	-16 94 91	-13 33 35
1 208 181	11 38 42	-15 111 94	-3 134 105	9 57 61	-3 103 107	-12 41 31	-11 47 52
3 552 531	13 17 29	-13 209 185	-1 65 49	11 37 39	-1 374 330	-10 51 52	-9 42 41
5 90 113	15 63 71	-11 107 88	1 451 395	13 19 23	1 87 90	-8 83 76	-7 42 40
7 116 134	K,L= 8 1	-9 205 196	7 114 109	K,L= 8 3	3 262 251	-6 126 110	-5 75 74
11 36 46	-16 18 20	-7 346 328	9 114 109	-16 44 50	5 114 114	-4 185 161	-3 85 88
15 57 54	-14 76 60	-5 386 359	11 54 56	-14 57 62	7 37 39	-2 247 214	-1 51 49
K,L= 2 1	-12 56 44	-3 339 359	13 14 21	-12 80 96	9 62 57	0 116 130	1 78 76
-16 63 64	-10 81 70	-1 135 192	15 28 37	-10 29 40	11 65 66	2 126 178	3 75 77
-14 69 56	-8 93 81	1 18 22	K,L= 2 3	-8 58 69	13 42 42	4 66 57	5 39 45

Table. 3 (Continued)

H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC
-6	24	24	-4	47	46	-19	53	52	-19	18	24	-13	100	98	K,L= 10		7	1	70	70	-3	113	120	-8	74	68
-2	56	55	-2	37	39	-17	88	89	-17	74	73	-11	106	105	-6	11	15	3	118	116	-1	110	107	-6	33	31
4	66	65	0	48	63	-15	81	83	-15	76	76	-9	104	102	-4	43	45	5	68	70	1	112	114	-4	44	49
6	28	33	K,L= 1		7	-13	51	55	-13	99	98	-7	103	95	-2	14	27	7	59	57	5	25	32	0	30	37
K,L= 7		6	-17	27	31	-11	48	54	-11	53	46	-5	53	53	K,L= 0		8	9	20	30	9	37	42	2	10	23
-17	15	25	-15	35	39	-9	169	182	-9	158	150	-3	39	37	-22	42	56	K,L= 2		8	K,L= 4		8	K,L= 7		8
-15	24	28	-13	44	42	-7	155	170	-7	87	83	-1	95	80	-20	28	28	-20	36	33	-20	15	20	-15	11	18
-13	16	21	-11	44	41	-5	120	132	-5	105	101	1	103	104	-18	35	39	-18	94	90	-18	37	41	-13	29	33
-11	61	50	-9	12	25	-3	67	77	-3	75	64	3	67	62	-16	33	36	-16	78	89	-16	38	31	-5	19	27
-9	48	46	-7	125	118	-1	117	114	-1	118	116	5	62	61	-14	136	140	-14	121	124	-14	48	40	K,L= 8		8
-1*	9	12	-5	61	73	1	101	97	1	93	82	7	25	26	-12	192	204	-12	119	127	-8	37	27	-14	21	21
1	21	27	-3	111	104	3	49	46	3	64	62	K,L= 8		7	-10	228	243	-10	60	65	-6	76	69	-12	20	23
K,L= 8		6	-1	134	142	5	21	27	7	94	98	-16	25	34	-8	246	265	-8	57	58	-4	64	52	-10	29	29
-16	24	29	1	134	121	7	73	85	9	41	45	-14	69	72	-4	140	155	-6	133	137	-2	96	80	-8	60	55
-14	51	46	5	24	23	9	46	53	K,L= 6		7	-12	88	93	-2	203	185	-4	49	50	0	67	61	-6	42	35
-10	27	33	K,L= 2		7	11	14	28	-18	51	47	-10	89	82	0	106	107	-2	90	90	2	46	43	-4	48	42
-4	66	65	-22	22	29	K,L= 4		7	-16	69	70	-8	71	63	2	194	206	0	35	28	10	10	20	-2	64	64
0*	10	20	-20	31	20	-18	64	59	-14	108	102	-6	48	42	4	134	140	2	49	61	K,L= 9		8	0	12	19
2	19	20	-18	44	48	-16	54	54	-12	111	114	-4	57	52	6	66	70	4	41	39	-19	42	43	2	51	54
K,L= 9		6	-16	69	61	-14	108	112	-10	134	140	-2	71	66	8	58	61	6	65	63	-17	64	53	4	24	30
-13	35	34	-14	46	43	-12	96	98	-8	202	202	0	78	74	K,L= 1		8	8	28	39	-15	62	53	K,L= 9		8
-11	15	22	-12	32	29	-10	20	32	-6	126	120	2	71	77	-21	37	33	10	35	47	-11	33	39	-11	18	22
-9	62	64	-10	65	59	-8	84	87	-4	53	47	4	57	60	-19	67	53	K,L= 3		8	-9	85	83	-9	48	42
-7	20	22	-8	184	187	-6	70	74	-2	41	42	6	41	47	-17	25	33	-21	18	23	-7	86	80	-7	58	63
-5	67	64	-6	133	138	-4	116	117	0	103	97	K,L= 9		7	-15	72	63	-19	46	41	-5	93	99	-5	51	49
-3	63	68	-4	28	32	-2	159	151	2	92	89	-13	38	40	-13	167	157	-17	51	47	-3	64	53	-3	51	54
-1	49	54	-2	47	50	0	104	104	4	28	39	-11	37	38	-11	147	151	-15	78	78	-1	31	38	-1	42	37
1	41	39	0	132	103	2	109	105	6	49	49	-9	57	58	-9	136	143	-13	69	60	3	32	40	1	34	36
K,L= 10		6	2	48	40	6	56	56	8	22	29	-7	16	18	-7	175	181	-11	93	100	7	14	29			
-10	32	34	4	34	36	8	112	118	K,L= 7		7	-5	24	29	-5	83	78	-9	33	37	9	11	19			
-8	52	52	K,L= 3		7	10	41	44	-17	20	23	-3	23	23	-3	111	109	-7	88	97	K,L= 6		8			
-6	26	27	-21	36	39	K,L= 5		7	-15	48	47	3	33	40	-1	54	43	-5	53	52	-12	51	39			

0.093 for all the observed reflections. The atomic scattering factors were taken from the "International Tables for X-ray Crystallography".[5] The final atomic parameters and their estimated standard deviations are listed in Table 2. The observed and calculated structure factors are compared in Table 3.

Discussion

A perspective drawing of the [Cu(hapt)] molecule is shown in Fig. 1. The bond lengths and angles in the molecule are listed in Table 4, together with their e.s.d.'s, they are also shown in Fig. 2.

The bis-(2-hydroxyacetophenone)trimethylenediimine group is coordinated to the copper atom as a tetradentate ligand through two phenolic oxygen atoms and two nitrogen atoms of the Schiff-base linkage. The coordination around the copper atom is a distorted tetrahedron. The Cu–O distances are 1.88 and 1.89 Å, and the Cu–N distances are 1.94 and 1.97 Å. These values agree well with those found in the related complexes.[6–8] The angle between the two planes defined by Cu, O(1), and N (1) and by Cu, O(2), and N(2) is 34.4°, being equal neither to 90°, a value expected for a regular tetrahedral environment, nor to 0° for a square-planar configuration. The distorted tetrahedral configu-

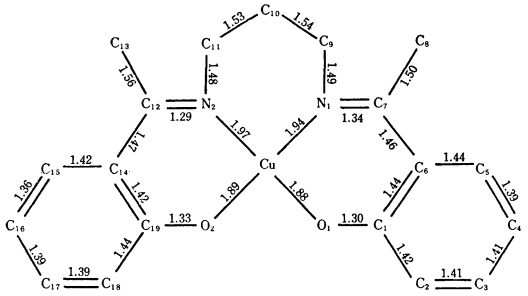


Fig. 2(a). Intramolecular bond length (in Å).

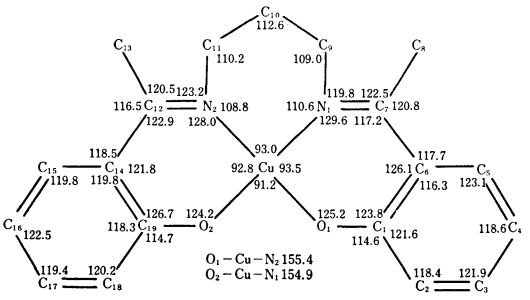


Fig. 2(b). Intramolecular bond angle (in degrees).

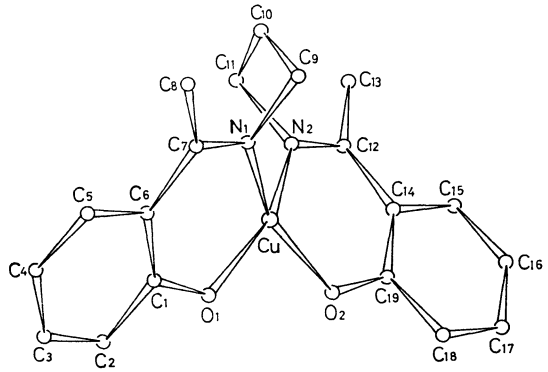


Fig. 1. Perspective drawing of the molecule.

5) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham (1962), p. 202.

6) E. C. Lingafelter, G. L. Simmons and B. Morosin, *Acta Cryst.*, **14**, 1222 (1961).

7) M. A. Jarski and E. C. Lingafelter, *ibid.*, **17**, 1109 (1964).

8) E. R. Boyko, *ibid.*, **21**, 614 (1966).

TABLE 4(a). INTRAMOLECUIAR BOND LENGTHS (IN Å) AND THEIR E.S.D.'S

2-haph moiety (I)		2-haph moiety (II)	
Cu - O(1)	1.88(0.02)	Cu - O(2)	1.89(0.01)
Cu - N(1)	1.94(0.02)	Cu - N(2)	1.97(0.02)
O(1)-C(1)	1.30(0.02)	O(2)-C(19)	1.33(0.02)
N(1)-C(7)	1.34(0.02)	N(2)-C(12)	1.29(0.02)
C(1)-C(2)	1.42(0.03)	C(18)-C(19)	1.44(0.02)
C(1)-C(6)	1.44(0.02)	C(14)-C(19)	1.42(0.02)
C(2)-C(3)	1.41(0.03)	C(17)-C(18)	1.39(0.03)
C(3)-C(4)	1.41(0.03)	C(16)-C(17)	1.39(0.03)
C(4)-C(5)	1.39(0.03)	C(15)-C(16)	1.36(0.03)
C(5)-C(6)	1.44(0.03)	C(14)-C(15)	1.42(0.03)
C(6)-C(7)	1.46(0.02)	C(12)-C(14)	1.47(0.03)
C(7)-C(8)	1.50(0.03)	C(12)-C(13)	1.56(0.03)
Trimethylenediamine ring			
N(1)-C(9)	1.49(0.02)		
N(2)-C(11)	1.48(0.03)		
C(9)-C(10)	1.54(0.04)		
C(10)-C(11)	1.53(0.04)		

TABLE 4(c). INTERMOLECULAR DISTANCES LESS THAN 3.6 Å

Atom 1	Atom 2	distance	e.s.d.
O(1)	N(2)	3.47	0.02
O(1)	C(12)	3.19	0.02
O(1)	C(13)	3.19	0.02
O(2)	C(13)	3.36	0.03
O(2)	C(15)	3.42	0.02
N(1)	O(2)	3.51	0.02
N(1)	C(19)	3.41	0.02
C(1)	N(2)	3.41	0.02
C(1)	C(11)	3.58	0.02
C(2)	C(11)	3.48	0.02
C(5)	O(1)	3.48	0.02
C(7)	O(2)	3.19	0.01
C(7)	C(19)	3.60	0.02
C(8)	O(1)	3.46	0.03
C(8)	O(2)	3.30	0.02
C(9)	C(18)	3.48	0.02
C(9)	C(19)	3.58	0.02

Atom 1: $(x.y,z)$
Atom 2: $(x, -y, z+1/2)$

TABLE 4(b). INTRAMOLECULAR BOND ANGLES (IN DEGREES) AND THEIR E. S. D.' S

Coordination angles			
O(1)-Cu-N(1)	93.5 (0.8)		
O(2)-Cu-N(2)	92.8 (0.7)		
O(1)-Cu-O(2)	91.2 (0.6)		
N(1)-Cu-N(2)	93.0 (0.6)		
O(1)-Cu-N(2)	155.4 (0.7)		
O(2)-Cu-N(1)	154.9 (0.7)		
2-haph moiety (I)		2-haph moiety (II)	
Cu - N(1)-C(7)	129.6 (1.1)	Cu - N(2)-C(12)	128.0 (1.2)
Cu - O(1)-C(1)	125.2 (1.2)	Cu - O(2)-C(19)	124.2 (1.0)
O(1)-C(1)-C(6)	123.8 (1.5)	O(2)-C(19)-C(14)	126.7 (1.3)
O(1)-C(1)-C(2)	114.6 (1.6)	O(2)-C(19)-C(18)	114.7 (1.2)
N(1)-C(7)-C(6)	117.2 (1.4)	N(2)-C(12)-C(14)	122.9 (1.5)
N(1)-C(7)-C(8)	122.5 (1.4)	N(2)-C(12)-C(13)	120.5 (1.5)
C(1)-C(6)-C(7)	126.1 (1.6)	C(12)-C(14)-C(19)	121.8 (1.6)
C(1)-C(2)-C(3)	118.4 (2.0)	C(17)-C(18)-C(19)	120.2 (1.4)
C(2)-C(3)-C(4)	121.9 (2.0)	C(16)-C(17)-C(18)	119.4 (1.7)
C(3)-C(4)-C(5)	118.6 (2.1)	C(15)-C(16)-C(17)	122.5 (2.1)
C(4)-C(5)-C(6)	123.1 (1.6)	C(14)-C(15)-C(16)	119.8 (2.1)
C(1)-C(6)-C(5)	116.3 (1.5)	C(15)-C(14)-C(19)	119.8 (2.1)
C(2)-C(1)-C(6)	121.6 (1.8)	C(14)-C(19)-C(18)	118.3 (1.5)
C(5)-C(6)-C(7)	117.7 (1.5)	C(12)-C(14)-C(15)	118.5 (1.6)
C(6)-C(7)-C(8)	120.8 (1.5)	C(13)-C(12)-C(14)	116.5 (1.7)
Trimethylenediamine ring			
Cu - N(1)-C(9)	110.6 (1.0)		
Cu - N(2)-C(11)	108.8 (1.3)		
N(1)-C(9)-C(10)	109.0 (1.6)		
N(2)-C(11)-C(10)	110.2 (1.8)		
C(9)-C(10)-C(11)	112.6 (1.2)		
C(7)-N(1)-C(9)	119.8 (1.3)		
C(11)-N(2)-C(12)	123.2 (1.6)		

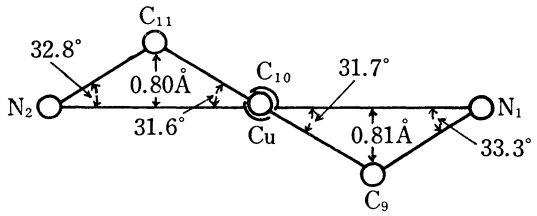


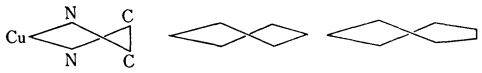
Fig. 3. Conformation of Cu(II)-trimethylenediamine ring.

rations are found in some *N*-substituted bis-salicylaldimine complexes of copper.[3,9-11] These authors claim that the substituent is sufficiently bulky to prevent the normal square-planar complex from being sterically feasible in the case of *N*-*t*-butyl[9] and *N*-isopropyl[10] complexes, and that the distortion in the *N*-ethyl[11] complex is due to packing forces in the crystal.[12] In the present compound, the two planar 2-hydroxyacetophenoneimine groups are joined by three methylene groups. Consequently, the central chelate ring is six-membered. The presence of this six-membered ring appears to give rise to the distortion of the square-planar coordination around the central copper atom. In fact, the related ethylenediamine analogue, *N*,*N*′-disalicylidene-ethylenediaminecopper,[2] exhibits a square-planar coordination. The conformation of the Cu(II)-trimethylenediamine ring is a twisted boat form, as is illustrated in Fig. 3. The six-membered chelate ring has approximately a twofold axis of rotation through the central copper atom and the central carbon atom C(10) of the ligand. The carbon atoms, C(9) and C(11), are 0.81 and 0.80 Å respectively apart from the plane defined by Cu, N(1), and N(2). It should be noted here that all the isolated metal-trimethylenediamine chelate rings

Table 5. Comparison of various fused-chelate ring structures

	a	b	c
Bond lengths and angles			
Cu–O	1.91, 2.03	1.88, 1.89	1.90, 1.90Å
Cu–N	1.94, 2.08	1.94, 1.97	1.94, 1.96Å
O–Cu–N	95°	93.5°	93.6°
O′–Cu–N′	90	92.8	93.6
O–Cu–O′	89	91.2	88.9
N–Cu–N′	82	93.0	96.1
O–Cu–N′	180	155.4	151.4
O′–Cu–N	180	154.9	154.6
Dihedral angle	0	34.4	37

Conformation of the central chelate ring



a: *N*,*N*′-disalicylidene-ethylenediaminecopper[2]
b: Present work
c: *N*,*N*′-(2, 2′-biphenyl) bis (salicylaldiminato) copper(II)[3]

Table 6. Least-squares planes

Coefficient of least-squares plane equations.

$A(x')+B(y')+C(z')+D=0$

	A	*B*	*C*	*D*
a: Coordination plane (I) [Cu, O(1), N(1)]	0.5285	0.2904	0.7977	−2.6264
b: Coordination plane (II) [Cu, O(2), N(2)]	0.5231	−0.3010	0.7974	−2.8562
c: Coordination plane (III) [Cu, N(1), N(2)]	0.7713	0.0007	0.6365	−1.4193
d: Chelate ring (I) [Cu, O(1), N(1), C(1) C(6), C(7)]	0.3761	0.3318	0.8651	−3.4027
e: Chelate ring (II) [Cu, O(2), N(2), C(12), C(14), C(19)]	0.3853	−0.3347	0.8600	−3.3655
f: Benzene ring (I) [C(1), C(2), C(3), C(4), C(5), C(6)]	0.2813	0.4024	0.8712	−3.8511
g: Benzene ring (II) [C(14), C(15), C(16), C(17), C(18), C(19)]	0.2676	−0.4099	0.8720	−3.3858
h: 2-haph moiety (I) [O(1), N(1), C(1), C(2), C(3), C(4), C(5), C(6), C(7)]	0.2825	0.3640	0.8875	−3.9227
i: 2-haph moiety (II) [O(2), N(2), C(12), C(14), C(15), C(16), C(17), C(18), C(19)]	0.2832	−0.3673	0.8859	−3.4897

$x'=ax+cz\cos\beta \qquad y'=by \qquad z'=cz\sin\beta$

9) T. P. Cheeseman, D. Hall and T. N. Waters, *J. Chem. Soc.*, **1966**, 685.
10) P. L. Orioli and L. Sacconi, *J. Amer. Chem. Soc.*, **88**, 277 (1966).
11) C. Panattoni, G. Bonbieri and R. Graziani, *Acta Cryst.*, **23**, 537 (1967).
12) D. Hall, R. H. Sumner and T. N. Waters, *J. Chem. Soc.*, **1969**, 420.

TABLE 7. DEVIATIONS FROM LEAS-SQUARES PLANES (Å × 10^3)

	d-plane	f-plane	h-plane		e-plane	g-plane	i-plane
Cu	130	(369)	(350)	Cu	−108	(−431)	(−346)
O(1)	−146	(−125)	−98	O(2)	138	(73)	87
N(1)	− 21	(221)	134	N(2)	42	(−261)	−117
C(1)	70	−11	2	C(19)	−61	4	16
C(2)	(243)	2	61	C(18)	(−254)	1	−50
C(3)	(365)	4	53	C(17)	(−403)	1	−58
C(4)	(325)	−1	−7	C(16)	(−378)	−9	−16
C(5)	(159)	−9	−60	C(15)	(−178)	14	68
C(6)	54	15	−29	C(14)	−48	−11	53
C(7)	−75	(47)	−48	C(12)	48	(−105)	25
C(8)	(−183)	(−37)	(−187)	C(13)	(263)	(96)	(280)

( ) not included in the least-squares calculations.

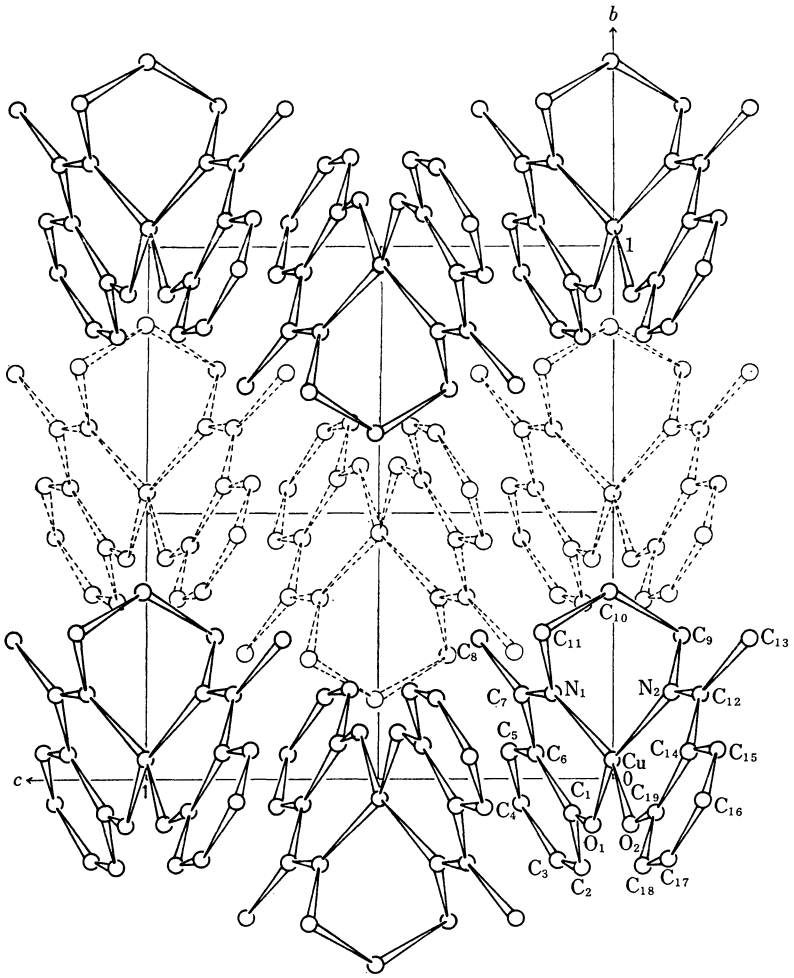


Fig. 4. Projection of the structure along the *a*-axis.

hitherto reported take a chair form.[13,14],*4 The reason for taking such a twisted boat form in the present compound may be that the arrangements of bonds around the two imino nitrogen atoms have

13) T. Nomura, F. Marumo and Y. Saito, This Bulletin, **42**, 1016 (1969).

14) E. Yasaki, I. Oonishi, H. Kawaguchi, S. Kawaguchi and Y. Komiyama, This Bulletin, **43**, 1354 (1970).

*4 The crystal structures of *trans*-$[Co(NO_2)_2(tn)_2]NO_2$ and *cis*-$[Co(NCS)_2(tn)_2]NCS$ were presented at the 22nd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1969.

to be planar.

The twofold symmetry of the fused central chelate ring is also observed in such related complexes as *N,N'*-disalicylidene-ethylenediaminecopper with a 6-5-6 fused chelate ring structure and *N,N'*-(2,2'-biphenyl)bis(salicylaldiminato)copper(II) with a 6-7-6 structure.[2,3] In Table 5, the shape and size of the central ring in the 6-*X*-6 fused chelate-ring structures are compared ($X=5$, 6, and 7). Obviously, the N–Cu–N' angle increases with the increase in X. The dihedral angles between the two coordination planes show the same tendency: 0° for $X=5$, 34.4° for $X=6$, and 37.0° for $X=7$. It seems likely that the extent of the distortion of square-planar coordination is related to the number of atoms in the central chelate ring.

Such a distorted-tetrahedral coordination around the central copper atom as is described above will certainly decrease the stability of the complex.[1]

The bond distances and angles within 2-hydroxyacetophenone moieties do not differ significantly from those reported for similar molecules.[6-8]

Equations for several least-squares planes are listed in Table 6, while the deviations from those planes are shown in Table 7. The two 2-hydroxyacetophenone moieties are approximately planar, and the deviations of the copper atom from these planes are 0.35 and 0.34 Å respectively. The angle between the two planes is 46.2°.

A projection of the structure along the a-axis is shown in Fig. 4. The molecules are alternately stacked with 2-hydroxyacetophenone groups parallel, but with Cu-C(10) directions opposite along the *c*-axis, thus forming columns. The short contacts in the columns occur between C(7) and O(2), (3.19 Å), and between C(12) and O(1), (3.19 Å). These columns of molecules are packed laterally with the usual van der waals contacts.

The numerical calculations were carried out on the HITAC 5020E at the Computer Centre of the University of Tokyo.

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