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The Structure of Coordination Compounds. II. The Crystal and Molecular Structure of the β Form of Anhydrous Copper 8-Hydroxyquinolinate

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The β form of anhydrous copper 8-hydroxyquinolinate crystallizes as dark tabular monoclinic crystals. The cell dimensions are:

$$a_0 = 10{\cdot}644 \pm 0{\cdot}004,\ b_0 = 8{\cdot}593 \pm 0{\cdot}003,\ c_0 = 15{\cdot}239 \pm 0{\cdot}004\ \text{Å};\ \beta = 102{\cdot}18^\circ.$$

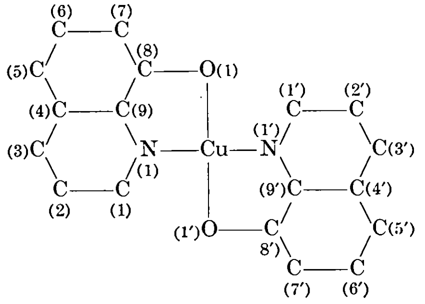
The space group is $P2_1/c$ with four molecules per unit cell. A spherical crystal was used in the measurement of the intensity of 2413 independent reflections. The data were refined by least squares with a final residual R of 7·1%.

The crystal is composed of dimer-like units similar to those reported in copper dimethylglyoxime. The copper atom is five-coordinate with 2 oxygen atoms at an average distance of 1·930 Å and 2 nitrogen atoms at an average distance of 1·972 Å. The fifth ligand is an oxygen atom from a second molecule. Since this oxygen–copper distance is 2·830 Å, the two atoms are only weakly bonded.

Introduction

The use of 8-hydroxyquinoline as a complexing agent is well known. However, the nature of the salts formed and the bonding between anion and cation is not well understood. For example, with cupric ion Jonassen (1962) found that the anhydrous as well as the dihydrated 8-hydroxyquinolinate could be obtained in an α and a β form. The β form of the dihydrate was reported by Merritt, Cady & Mundy (1954) to be isomorphous with the zinc 8-hydroxyquinolinate dihydrate. They also suggested that the anydrous β form might be tetrahedral. This assumption was based on the unit cell and space group determination by Mundy (1948) which indicated that the molecule did not possess a center of symmetry. And, in addition, Liu & Bailar (1951) reported a separation of the zinc complex of 8-hydroxyquinoline-5-sulfonic acid into optical isomers, suggesting that the zinc and possibly the copper 8-hydroxyquinolinate were tetrahedral. The infrared measurements by Charles, Freiser, Friedel, Hilliard & Johnston (1956) of a number of metal salts of 8-hydroxyquinoline and its derivatives did not resolve the question of the structure of these chelates. Chatterjee (1959) studied the ultraviolet absorption of 8-hydroxyquinoline and the copper salt and concluded that the complex was planar with an appreciable amount of double bond character in the metal–oxygen bond.

To resolve the question of the configuration of the copper complex, an X-ray structure determination was required. The β form of copper 8-hydroxyquinolinate was thus chosen as the second structure in the author's program devoted to the structure of coordination compounds. The molecular formula of copper 8-hydroxyquinolinate and the atomic numbering are:



Jonassen (1962) has indicated that the α form is being investigated elsewhere.

Experimental

The β form of anhydrous copper 8-hydroxyquinolinate is obtained as very dark, well-developed tabular crystals. Weissenberg photographs indicated that the crystals were monoclinic and elongated along the $\tilde{b}$ axis. A large crystal was ground to a sphere 0·2 mm in diameter with a modified version of the crystal grinder described by Bond (1951). After an attempt to mount the spherical crystal with the $\tilde{b}$ axis parallel to the axis of rotation, the crystal was found to be aligned with the $\tilde{a}$ axis parallel to the axis of rotation. The systematic absences observed on the Weissenberg photographs of the two crystals were:

hkl	no absences,
$h0l$	absent when l is odd,
$0k0$	absent when k is odd.

The space group is thus uniquely determined to be $P2_1/c$ (C^5_{2h}). Weissenberg photographs were also taken about the $\tilde{b}$ axis with the spherical crystal to check for possible damage which might have occurred during the grinding process.

Determination of the unit-cell dimensions and intensity measurements were carried out by use of the General Electric single-crystal orienter with molybdenum radiation ($\alpha_1=0{\cdot}70926$ Å and $\alpha_2=0{\cdot}71354$ Å). The unit-cell dimensions were determined by using a narrow beam with a narrow slit at the counter window. The average values of these measurements are given below:

$$a=10{\cdot}644\pm0{\cdot}004,\ b=8{\cdot}593\pm0{\cdot}008\ ,$$
$$c=15{\cdot}239\pm0.004\text{ Å};\ \beta=102{\cdot}18^\circ\ .$$

These values are in good agreement with the values reported by Mundy (1948):

$$a=10{\cdot}66,\ b=8{\cdot}65,\ c=15{\cdot}24\text{ Å};\ \beta=101{\cdot}6^\circ\ .$$

The density reported by Mundy (1948) of 1·707 g.cm^{-3} suggests 3·98 molecules per unit cell; the density calculated for four molecules is 1·715 g.cm^{-3}.

Intensity measurements were made with a scintillation counter and pulse height selector. The stationary crystal — stationary counter technique was employed in measuring the 2413 reflections with $2\theta\le50{\cdot}0^\circ$ (molybdenum radiation). The background measurements, corrections for $\alpha_1-\alpha_2$ splittings, and the reduction of data to a set of F^2 (observed) values have been described previously by the author (Palenik, 1964).

Determination of the structure

A sharpened three-dimensional Patterson synthesis with the origin peak intact was computed. The position of the copper atom was determined from the Patterson synthesis. A Fourier synthesis was computed with the use only of the contribution of the copper atoms to the structure factor for determining the phases. A Buerger Minimum Function was also computed with the copper–copper inversion peak as the superposition point. A comparison of the Fourier synthesis and Minimum Function indicated probable positions for the twenty-two atoms in the hydroxyquinolinate groups. The presence of a number of large peaks in the Fourier synthesis which were not assigned to atom positions suggested a cautious approach. The second Fourier synthesis was calculated with the use of the copper atom and eight atoms of one hydroxyquinolinate anion for determining the phases. A careful check of the second Fourier synthesis revealed that the peak heights of the postulated atoms increased or remained constant, while the heights of the doubtful peaks all decreased. A third Fourier synthesis was calculated in which all of the twenty-three independent atoms were used in the structure factor calculation for determining the phases. A new set of coordinates was obtained from the third Fourier synthesis and provided the starting parameters for the least-squares refinement. The value of R, the usual residual, was 19·1% for the structure factor calculation which used approximate values of the scale and temperature factors.

In the above structure factor calculations and the following least-squares refinement, the following scattering factors were used: neutral copper from Freeman & Watson (1961), oxygen and nitrogen from Hoerni & Ibers (1954), and carbon and hydrogen from McWeeny (1951).

Refinement of the trial structure

The first stage of the refinement was carried out by least-squares using individual isotropic thermal parameters. The full matrix was calculated for each cycle. The weighting scheme chosen was:

$$\begin{array}{ll} \text{if}\quad F_o<11{\cdot}3 & \sqrt{w}=F_o/11{\cdot}3 \\ \text{if}\quad 11{\cdot}3\le F_o\le45{\cdot}4 & \sqrt{w}=1{\cdot}0 \\ \text{if}\quad F_o>45{\cdot}4 & \sqrt{w}=45{\cdot}4/F_o\ . \end{array}$$

The above weighting reflects our prejudice regarding the accuracy of the values of F_o. Three cycles dropped R, the usual residual, to 9·9%. At this point anisotropic thermal parameters were introduced in the refinement process.

If anisotropic thermal parameters are included, it is necessary to determine 208 independent variables. Because of the large number of variables, it was necessary to approximate the full matrix with three-by-three blocks for the positional parameters and with six-by-six blocks for the thermal parameters. Partial shifts of 0·75 and 0·50 were used for the positional and thermal parameters respectively. Since the isotropic refinement had included the interaction between the scale and temperature factors, the scale factor (G) was shifted by 0·25 of the amount calculated by dividing $\Sigma w\Delta F(\delta|F_c|/\delta G)$ by $\Sigma w(\delta|F_c|/\delta G)^2$. The shifts for all parameters were tabulated for each cycle and carefully surveyed to determine if any trends in the shifts were apparant. A total of ten cycles was calculated before it was felt that no trends in the shifts were apparent. R was 8·0%.

A difference Fourier synthesis was calculated using the last least-squares parameters for the heavier atoms. Approximate hydrogen positions were computed on the assumption that the C–H distance was 1 Å and that the hydrogens could be found on extensions of the cross-ring vectors. A reasonable fit to positive areas in the difference map was found for all twelve independent hydrogen atoms.

A total of six additional least-squares cycles was calculated using the block approximation. Only the heavier atoms were refined. The hydrogen atoms were fixed, but their contribution to the structure factor was calculated for each cycle. The final value of R was 7·1%.

Table 1. *Final atomic parameters for the heavier atoms and their probable errors in fractions of the cell edges*

The temperature factor for each atom is of the form $T_i = \exp\{-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)\}$. All values have been multiplied by 10^5

	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	01438	30107	18646	00782	00659	00200	-00059	00122	00093
C(2)	-06689	41378	21040	00652	00856	00312	-00380	00279	-00185
C(3)	-15094	48836	14446	00554	00764	00370	-00083	00281	-00163
C(4)	-15731	45173	05330	00403	00478	00318	-00186	00196	00045
C(5)	-23886	52140	-02067	00451	00864	00383	00258	00089	00143
C(6)	-23947	47282	-10601	00477	00865	00336	00169	-00045	00290
C(7)	-15588	35180	-12224	00472	00953	00238	-00103	-00078	-00044
C(8)	-07235	28056	-05206	00295	00529	00292	00188	00001	00141
C(9)	-07372	33264	03627	00478	00413	00289	-00010	00182	00061
C(1′)	24356	-02717	-09029	00642	00678	00283	-00183	00160	00007
C(2′)	33333	-12975	-11507	00580	00911	00301	-00118	00133	-00282
C(3′)	42187	-20009	-05062	00554	01084	00360	00259	00120	-00078
C(4′)	42936	-17037	04182	00460	00634	00338	00034	00179	-00026
C(5′)	51677	-23381	11419	00481	00885	00359	00123	-00033	-00000
C(6′)	51526	-19316	20034	00691	00613	00363	00018	-00077	00158
C(7′)	42055	-08471	21928	00585	00668	00303	-00096	-00010	00175
C(8′)	33166	-02029	15084	00398	00519	00280	00030	00121	00111
C(9′)	33685	-06350	06076	00398	00474	00277	-00181	00049	00041
σ	00054	00068	00039	00052	00080	00028	00107	00062	00078
N(1)	01129	26139	10248	00596	00642	00272	-00124	00160	00041
N(1′)	24512	00210	-00438	00427	00536	00261	-00152	00042	-00103
σ	00043	00053	00030	00042	00061	00022	00084	00048	00059
O(1)	00542	16458	-06193	00712	00879	00260	00453	00003	-00153
O(1′)	24161	07830	16212	00592	00938	00266	00058	00156	-00056
σ	00038	00047	00026	00039	00060	00018	00079	00043	00053
Cu	12305	12074	05064	00456	00699	00227	00264	00039	-00060
σ	00006	00008	00004	00006	00009	00003	00013	00006	00009

A second difference Fourier synthesis was calculated with the use of only the heavier atoms in the structure factor calculation. New hydrogen atom positions were determined from the difference Fourier synthesis. At this point the refinement was terminated.

Results

The final set of positional and thermal parameters for the heavier atoms (hydrogens excluded) is presented in Table 1. Since there are two crystallographic 8-hydroxyquinolinate ions, primes are used in Table 1 to distinguish between chemically equivalent atoms in the two anions. An estimate of the standard deviations for each atom was made using the inverse of the appropriate 3×3 or 6×6 matrices. The values for like atoms were averaged to give the final deviations quoted in Table 1. The individual values did not differ significantly from the mean value.

The hydrogen positions obtained from the second difference Fourier synthesis together with their apparent peak heights are given in Table 2. The distance of the hydrogen from the carbon atom to which it is bonded is also given in Table 2. The final set of structure factors calculated with the use of the parameters given in Tables 1 and 2 is presented in Table 3.

The pertinent intramolecular distances and angles are tabulated in Table 4 and illustrated in Fig. 1.

Table 2. *Probable hydrogen positions, peak heights and carbon–hydrogen distances*

Atom [Atom i]*	X	Y	Z	Height (e.Å^{-3})	Distance (Å)
H(1) [C(1)]	0·082	0·269	0·238	0·6	0·99
H(2) [C(2)]	-0·072	0·416	0·272	0·8	0·95
H(3) [C(3)]	-0·220	0·568	0·156	0·5	1·05
H(4) [C(5)]	-0·299	0·592	-0·010	0·4	0·92
H(5) [C(6)]	-0·281	0·511	-0·151	0·4	0·80
H(6) [C(7)]	-0·173	0·323	-0·185	0·7	0·97
H(7) [C(1′)]	0·147	-0·002	-0·137	0·5	1·14
H(8) [C(2′)]	0·303	-0·142	-0·194	0·7	1·18
H(9) [C(3′)]	0·485	-0·273	-0·056	0·5	0·94
H(10) [C(5′)]	0·601	-0·312	0·104	0·4	1·16
H(11) [C(6′)]	0·560	-0·240	0·246	0·7	0·86
H(12) [C(7′])	0·422	-0·059	0·286	0·8	1·04

* Denotes atom to which the hydrogen is bonded.

The primed atoms in Fig. 1 refer to the primed coordinates in Table 1. The intermolecular distances less than 4·0 Å, representing van der Waals contacts, are tabulated in Table 5. A packing drawing of the complex is shown in Fig. 2.

The thermal parameters given in Table 1 were converted to mean square displacements with the results given in Table 6. A number of least-squares planes were calculated through various heavy atoms and the results tabulated in Table 7.

Table 3. *Observed and calculated structure factors*

The values of h and k are given above each group with the values of l listed, F(observed) and F(calculated) given in that order. A negative F(observed) indicates an unobserved reflection

0, 0		
2	1704	1795
4	125	-114
6	350	-349
8	800	-797
10	648	-655
12	607	-603
14	172	-123
16	155	131
1, 0		
-16	123	-112
-14	294	-292
-12	494	-485
-10	491	-494
-8	105	-115
-6	299	254
-4	513	513
-2	1609	1721
0	1237	1274
2	145	159
4	292	-298
6	754	-758
8	1015	-1063
10	404	-407
12	50	16
14	104	100
16	358	348
2, 0		
-18	23	-30
-16	303	-278
-14	495	-513
-12	447	-434
-10	39	-32
-8	398	-315
-6	275	-171
-4	1346	1329
-2	162	124
0	227	224
2	782	-751
4	547	-665
6	838	-761
8	620	-702
10	35	3
12	241	-231
14	338	333
16	385	373
3, 0		
-18	144	-138
-16	245	-231
-14	232	-224
-12	100	104
-10	334	326
-8	159	158
-6	565	530
-4	602	597
-2	302	-291
0	508	-465
2	445	-486
4	877	-950
6	508	-524
8	98	69
10	346	347
12	509	530
14	310	300
16	134	116
4, 0		
-18	180	-159
-16	128	-114
-14	34	-68
-12	429	430
-10	697	666
-8	724	713
-6	346	339
-4	96	-71
-2	291	-387
0	131	-93
2	656	-663
4	472	-490
6	289	268
8	302	314
10	961	1021
12	596	612
14	86	74
5, 0		
-16	24	-2
-14	303	284
-12	511	519
-10	430	393
-8	220	216
-6	430	-406
-4	524	-658
-2	474	-449
0	308	-303
2	144	-128
4	338	358
6	409	443
8	313	285
10	291	295
12	93	96
14	181	-176
6, 0		
-16	413	386
-14	321	314
-12	241	232
-10	52	-28
-8	285	-239
-6	780	-814
-4	1293	-1266
-2	452	-451
0	116	-82
2	44	-13
4	63	94
6	409	402
8	257	248
10	51	18
12	269	-271
7, 0		
-16	356	322
-14	187	171
-12	51	-51
-10	459	-451
-8	563	-560
-6	601	-617
-4	297	-285
-2	51	-21
0	452	419
2	626	664
4	343	356
6	166	148
8	119	-87
10	210	-224
12	249	-246
8, 0		
-16	125	114
-14	75	-72
-12	274	255
-10	55	24
-8	505	-510
-6	231	-222
-4	241	-219
-2	404	401
0	678	695
2	435	456
4	177	153
6	88	52
8	109	30
10	204	-215
9, 0		
-14	200	-184
-12	76	-53
-10	264	-256
-8	86	-63
-6	110	84
-4	217	225
-2	572	561
0	548	526
2	196	188
4	149	-161
6	254	-248
8	347	-361
10, 0		
-12	166	-154
-10	117	81
-8	89	79
-6	307	306
-4	307	299
-2	326	310
0	253	-221
2	413	-441
4	169	-160
6	408	-423
11, 0		
-12	90	56
-10	148	139
-8	147	115
-6	227	217
-4	221	214
-2	61	-63
0	336	-339
2	189	-181
4	231	-215
12, 0		
-8	127	115
-6	157	151
-4	112	-95
-2	59	38
0	241	227
2	141	-119
0, 1		
1	1126	1045
2	402	-376
3	370	356
4	396	-396
5	58	20
6	468	-465
7	401	-400
8	352	-336
9	365	-573
10	138	61
11	268	-272
12	68	23
13	72	57
14	109	108
15	54	33
16	218	206
17	182	163
1, 1		
-17	79	-58
-16	150	-146
-15	122	-120
-14	109	-110
-13	413	-415
-12	115	111
-11	521	-525
-10	386	356
-9	159	-184
-8	225	289
-7	611	621
-6	358	374
-5	111	61
-4	249	-249
-3	737	770
-2	672	712
-1	373	314
0	161	187
1	645	-699
2	797	-781
3	509	518
4	149	-115
5	513	-503
6	511	-549
7	833	-855
8	225	251
9	501	-534
10	106	104
11	307	322
12	120	-101
13	314	307
14	147	144
15	137	130
16	119	107
17	296	264
2, 1		
-18	183	-155
-17	139	-126
-16	75	-70
-15	248	-248
-14	105	105
-13	395	-418
-12	359	355
-11	293	-283
-10	443	439
-9	173	165
-8	379	373
-7	311	275
-6	117	108
-5	461	427
-4	314	-317
-3	851	864
-2	801	-788
-1	183	166
0	769	-736
1	282	-293
2	357	-353
3	335	-341
4	113	-93
5	690	-733
6	316	333
7	616	-636
8	467	466
9	116	-102
10	325	352
11	79	-71
12	76	62
13	109	103
14	56	24
15	246	242
16	69	-47
3, 1		
-18	34	7
-17	145	-133
-16	33	-30
-15	43	-20
-14	177	182
-13	50	-11
-12	478	476
-11	224	198
-10	227	227
-9	201	209
-8	395	-359
-7	491	518
-6	445	-482
-5	547	529
-4	624	-546
-3	225	260
-2	282	236
-1	719	684
0	189	218
1	326	-270
2	272	-272
3	850	-871
4	885	828
5	1059	-1039
6	767	742
7	60	76
8	448	468
9	55	47
10	150	-156
11	108	-90
12	350	-351
13	262	261
14	91	-68
15	117	118
16	184	-158
4, 1		
-17	96	-87
-16	144	134
-15	65	68
-14	326	338
-13	273	273
-12	278	267
-11	390	385
-10	46	10
-9	295	270
-8	197	-199
-7	382	445
-6	580	-574
-5	136	113
-4	746	-751
-3	337	-332
-2	332	-331
-1	294	-255
0	37	32
1	331	-366
2	228	270
3	432	-454
4	596	648
5	50	42
6	545	564
7	289	297
8	209	208
9	247	268
10	39	42
11	282	298
12	216	-273
13	246	235
14	269	-262
15	39	23
5, 1		
-17	72	-64
-16	72	55
-15	97	77
-14	122	103
-13	280	281
-12	56	32
-11	345	327
-10	389	-389
-9	137	159
-8	606	-607
-7	186	-201
-6	582	-579
-5	398	-380
-4	52	9
-3	867	-862
-2	444	443
-1	481	-542
0	175	216
1	220	-199
2	487	449
3	555	513
4	808	819
5	519	534
6	197	204
7	301	304
8	126	-100
9	266	279
10	239	-255
11	36	22
12	375	-368
13	33	24
14	127	-121
6, 1		
-17	110	79
-16	53	4
-15	220	209
-14	53	4
-13	98	99
-12	138	-133
-11	74	80
-10	279	-273
-9	96	-96
-8	372	-391
-7	403	-413
-6	263	-249
-5	607	-600
-4	168	127
-3	503	-490
-2	232	216
-1	219	-232
0	408	472
1	94	94
2	429	437
3	456	476
4	180	197
5	337	336
6	99	-63
7	208	209
8	187	-174
9	149	-115
10	241	-234
11	125	-109
12	249	-259
13	214	-208
7, 1		
-16	106	-90
-15	186	168
-14	179	-168
-13	19	24
-12	160	-159
-11	134	-124
-10	399	-404
-9	176	-158
-8	100	-95
-7	515	-534
-6	163	157
-5	50	-31
-4	286	302
-3	281	263
-2	471	478
-1	141	143
0	258	242
1	279	289
2	36	32
3	333	347
4	145	-152
5	230	240
6	210	-196
7	127	-81
8	195	-173
9	67	-75
10	165	-161
11	211	-210
12	81	-63
8, 1		
-16	173	-162
-15	71	64
-14	89	-87
-13	39	-9
-12	161	-161
-11	59	-45
-10	106	-100
-9	275	-278
-8	248	226
-7	314	-308
-6	289	298
-5	110	100
-4	307	299
-3	218	224
-2	179	195
-1	399	400
0	109	52
1	369	362
2	248	-225
3	216	232
4	258	-251
5	114	48
6	203	-223
7	112	-108
8	153	-132
9	220	-228
10	107	33
11	185	-191
9, 1		
-15	76	-74
-14	55	-38
-13	186	-175
-12	225	208
-11	503	-514
-10	217	202
-9	224	-224
-8	285	282
-7	53	37
-6	108	102
-5	43	26
-4	48	34
-3	211	209
-2	107	23
-1	459	459
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1	225	-279
2	204	-171

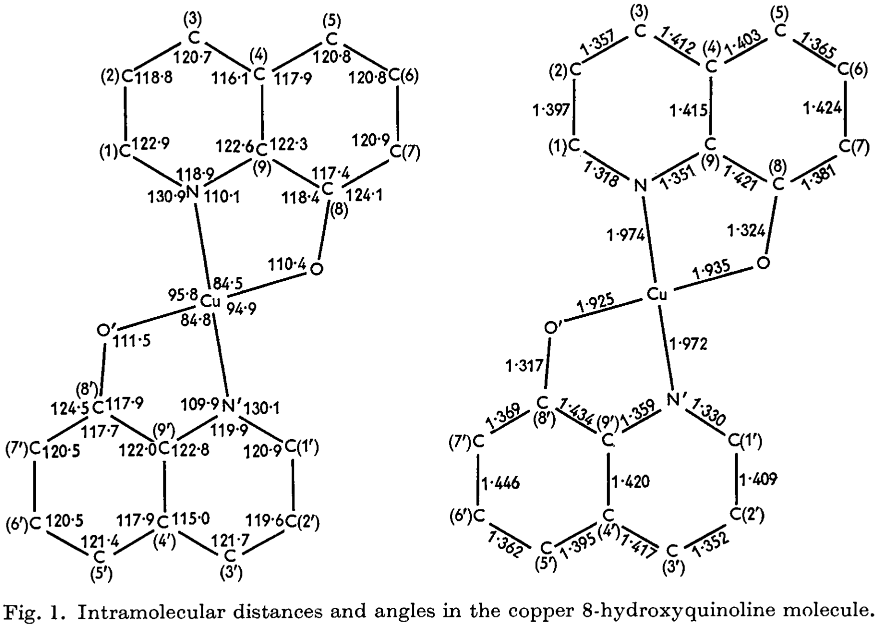

Fig. 1. Intramolecular distances and angles in the copper 8-hydroxyquinoline molecule.

Discussion

The copper atom is bonded to two 8-hydroxyquinolinate anions through the hydroxyl oxygen and ring nitrogen atoms. The two anions are in the *trans* configuration with respect to each other. The two copper–oxygen bond lengths are 1·925 and 1·935 Å; the copper–nitrogen distances are 1·972 and 1·974 Å.

Barclay & Kennard (1961*a*) have tabulated the copper–oxygen distances in a number of different compounds, but there is a wide variation in the values. The average value of the copper–oxygen bond distance of 1·930 Å found in the present study is in agreement with the results obtained in other three-dimensional studies: Barclay & Kennard (1961*a*) found 1·93 and 1·99 Å in anhydrous copper formate, Jarvis (1961)

Table 4. *Intramolecular distances and angles*

Distance	*A*	*B*
Cu–O(1)	1·935 Å	1·925 Å
Cu–N(1)	1·974	1·972
N(1)–C(1)	1·318	1·330
C(1)–C(2)	1·397	1·409
C(2)–C(3)	1·357	1·352
C(3)–C(4)	1·412	1·417
C(4)–C(5)	1·403	1·395
C(5)–C(6)	1·365	1·362
C(6)–C(7)	1·424	1·446
C(7)–C(8)	1·381	1·369
C(8)–C(9)	1·421	1·434
C(9)–C(4)	1·415	1·420
C(9)–N(1)	1·351	1·359
C(8)–O(1)	1·324	1·317
N(1)–O(1′)	2·893	
O(1)–N(1′)	2·878	
O(1)–C(1′)	3·129	
C(1)–O(1′)	3·167	

Angle	*A*	*B*
O(1)–Cu–N(1)	84·5°	84·8°
N(1)–C(1)–C(2)	122·9	120·9
C(1)–C(2)–C(3)	118·8	119·6
C(2)–C(3)–C(4)	120·7	121·7
C(3)–C(4)–C(5)	126·0	127·1
C(4)–C(5)–C(6)	120·8	121·3
C(5)–C(6)–C(7)	120·8	120·5
C(6)–C(7)–C(8)	120·9	120·5
C(7)–C(8)–C(9)	117·4	117·7
N–C(9)–C(4)	122·6	122·8
C(8)–C(9)–C(4)	122·3	122·0
C(1)–N–Cu	130·8	130·1
C(9)–N–Cu	110·1	109·9
C(9)–C(8)–O(1)	118·4	117·9
C(7)–C(8)–O(1)	124·1	124·5
C(8)–O(1)–Cu	110·4	111·5
O(1)–Cu–N(1′)	94·9	
O(1)–Cu–O(1′)	179·3	
N(1)–Cu–N(1′)	173·3	
N(1)–Cu–O(1′)	95·8	

A refers to the unprimed coordinates. *B* refers to the primed coordinates.

The probable error in the light atom–light atom distances is ±0·009 Å. The probable error of the bond angles is ±0·6°.

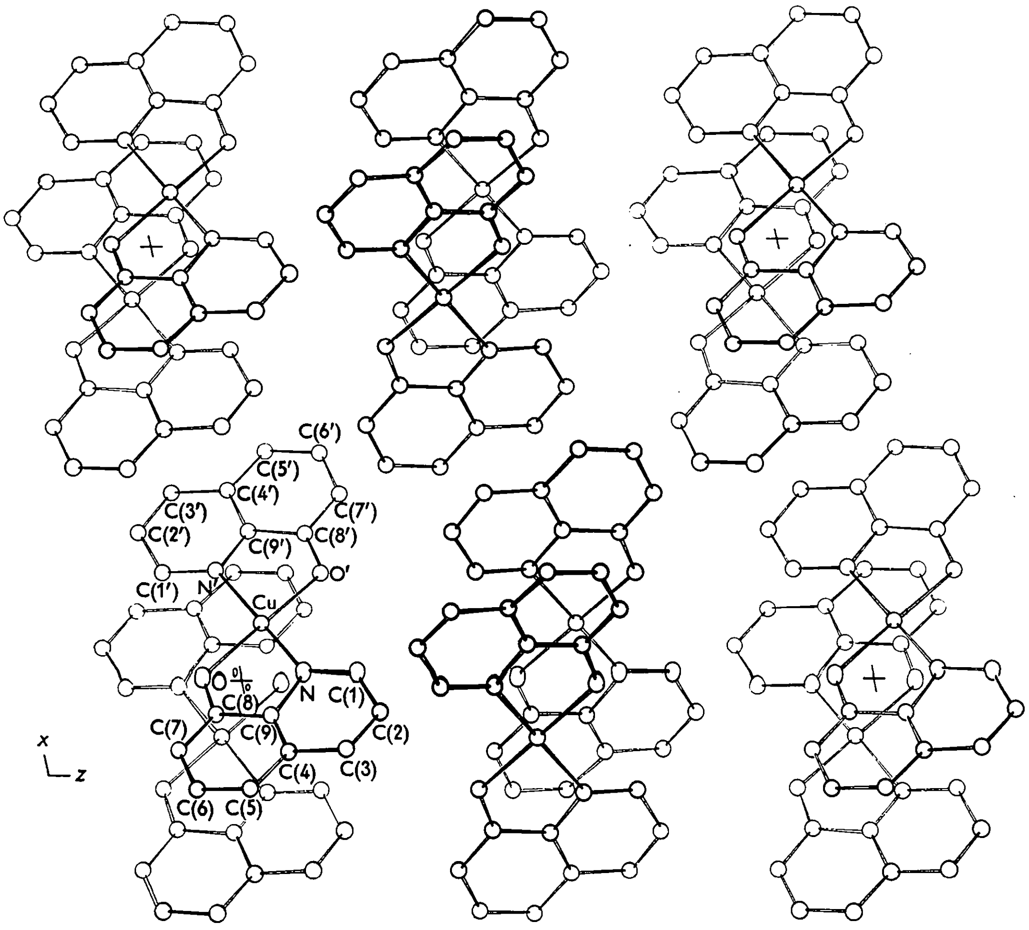

Fig. 2. Projection down the *b* axis illustrating the packing of the dimer-like units.

Table 5. *Intermolecular distances**

X	*Y*	Distance	*X*	*Y*	Distance
Cu	Cu(*A*)	3·441 Å	Cu	C(5)(*B*)	3·380 Å
Cu	O(1)(*A*)	2·830	N(1)	C(6)(*B*)	3·326
Cu	N(1′)(*A*)	3·975	C(4)	C(8)(*B*)	3·360
Cu	C(8)(*A*)	3·491	C(1′)	C(5′)(*C*)	3·473
O(1)	O(1)(*A*)	3·416	C(2′)	C(5′)(*C*)	3·507
O(1)	O(1′)(*A*)	3·451	C(3′)	C(4′)(*C*)	3·545
O(1)	N(1)(*A*)	3·710	C(3′)	C(9′)(*C*)	3·452
O(1)	N(1′)(*A*)	3·365	O(1)	C(2)(*D*)	3·458
N(1)	C(1′)(*A*)	3·351	C(2′)	C(7)(*D*)	3·692
N(1′)	C(8)(*A*)	3·269	C(2)	O(1′)(*E*)	3·280
N(1′)	C(9)(*A*)	3·386	C(3)	O(1′)(*E*)	3·379
C(7)	C(8′)(*A*)	3·385	C(2)	C(1)(*E*)	3·673
C(7)	C(9′)(*A*)	3·389	C(7′)	C(6′)(*F*)	3·596
C(8)	C(9′)(*A*)	3·356	O(1′)	C(6′)(*F*)	3·558
C(9)	C(1′)(*A*)	3·386	C(8′)	C(6′)(*F*)	3·760

* The distances quoted are from *X* in the molecule specified by the parameters in Table 1 to *Y* in the molecule specified by the letter in parenthesis. Molecules *A*–*F* are located as follows:

A $\bar{x}, \bar{y}, \bar{z}$ *D* $x, \frac{1}{2}-y, \frac{1}{2}+z$
B $\bar{x}, 1-y, \bar{z}$ *E* $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$
C $1-\bar{x}, \bar{y}, \bar{z}$ *F* $1-x, \frac{1}{2}+y, \frac{1}{2}-z$.

1·93 Å in copper(II) bis(phenylazo-β-naphthol), Barclay & Kennard (1961*b*) 1·98 Å in monopyridine copper acetate, and Freeman, Lovell, Robinson, Schoone & Sime (1962) 1·93 and 1·99 Å in glycylglycylglycinocopper(II) chloride 1·5 hydrate, and 1·93 Å in sodium glycylglycylglycino cuprate(II) monohydrate.

The average value of 1·973 Å found in this study for the copper–nitrogen bond distance appears to be slightly shorter than the value found in other three-dimensional studies. Freeman *et al.* (1962) reported values of 2·00, 2·03, 1·99 and 1·84 Å, Jarvis (1961) found 2·01 Å, and Barclay & Kennard (1961*a*) reported 2·12 Å. The two extreme values given above of 1·84 and 2·12 Å are probably a consequence of the geometry of the structure and should not be regarded as normal. Numerous two-dimensional studies have been reported which find a copper–nitrogen distance of about 2·0 Å, but the majority are probably of low accuracy.

The copper–nitrogen bond is 0·043 Å longer than the copper–oxygen bond. The difference is close to the value 0·045 Å predicted by the Schomaker & Stevenson correction to the additivity of single-bond radii. The basic assumption is that the electronegativities of oxygen and nitrogen are not changed relative to one another. Lingafelter, Simmons, Morosin, Scherin-

Table 6. *Mean square displacements from the thermal parameters*

Atom	$\sqrt{(r^2)}$*	Direction cosines†			Atom	$\sqrt{(r^2)}$*	Direction cosines†		
O(1)	229	−7808	−5368	3198	O(1′)	191	−4145	−8737	2546
	164	−4394	1079	−8918		179	−9026	3590	−2377
	158	−4442	8368	3201		171	−1163	3283	9374
N(1)	184	9320	−3188	−1725	N(1′)	180	4981	1184	−8590
	175	2121	0937	9728		159	7248	−6007	3374
	151	2940	9432	−1549		129	4761	7906	3851
C(1)	210	9943	−1055	−0126	C(1′)	193	9354	−3416	−0915
	163	0928	8042	5871		178	0886	−0240	9958
	142	0518	5849	−8094		154	3424	9395	−0078
C(2)	213	−5861	5876	−5579	C(2′)	208	0802	7036	−7061
	177	−6096	1338	7813		182	9699	−2185	−1076
	158	−5337	−7981	−2798		156	2300	6762	6999
C(3)	209	1604	−3299	9303	C(3′)	216	−4463	−6988	5590
	169	9869	0721	−1445		195	−0993	−5822	−8070
	163	0194	−9413	−3371		166	−8893	4157	−1905
C(4)	189	0164	−0850	−9962	C(4′)	195	−0818	−0637	9946
	157	8262	−5600	0614		160	−8878	−4489	−1017
	121	5631	8241	−0610		152	−4530	8913	0198
C(5)	214	−2163	2488	9441	C(5′)	216	−5282	−1111	8418
	187	−5422	−8348	0958		183	−1501	−9636	−2214
	145	−8119	4912	−3155		153	−8357	2433	−4923
C(6)	219	−4003	4391	8043	C(6′)	233	−7196	1272	6826
	182	−6662	−7421	0736		176	−6768	−3481	−6486
	138	−6292	5064	−5896		146	−1551	9288	−3366
C(7)	194	−7343	3904	5553	C(7′)	211	−6763	3123	6671
	189	−2136	−9094	3568		166	−7360	−3245	−5942
	137	−6443	−1434	−7512		149	−0309	8928	−4493
C(8)	190	−3298	1892	9249	C(8′)	181	−1755	2566	9505
	150	−5897	−8064	−0453		148	−9771	−1634	−1363
	111	−7373	5603	−3774		136	−1203	9526	−2794
C(9)	181	−0320	−1125	−9931	C(9′)	185	4699	−1992	−8600
	161	−9974	0679	0244		152	7200	−4772	5039
	123	−0647	−9913	1144		123	5107	8559	0808
Cu	187	−6818	−6037	4133					
	155	−0990	−4836	−8697					
	140	−7248	6338	−2700					

* Values $\times 10^3$. † Values $\times 10^4$. (The cosines are given with respect to *a*, *b*, *c**).

Table 7. *Least-squares planes*†

Atom	Plane and deviations ($\times 10^3$) from the plane				
	I	II	III	IV	V
N(1)	−022	231	−038	230	−052
O(1)	073	460	040	459	052
C(1)	−014	178	−022	176	—
C(2)	021	066	028	064	—
C(3)	018	−020	030	−022	—
C(4)	−006	016	−002	014	—
C(5)	−025	−077	−017	−079	—
C(6)	−004	014	−005	012	—
C(7)	016	185	001	183	—
C(8)	017	264	−003	263	—
C(9)	000	173	−010	171	—
N(1′)	−629	025	−684	025	−052
O(1′)	−523	002	−562	001	052
C(1′)	−717	−006	−780	−006	—
C(2′)	−880	−021	−957	−021	—
C(3′)	−941	003	−1024	003	—
C(4′)	−881	007	−956	008	—
C(5′)	−949	015	−1029	016	—
C(6′)	−904	−007	−975	−007	—
C(7′)	−755	−011	−813	−012	—
C(8′)	−670	−005	−721	−005	—
C(9′)	−740	−002	−801	−002	—
Cu	−216	240	−252	239	062

±Plane	Direction cosines ($\times 10^4$) with respect to			Distance to origin	Description of plane
	a	*b*	*c**		
I	−7233	−6882	0572	−1·285	N(1)–6(9) Quinoline ring only
II	−6477	−7607	0419	−1·741	N(1′)–C(9′) Quinoline ring only
III	−7297	−6810	0605	−1·246	O(1)–C(9) Quinoline ring and hydroxyl
IV	−6475	−7609	0418	−1·740	O(1′)–C(9′) Quinoline ring and hydroxyl
V	−5690	−8127	1252	−1·463	2 Nitrogen and 2 oxygens only

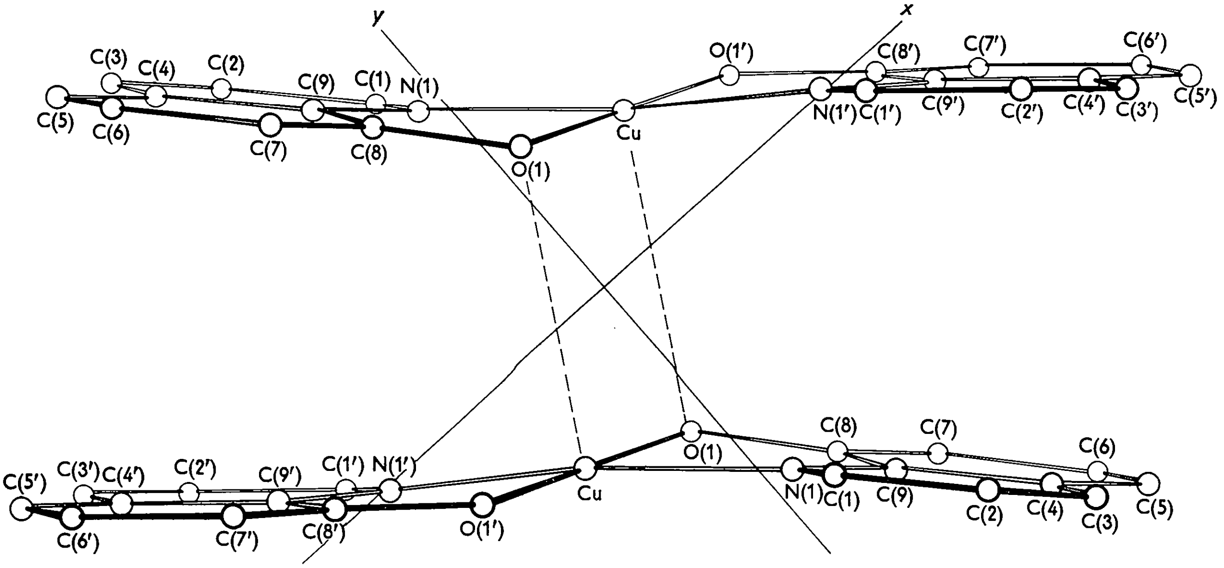

Fig. 3. Projection of two molecules related by center of symmetry on the (001) plane. The fifth bond formed by the copper atom to the oxygen atom of another molecule is shown by the dotted lines.

ger & Freiburg (1961) have attributed the inequality of the copper–oxygen and copper–nitrogen distances in the α form of bis(N-methylsalicylaldiminato)copper to steric hindrance. The equality of the nickel–oxygen and nickel–nitrogen bond distances in bis(salicylaldiminato)nickel reported by Stewart & Lingafelter (1959) is cited in support of Lingafelter's views. The two structures were determined from projections by the use of only a small number of independent reflections. Therefore, Lingafelter's conclusions are based on incomplete results and can be accepted only after a careful three-dimensional analysis is carried out on both structures.

The structure can be regarded as a planar configuration which has been distorted to relieve steric strain between the oxygen and nitrogen atoms from opposite anions. The nitrogens are twisted out of the plane in such a manner that a fifth ligand can approach without large steric repulsion. The result is definitely not a square coplanar configuration around the copper atom. The copper atom forms four normal bonds to the two anions and a fifth longer bond to an oxygen of another molecule related to the first by a center of symmetry. The result is a dimer-type unit, illustrated in Fig. 3, similar to that reported by Frasson, Bardi & Bezzi (1959) for bis(dimethylglyoximato)copper(II).

The distorted tetragonal pyramidal coordination for copper has also been reported for anhydrous copper formate and dichloro(dimethylglyoxime)copper(II) by Barclay & Kennard (1961), in N,N'-ethylene bis(salicylideneiminato)copper(II) by Hall & Waters (1960), and in glycylglycylglycinocopper(II) chloride 1·5 hydrate and sodium glycylglycylglycino cuprate(II) monohydrate by Freeman *et al.* (1962).

The two quinoline rings are planar within experimental error. The hydroxyl oxygen atoms, however, are not both coplanar with their respective quinoline rings. The oxygen which provides the fifth ligand for the copper atom is definitely displaced from the plane of the ring. The other hydroxyl oxygen atom, however, is coplanar with its quinoline ring. It appears that the oxygen bends out of the plane of the ring as a consequence of the additional attraction to the copper atom. This effect is rather surprising since the copper–oxygen distance of 2·830 Å implies only a weak bond. It is known, however, that angular distortions can be brought about with only a small expenditure of energy relative to a change in bond distance.

The quinoline rings are not parallel but their least-squares planes are inclined at the small angle of 6°. A comparison of chemically equivalent but crystallographically independent bonds in the two rings is very favorable. The largest difference is 0·022 Å with an average difference of 0·009 Å. It is felt that this average difference represents a good estimate of the accuracy of the light atom — light atom distances.

Unfortunately the only comparison of the quinoline ring available is found in the structure of zinc hydroxyquinolinate dihydrate reported by Merritt, Cady & Mundy (1954). While three-dimensional data were collected, the structure was not completely refined, and a direct comparison is difficult. A refinement of this structure was undertaken and the results will be reported in the near future.

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