356. *The Crystal Structure of Acetylacetone-mono-(*o*-hydroxyanil)copper*(II)

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The crystal structure of acetylacetone-mono-(*o*-hydroxyanil)copper(II) has been determined by *X*-ray diffraction methods; refinement was carried out by differential syntheses with three-dimensional data. The triclinic unit cell ($a = 8{\cdot}914 \pm 0{\cdot}010$, $b = 10{\cdot}485 \pm 0{\cdot}10$, $c = 11{\cdot}733 \pm 0{\cdot}010$ Å, $\alpha = 101{\cdot}6 \pm 0{\cdot}3$, $\beta = 110{\cdot}6 \pm 0{\cdot}3$, $\gamma = 92{\cdot}5 \pm 0{\cdot}3°$; Space group $P\bar{1}$) contains four units of composition $C_{11}H_{11}NO_2Cu$. The acetylacetone-mono-(*o*-hydroxyanil)copper(II) molecule is a dimer with the two copper atoms of the asymmetric unit bridged together by the phenolic oxygen atoms of the ligand molecules; the copper–copper distance is 2·99 Å. The crystal is built up of these dimers which are arranged in layers and held together by van der Waals forces. Association between pairs of molecules takes place through a weak bond between the copper atom of one molecule and an oxygen atom of the other (Cu–O distance 2·64 Å). Although each copper atom is covalently bonded to an identical group of atoms (one nitrogen and three oxygen) at the corners of a somewhat distorted square they have different environments; one copper having a distorted square-pyramidal configuration whereas the other has a square-planar co-ordination. The analysis shows that the complex formation takes place with the ligand in the ketamine form. The structure does not provide an unambiguous explanation of the demagnetisation observed in the compound.

THE magnetic behaviour of some so-called trico-ordinated copper(II) complexes derived from certain Schiff's bases [such as acetylacetone-mono-(*o*-hydroxyanil)copper(II) (I; R = Me) benzoylacetone-mono-(*o*-hydroxyanil)copper(II) (I; R = Ph) and salicylal-mono-(*o*-hydroxyanil)copper(II) (II)] was reported by Kishita, Muto, and Kubo [1] to be anomalous; the magnetic moments at room temperature are 1·37, 1·11, and 1·34 B.M., respectively. They attributed the demagnetisation to the occurrence of trico-ordinated copper(II) and possibly to direct copper–copper interaction in the solid state due to dimerisation. The magnetic moments of the monopyridine complexes of these three

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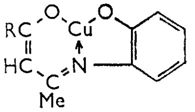
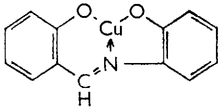
[1] Kishita, Kubo, and Muto, *Naturwiss.*, 1957, **44**, 372, 612; *Austral. J. Chem.*, 1957, **10**, 386; 1958, **11**, 309.

compounds, 1·81, 1·84, and 1·84 B.M., respectively, are normal for copper(II) compounds. On the basis of their green colour, the alleged presence of orbital contribution to the magnetic susceptibility, and the terdentate nature of the ligand, it was suggested that the arrangement about the copper atom in the pyridine complexes was tetrahedral.


(I)


(II)

Harris and Kokot [2] have critically re-examined the above work and have measured the magnetic susceptibility of the compounds (I; R = Me or Ph; II) over a wide range of temperatures. The magnetic susceptibility of (I; R = Me) closely parallels that of copper(II) acetate monohydrate.[3] Although both the other compounds exhibit antiferromagnetism there are some features which are different from those in copper(II) acetate monohydrate. Harris and Kokot concluded that an infinite polymeric structure was unlikely for these compounds because of their solubility in organic solvents. These compounds cannot be assigned bridged binuclear structures of the type found for copper(II) acetate monohydrate,[4] hence there is a possibility that their antiferromagnetic behaviour may be explained without the necessity to postulate a delta bond between the copper atoms. The crystal structure of one of these substances (I; R = Me) was undertaken in an attempt to determine the stereochemistry of the copper atoms and to explain the magnetic behaviour of these compounds.

EXPERIMENTAL

Acetylacetone-mono-(*o*-hydroxyanil)copper(II) was prepared according to the method of Kishita *et al.*[1] (Found: C, 52·2; H, 4·2; N, 5·4; Cu, 25·2. Calc. for $C_{11}H_{11}CuNO_2$: C, 52·2; H, 4·4; N, 5·5; Cu, 25·2%). Suitable crystals for the *X*-ray analysis were obtained from bromobenzene solution. Most of the dark green crystals were rod-like, elongated in the direction of the *a* axis.

Accurate cell dimensions were determined from single-crystal Straumanis oscillation photographs (about the *b*-axis) and zero-layer Weissenberg photographs (about the *a*- and the *b*-axes); the latter were calibrated using sodium chloride powder lines. Intensities were estimated visually from equi-inclination Weissenberg photographs taken about each of the principal axes. The crystals used were almost cylindrical with the approximate dimensions 0·10 mm. (diam.) × 0·20 mm., 0·15 mm. × 0·15 mm., and 0·10 mm. × 0·10 mm. for the *a*-, *b*-, and *c*-axes, respectively. Corrections for the Lorentz and polarisation factors were obtained using a Cochran chart; [5] no allowance was made for absorption or extinction. The intensities were placed on the same arbitrary scale by internal correlation. Values were obtained for 2280 of the possible 2690 independent reflections.

Crystal Data.—$C_{11}H_{11}CuNO_2$; $M = 252{\cdot}8$; triclinic; $a = 8{\cdot}914 \pm 0{\cdot}010$, $b = 10{\cdot}485 \pm 0{\cdot}010$, $c = 11{\cdot}733 \pm 0{\cdot}010$ Å, $\alpha = 101{\cdot}6 \pm 0{\cdot}3$, $\beta = 110{\cdot}6 \pm 0{\cdot}3$, $\gamma = 92{\cdot}5 \pm 0{\cdot}3°$; $U = 997{\cdot}76$ Å^3; $D_m = 1{\cdot}68 \pm 0{\cdot}01$ (by flotation); $Z = 4$; $D_c = 1{\cdot}683$ g. cm.$^{-3}$; $F(000) = 508$, space group $P\bar{1}$ (C_i^1; No. 2). Cu-radiation, unfiltered, single-crystal oscillation and equi-inclination Weissenberg photographs; $\mu = 30{\cdot}2$ cm.$^{-1}$. Intensity data were collected from $0kl \longrightarrow 5kl$, $h0l \longrightarrow h4l$, $hk0 \longrightarrow hk6$.

Structure Determination.—From all the observed data, an unmodified three-dimensional Patterson synthesis was computed at intervals of approximately 0·25 Å along each axis. The number and relative heights of the copper–copper vectors in the resulting vector map suggested that the space group was $P\bar{1}$. One of the copper atoms being used as a searcher, all the atoms of the asymmetric unit (other than the hydrogen atoms) were easily recognised. From the

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[2] Barclay, Harris, Hoskins, and Kokot, *Proc. Chem. Soc.*, 1961, 264; Harris and Kokot, personal communication.

[3] Figgis and Martin, *J.*, 1956, 3837.

[4] van Niekerk and Schoening, *Acta Cryst.*, 1953, **6**, 227.

[5] Cochran, *J. Sci. Inst.*, 1948, **25**, 253.

TABLE 1

Calculated structure factors and observed structure amplitudes (Scale: 1/2 absolute)

l	F_c	$\|F_o\|$
	0, 0, *l*	
1	75	57
2	−5	6
3	−4	5
4	3	5
5	43	46
6	33	31
7	6	8
8	−6	7
9	−7	8
10	−7	8
	0, 1, *l*	
−13	3	5
−12	5	7
−11	−3	4
−10	−8	8
−9	−4	4
−8	8	11
−7	22	20
−6	43	41
−5	16	18
−4	−4	3
−3	5	7
−2	19	20
−1	69	56
0	60	63
1	14	14
2	−4	7
3	−6	7
4	2	3
5	19	19
6	14	15
7	3	5
8	−13	16
9	−12	14
10	−5	7
	0, 2, *l*	
−13	6	6
−12	−6	8
−11	−1	6
−9	7	9
−8	17	19
−7	30	30
−6	7	7
−5	−12	12
−3	6	7
−2	20	21
0	−28	32
1	16	20
2	−17	21
3	−10	12
4	3	6
5	3	4
6	−5	6
7	−30	31
8	−22	21
9	−12	12
	0, 3, *l*	
−14	7	4
−13	6	6
−12	3	4
−10	6	7
−9	18	17
−8	22	23
−7	26	22
−6	−4	8
−5	−11	10
−4	6	6
−3	15	18
−2	22	23
−1	−6	10
0	−8	9
1	−30	30
2	−25	26
3	−25	26
4	−3	5
5	−9	12
6	−22	24
7	−23	24
8	−8	8
10	3	5
	0, 4, *l*	
−13	6	5
−11	−4	4
−10	4	5
−9	20	19
−8	25	24
−7	4	4
−6	−11	11
−5	−17	18
−3	9	11
−2	4	4
−1	−20	23
0	−28	28
1	−5	5
3	−4	8
5	−14	18
6	−4	9
7	10	17
9	5	7
10	6	8
	0, 5, *l*	
−10	4	4
−9	10	10
−8	7	10
−7	−15	15
−6	−12	15
−5	−11	12
−4	−19	22
−3	−6	7
−2	−13	15
−1	−36	36
0	−37	40
1	4	10
4	−6	8
5	−18	20
7	10	12
9	12	14
10	6	8
	0, 6, *l*	
−10	5	5
−8	−16	15
−7	−24	24
−6	−15	16
−5	−6	6
−4	−11	13
−3	−12	14
−2	−31	31
−1	−36	38
0	−20	21
1	−10	10
2	6	9
3	4	7
4	−7	9
5	−12	12
6	−6	7
7	7	7
8	17	19
9	11	12
	0, 7, *l*	
−9	−11	11
−8	−20	19
−7	−18	18
−6	−5	7
−5	3	6
−4	4	7
−3	−7	10
−2	−18	19
−1	−15	16
0	−1	5
2	15	16
3	8	10
4	−7	7
5	−6	7
7	13	17
8	12	15
	0, 8, *l*	
−11	−6	6
−10	−9	8
−9	−13	11
−8	−9	8
−7	−5	5
−5	4	7
−4	−5	5
−3	−8	11
−2	−6	7
0	15	17
1	20	20
2	13	15
3	4	6
5	4	7
6	11	12
7	12	14
8	6	6
	0, 9, *l*	
−11	−6	5
−10	−10	8
−9	−14	13
−8	−8	8
−6	5	7
−5	5	8
−4	−6	8
−3	−11	13
−2	4	8
−1	21	23
0	22	23
1	16	15
3	−7	7
5	7	8
6	6	5
	0, 10, *l*	
−10	−6	6
−9	−6	6
−8	3	4
−7	12	13
−6	9	11
−5	7	8
−4	3	5
−3	−6	6
−2	7	10
−1	13	17
0	10	10
2	−7	6
3	−8	6
	0, 11, *l*	
−9	2	3
−8	8	7
−7	10	8
−6	7	6
−5	3	3
−4	1	5
−2	8	7
−1	8	8
0	5	6
2	−6	6
	0, 12, *l*	
−8	8	6
−7	6	5
−6	3	4
−5	−3	4
−4	−4	6
−3	6	8
−2	8	9
−1	4	7
0	−4	7
	1, −12, *l*	
3	7	−7
	1, −11, *l*	
−3	−8	8
2	−12	12
3	−9	10
4	6	7
5	9	9
6	10	9
	1, −10, *l*	
−4	−12	11
−3	−8	8
−2	6	5
−1	9	10
0	5	7
2	−13	13
3	4	6
4	19	16
5	17	16
6	10	10
	1, −9, *l*	
−6	−6	7
−5	−9	8
−4	−7	8
−3	9	8
−2	17	14
−1	14	13
0	3	5
1	−7	6
2	5	8
3	8	8
4	17	19
5	17	18
6	6	8
	1, −8, *l*	
−6	3	7
−4	8	11
−3	22	20
−2	19	18
−1	13	13
2	12	16
3	17	21
4	19	21
5	9	12
	1, −7, *l*	
−9	9	9
−8	8	8
−7	5	5
−6	6	6
−5	11	11
−4	24	24
−3	26	25
−2	17	16
−1	7	8
1	6	10
2	17	20
3	21	21
4	−3	7
5	−13	15
6	−16	15
	1, −6, *l*	
−10	13	13
−9	12	13
−8	6	6
−6	−6	8
−5	21	23
−4	28	25
−3	14	15
−2	5	7
−1	−5	5
1	12	15
2	15	16
3	−16	18
4	−27	25
5	−18	17
6	−12	14
	1, −5, *l*	
−5	16	17
−4	17	19
−1	−8	9
0	−7	10
2	−4	7
3	−30	32
4	−26	26
5	−19	22
6	−6	9
	1, −4, *l*	
−11	12	11
−10	8	9
−8	−3	5
−7	3	5
−6	13	15
−5	9	10
−4	3	5
−3	−26	24
−2	−30	26
−1	−9	10
0	5	4
1	6	7
2	−31	31
3	−21	22
4	−20	19
5	−9	8
6	8	8
7	5	5
8	3	5
10	−8	8
11	5	7
12	13	10
13	10	8
	1, −3, *l*	
−12	11	11
−11	8	7
−10	−6	7
−9	−12	13
−8	−11	14
−7	1	5
−6	8	7
−5	−2	4
−4	−28	29
−3	−38	36
−2	−24	23
−1	15	15
0	30	30
1	16	15
2	−23	23
3	−18	18
4	−7	8
5	3	2
6	20	19
7	10	11
10	3	4
11	9	9
12	12	11
13	8	6
	1, −2, *l*	
−11	−5	6
−10	−19	19
−9	−14	14
−8	−5	7
−6	−4	8
−5	−29	28
−4	−36	31
−3	−16	14
−2	−7	10
−1	6	3
0	12	13
1	−12	11
3	−21	22
5	29	26
6	34	32
7	16	16
11	9	10
12	10	11
	1, −1, *l*	
−12	−6	7
−11	−11	12
−10	−7	10
−9	−6	6
−8	−3	5
−6	−16	17
−5	−58	51
−4	−35	32
−3	−13	13
−2	−7	8
−1	37	31
0	7	10
1	−27	24
2	15	14
3	14	14
4	27	26
5	54	47
6	23	23
7	6	7
8	4	4
9	4	5
10	5	5
11	9	10
12	5	4
	1, 0, *l*	
−13	−3	5
−12	−12	13
−11	−14	16
−10	−3	6
−8	4	5
−7	−2	4
−6	−23	23
−5	−29	27
−4	−5	7
−3	29	28
−2	19	19
−1	40	34
0	10	12
1	−6	8
2	2	5
3	15	16
4	30	29
5	31	31
6	8	12
7	−3	5
9	9	9
10	16	16
11	5	5
	1, 1, *l*	
−13	−7	7
−12	−15	14
−11	−15	14
−10	−6	7
−9	8	8
−8	8	11
−6	−12	13
−5	4	10
−4	3	3
−3	20	20
−2	32	26
0	1	4
1	−4	7
2	14	20
3	35	33
4	29	32
5	4	4
7	−3	5
8	4	7
9	8	10
10	6	6
11	−7	6
12	−13	10
	1, 2, *l*	
−13	−9	9
−12	−14	12
−11	−8	8
−10	7	7
−9	9	10
−8	5	7
−7	2	5
−6	−4	3
−5	9	6
−4	14	18
−3	17	18
−2	47	47
−1	−3	7
0	−2	1
1	10	14
2	26	28
3	27	27
4	−5	8
5	−18	20
6	−17	20
7	−3	5
10	−7	8
11	−11	11
	1, 3, *l*	
−14	−2	2
−13	−7	6
−12	−3	4
−11	7	6
−10	19	20
−9	16	17
−8	10	11
−7	−3	6
−6	4	6
−5	19	18
−4	25	25
−3	33	27
−2	3	3
−1	−11	17
0	−3	4
2	−9	13
3	−2	5
4	−22	27
5	−28	31
6	−10	15

TABLE 1 (*Continued*)

l	F_c	$\lvert F_o \rvert$
	1, 3, l	
10	−11	13
11	−10	12
	1, 4, l	
−12	7	8
−11	8	9
−10	9	10
−9	25	25
−8	8	10
−7	−5	6
−6	9	11
−5	14	11
−4	32	30
−3	27	29
−2	−27	25
−1	−27	29
0	−6	11
2	−8	11
3	−17	19
4	−35	34
5	−34	36
9	−8	10
10	−13	16
	1, 5, l	
−9	7	9
−8	−8	8
−6	12	13
−5	8	8
−4	0	3
−3	−33	32
−2	−32	37
−1	−21	24
0	−2	4
1	−2	4
2	−16	19
3	−32	35
4	−31	34
5	−16	19
6	−4	5
8	−4	5
9	−8	9
10	−5	6
	1, 6, l	
−10	−8	9
−9	−25	24
−8	−10	13
−5	−14	17
−4	−38	39
−3	−38	37
−2	−22	25
0	3	3
1	−8	11
2	−20	25
3	−28	31
4	−13	15
5	3	5
7	3	6
	1, 7, l	
−10	−16	16
−9	−13	15
−8	2	4
−7	3	4
−6	−4	8
−5	−20	23
−4	−28	29
−3	−20	21
−2	−15	18
−1	8	9
0	3	4
1	−9	11
2	−18	22
3	−15	19
4	6	8
5	12	14
6	10	13
7	4	5
	1, 8, l	
−11	−4	4
−10	−9	9
−6	−7	10
−5	−20	24
−4	−27	27
−3	−11	14
−2	18	20
−1	11	15
1	−6	7
2	−5	8
3	9	13
4	15	21
5	9	13
6	6	8
	1, 9, l	
−11	−8	6
−10	−9	8
−9	−7	8
−8	4	5
−6	−9	11
−5	−12	13
−4	−13	16
−3	11	11
−2	23	26
−1	3	6
2	3	5
3	11	16
4	9	12
5	6	8
	1, 10, l	
−6	−6	11
−5	−3	5
−3	6	8
2	6	8
3	9	11
4	8	9
5	4	5
	1, 11, l	
−5	4	5
−4	9	11
−3	6	6
−2	6	6
−1	6	10
1	3	6
2	7	9
3	6	7
	1, 12, l	
−7	3	5
−5	11	11
−4	12	11
−3	7	6
−2	5	8
−1	0	8
	2, −12, l	
0	−7	7
1	−11	11
2	−8	6
	2, −11, l	
0	−15	16
1	−17	17
2	−6	12
3	7	7
4	8	9
	2, −10, l	
−5	−4	4
−2	−5	6
−1	−9	11
0	−9	9
1	−2	7
3	7	8
4	7	7
	2, −9, l	
−5	6	6
−4	11	9
−2	−6	5
0	4	6
1	15	15
2	15	22
3	7	8
	2, −8, l	
−5	8	10
−4	11	12
−3	5	7
−2	1	3
−1	8	8
0	12	12
1	26	23
2	25	24
3	10	11
4	7	7
5	6	5
6	9	9
	2, −7, l	
−7	−5	5
−6	0	4
−5	14	14
−4	9	11
−3	5	6
−2	4	4
−1	0	2
0	23	22
1	24	24
2	9	10
4	7	10
5	6	9
6	8	10
	2, −6, l	
−7	−4	7
−6	6	7
−5	15	15
−4	6	8
−3	6	7
−2	5	6
−1	8	8
0	24	23
1	17	18
2	−4	5
3	−14	15
4	−8	9
5	7	9
6	9	9
	2, −5, l	
−8	9	8
−7	22	19
−6	20	18
−5	8	10
−4	3	4
−3	6	6
−2	17	16
−1	23	21
0	7	7
1	7	9
2	−12	13
3	−21	22
4	−15	17
5	7	7
6	10	12
	2, −4, l	
−10	2	5
−9	9	10
−8	17	18
−7	29	29
−6	3	5
−5	−13	15
−4	−13	14
−3	−2	3
−2	14	15
−1	1	2
0	5	5
1	−17	14
2	−20	17
3	−10	10
4	−4	7
5	10	12
6	1	5
7	−17	17
8	−10	10
9	−6	7
	2, −3, l	
−10	4	6
−9	11	11
−8	11	14
−7	−1	4
−6	−15	16
−5	−28	28
−4	−17	21
−3	−6	8
−2	3	4
−1	1	2
0	−41	36
1	−75	50
2	−38	31
3	−10	10
4	6	5
5	−2	5
6	−25	25
7	−17	17
8	−7	6
9	6	5
10	9	7
11	7	5
	2, −2, l	
−11	2	5
−9	6	6
−8	7	7
−7	−5	7
−6	−30	28
−5	−51	46
−4	−22	23
−3	−6	8
−2	11	9
−1	27	23
0	−152	113
1	−78	62
2	−12	10
3	4	6
4	11	12
5	−20	21
6	−21	21
8	5	5
9	8	7
10	8	6
11	4	4
	2, −1, l	
−12	−10	11
−11	−4	7
−8	−6	10
−7	−19	18
−6	−47	48
−5	−29	29
−4	−4	5
−3	−2	4
−2	−1	3
−1	−34	26
0	−41	32
1	−8	8
2	7	9
3	12	12
4	7	11
5	−7	8
6	−5	8
7	2	7
8	15	16
9	13	12
10	4	5
	2, 0, l	
−12	−11	13
−11	−5	6
−9	−5	7
−8	−18	20
−7	−34	32
−6	−16	16
−5	6	13
−3	−2	3
−2	−22	21
0	46	42
1	−14	20
2	12	16
3	17	17
5	4	5
6	6	6
7	25	26
8	25	24
9	15	14
11	−4	4
	2, 1, l	
−12	−8	9
−11	−3	4
−10	−2	4
−9	−10	13
−8	−19	20
−7	−33	31
−5	9	5
−4	6	10
−3	3	6
−2	−27	24
0	17	19
1	30	32
2	23	26
3	8	12
4	−4	5
5	4	6
6	18	19
7	19	20
8	6	5
10	−5	6
11	−4	4
	2, 2, l	
−14	−12	12
−13	−10	11
−11	5	5
−9	−13	15
−8	−23	23
−7	−4	5
−6	12	11
−5	20	18
−4	9	10
−2	−1	3
−1	18	25
0	32	31
1	14	13
2	−9	15
3	−6	7
4	−6	7
5	7	10
6	4	10
7	−12	18
8	−4	4
9	−8	8
10	−9	10
	2, 3, l	
−14	−8	7
−12	8	9
−9	−11	12
−8	−10	14
−7	23	22
−6	19	19
−5	9	9
−4	16	17
−3	3	5
−2	14	13
−1	41	40
0	48	50
1	−2	7
2	−6	10
3	−11	14
4	−5	8
5	14	18
6	2	5
7	−9	13
8	−9	10
9	−15	15
10	−10	11
	2, 4, l	
−13	8	5
−12	7	9
−11	−4	6
−10	−3	5
−9	2	5
−8	18	17
−7	32	27
−6	24	22
−4	5	8
−3	1	3
−2	21	24
−1	37	38
0	26	27
1	12	13
2	−14	16
3	−19	24
4	−6	9
5	7	10
6	10	11
7	−2	8
8	−18	22
9	−13	15
10	−4	4
	2, 5, l	
−9	15	15
−8	26	26
−7	23	21
−6	9	11
−5	−10	14
−4	−19	22
−2	15	17
−1	11	14
0	−3	6
1	−2	5
2	−24	27
3	−19	21
4	−3	5
6	3	6
7	−9	13
8	−14	17
9	−5	6
	2, 6, l	
−11	6	7
−10	8	9
−9	16	15
−8	13	13
−7	6	6
−5	−10	12
−4	−7	12
−3	4	7
−2	9	10
0	−19	22
1	−27	31
2	−22	28
3	−9	13
4	3	4
5	−5	6
6	−11	14
7	−12	16
8	−7	9
	2, 7, l	
−10	8	9
−9	15	14
−8	11	11
−7	−6	6
−6	−10	14
−5	−15	19
−4	−5	8
−3	6	8
−2	−2	4
−1	−19	25
0	−24	30
1	−23	26
2	−5	9
3	9	9
4	3	6
5	−4	6
6	−4	6
	2, 8, l	
−9	7	8
−7	−16	15
−6	−15	17
−5	−15	16
−4	−10	13
−3	5	6
−2	−5	8
−1	−11	14
0	−9	10
1	−7	8
2	6	6
3	11	15
	2, 9, l	
−8	−7	10
−7	−10	10
−6	−9	9
−5	−3	6
−4	−2	6
−2	−5	5
0	−4	6
1	2	6
2	8	12
	2, 10, l	
−8	−8	8
−7	−8	8
−6	−4	7
−5	7	10
−4	11	13
−3	−4	5
−2	−6	6
−1	−3	5
0	8	10
1	15	21
2	8	11
	2, 11, l	
−7	−2	6

TABLE 1 (*Continued*)

l	F_c	$\|F_o\|$
	2, 11, l	
−6	5	7
−5	12	14
−4	9	11
−2	3	6
−1	7	10
0	13	16
1	13	15
2	5	6
	2, 12, l	
−6	9	11
0	9	11
	3, −12, l	
0	−6	5
	3, −11, l	
−2	−10	10
−1	−12	13
0	−5	6
4	−7	5
5	−9	8
	3, −10, l	
−3	−13	13
−2	−12	11
−1	−10	11
0	−3	4
1	2	7
3	−7	8
4	−7	8
	3, −9, l	
−8	−8	6
−7	−7	6
−6	−5	5
−5	−5	5
−4	−15	12
−3	−17	14
−2	−11	10
−1	−5	6
2	−7	8
3	−13	13
4	3	4
5	12	11
6	15	10
	3, −8, l	
−6	7	7
−5	−8	8
−4	−15	12
−3	−8	7
−2	0	3
−1	9	8
0	8	7
3	6	8
4	17	16
5	16	13
6	13	11
	3, −7, l	
−5	−8	9
−4	−10	9
−3	2	3
−2	8	7
−1	15	13
0	10	11
2	3	5
3	20	19
4	20	19
5	17	15
6	7	8
	3, −6, l	
−10	−6	5
−6	−10	10
−5	−5	5
−3	18	15
−2	28	23
−1	14	14
0	−3	3
1	−12	14
2	7	6
3	12	13
4	17	15
5	10	9
6	−6	7
	3, −5, l	
−12	−8	7
−11	−7	5
−10	5	4
−9	14	13
−8	18	16
−7	4	7
−6	−10	8
−4	18	16
−3	30	24
−2	27	22
−1	−4	6
0	−27	24
1	−21	19
2	4	5
3	6	6
4	6	8
6	−16	15
	3, −4, l	
−11	4	5
−10	16	16
−9	15	15
−8	9	11
−5	15	16
−4	30	28
−3	17	17
−2	11	11
−1	−1	4
0	−17	15
1	−3	3
2	−5	4
3	6	7
4	−2	7
5	−19	17
6	−27	24
7	−17	14
8	−4	5
	3, −3, l	
−12	4	6
−11	10	12
−10	8	12
−9	6	8
−7	−4	6
−6	3	5
−5	35	34
−4	27	26
−3	8	8
−2	−4	3
−1	−30	26
0	−17	20
1	5	7
2	−13	12
3	−11	9
4	−18	18
5	−35	30
6	−18	17
7	−6	5
11	−6	5
	3, −2, l	
−12	9	10
−11	14	16
−10	6	7
−9	2	5
−8	−7	8
−7	−11	13
−6	1	4
−5	12	14
−4	3	4
−3	−20	20
−2	−27	26
−1	−45	41
0	−23	21
1	−4	4
2	−5	5
3	−16	14
4	−23	20
5	−22	20
6	−6	8
7	3	5
	3, −1, l	
−12	12	12
−11	16	15
−10	9	9
−9	−9	10
−8	−13	15
−7	−5	9
−6	0	4
	3, −1, l	
−5	−16	19
−4	−8	8
−3	−15	15
−2	−22	20
−1	−7	6
0	−19	19
1	−13	15
2	−10	14
3	−27	24
4	−24	21
7	5	5
9	−5	6
10	−6	6
	3, 0, l	
−13	5	6
−12	9	9
−11	8	9
−10	−4	5
−9	−14	17
−8	−13	15
−7	−6	8
−6	−1	3
−5	−14	13
−4	−15	18
−3	−14	16
−2	−36	32
−1	12	14
0	9	11
1	−7	8
2	−16	17
3	−22	21
4	2	4
5	21	23
6	21	22
7	6	7
	3, 1, l	
−11	−9	8
−10	−20	19
−9	−19	21
−8	−18	20
−7	−3	5
−5	−15	14
−4	−23	22
−3	−31	28
−2	−7	6
−1	23	23
0	23	24
1	7	9
2	8	12
4	16	19
5	30	28
6	20	21
7	5	5
	3, 2, l	
−12	−7	9
−11	−8	10
−10	−6	8
−9	−23	25
−8	−10	15
−7	6	8
−6	−5	7
−5	−9	9
−4	−28	24
−3	−29	30
−2	28	26
−1	32	31
0	16	18
1	3	5
2	5	8
3	10	13
4	26	27
5	33	32
6	8	9
7	2	4
	3, 3, l	
−12	−8	9
−11	−4	5
−10	1	3
−9	−2	5
−8	15	14
−7	8	11
−6	−5	7
−5	−2	4
−4	2	5
−3	38	36
−2	46	50
	3, 3, l	
−1	36	36
0	7	10
1	−7	9
2	3	6
3	26	30
4	29	32
5	16	20
7	−5	6
8	−2	5
	3, 4, l	
−13	−5	4
−12	−9	7
−11	−7	7
−10	11	12
−9	38	34
−8	24	25
−7	4	7
−6	−3	4
−5	10	13
−4	43	42
−3	52	48
−2	32	33
−1	10	13
0	−1	3
1	−2	5
2	9	14
3	25	29
4	13	17
5	−2	5
7	−8	10
	3, 5, l	
−10	17	17
−9	24	24
−8	6	8
−5	11	15
−4	28	30
−3	27	28
−2	22	26
−1	−7	7
0	−6	8
1	2	3
2	11	17
3	14	18
4	−6	9
5	−13	16
6	−9	12
7	−5	8
	3, 6, l	
−11	5	6
−10	12	13
−9	10	10
−8	5	6
−7	−4	4
−6	3	5
−5	14	17
−4	26	29
−3	17	20
−2	−19	20
−1	−20	26
0	−9	12
2	2	5
3	−10	14
4	−17	22
5	−11	15
6	−7	8
	3, 7, l	
−12	6	7
−11	12	13
−10	15	15
−9	13	13
−8	−3	4
−7	−5	6
−6	5	6
−5	10	12
−4	17	19
−3	−7	8
−2	−29	32
−1	−7	10
0	−3	5
2	−3	5
3	−13	17
4	−10	13
5	−7	8
	3, 8, l	
−12	9	10
	3, 8, l	
−11	11	11
−10	5	5
−8	−6	7
−4	−2	1
−3	−5	7
−1	−5	6
0	−3	6
2	−4	5
3	−7	9
4	−8	8
5	−4	7
	3, 9, l	
−12	4	4
−10	−8	7
−9	−14	13
−6	−3	5
−5	−7	9
−4	−16	20
−3	−8	10
−1	−7	10
2	−6	10
3	−5	7
	3, 10, l	
−11	−7	7
−10	−13	11
−9	−13	12
−8	−5	6
−7	−3	5
−6	−7	10
−5	−12	18
−4	−18	20
−3	−11	12
−2	−4	8
−1	3	4
0	4	6
	3, 11, l	
−9	−5	5
−8	−2	4
−6	−3	5
−5	−10	13
−4	−11	14
−3	−2	5
−2	8	11
−1	7	10
0	3	3
	4, −11, l	
0	−4	5
1	−11	10
	4, −10, l	
0	−7	5
1	−16	12
3	−5	5
	4, −9, l	
−5	−9	7
−4	−8	7
0	−13	9
1	−15	13
2	−8	7
	4, −8, l	
−6	−8	6
−5	−13	10
−4	−5	6
−1	−6	7
0	−16	13
1	−12	12
2	1	3
3	9	8
4	12	9
	4, −7, l	
−8	−6	6
−7	−16	13
−6	−16	13
−5	−6	6
−2	−5	7
−1	−12	11
2	6	5
3	15	12
4	15	13
6	−8	8
	4, −6, l	
−9	−5	5
−8	−11	10
−7	−23	17
−6	−5	5
−5	14	12
−4	17	14
−3	12	11
−2	−3	4
−1	−5	6
1	14	13
2	16	15
3	10	10
4	6	5
6	−4	5
	4, −5, l	
−11	4	4
−9	−6	5
−8	−8	9
−6	7	8
−5	22	19
−4	22	18
−3	14	13
−2	2	5
−1	−7	9
0	15	15
1	47	37
2	32	26
3	10	10
4	−5	4
6	11	12
	4, −4, l	
−12	6	4
−11	7	10
−10	4	6
−7	3	5
−6	16	15
−5	35	33
−4	24	24
−3	12	14
−2	−2	2
−1	3	6
0	60	46
1	42	32
2	12	9
3	−5	6
4	−15	13
5	4	5
6	9	9
8	−4	3
9	−8	7
10	−8	6
	4, −3, l	
−12	11	11
−11	9	11
−10	6	8
−8	3	8
−7	12	15
−6	35	33
−5	27	28
−4	8	8
−2	−3	4
−1	16	18
0	19	19
1	−4	5
2	−12	10
3	−15	13
4	−11	12
7	−4	6
8	−14	11
9	−13	10
10	−6	5
	4, −2, l	
−13	9	8
−12	13	12
−11	8	10
−10	1	5
−8	10	12
−7	23	23
−6	15	15
−5	−2	6
−4	−4	5
−3	−6	7
−2	12	13
−1	5	5
0	−30	28
1	−2	3

TABLE 1 (*Continued*)

l	F_c	$\|F_o\|$
2	−14	13
3	−19	16
4	−5	5
5	−2	4
6	−2	6
7	−15	13
8	−20	16
9	−15	10
	4, −1, l	
−14	8	7
−13	11	12
−12	10	11
−11	6	8
−9	2	4
−8	10	13
−7	24	24
−6	1	4
−5	−10	9
−4	−12	12
−3	−15	15
−2	16	12
−1	4	6
0	−20	19
1	−27	25
2	−21	21
3	−8	9
4	8	9
5	3	4
6	−8	10
7	−10	12
	4, 0, l	
−14	11	8
−13	11	11
−9	7	10
−8	17	18
−7	3	5
−6	−15	16
−5	−23	22
−4	−13	13
−3	−4	5
−2	4	4
−1	−6	7
0	−29	27
1	−28	26
2	1	3
3	10	11
4	14	15
5	3	6
6	−3	6
7	9	11
8	6	7
9	8	6
10	8	7
	4, 1, l	
−14	7	8
−12	−10	10
−11	−6	8
−9	13	13
−8	13	14
−7	−22	20
−6	−26	25
−5	−14	11
−4	−6	6
−3	9	13
−2	−4	6
−1	−24	23
0	−37	32
1	−9	9
2	3	6
3	14	15
4	14	15
5	−2	4
7	4	6
9	12	10
	4, 2, l	
−13	−10	10
−12	−10	12
−8	−14	15
−7	−31	30
−6	−29	27
−5	−8	8
−4	2	7
−3	5	12
−1	−21	23
0	−19	19
1	−10	10
2	13	12
3	24	24

l	F_c	$\|F_o\|$
	4, 2, l	
4	15	16
6	−6	7
7	−2	6
8	13	12
9	12	10
	4, 3, l	
−14	−11	10
−13	−13	11
−12	−11	11
−11	−5	6
−9	−12	15
−8	−26	22
−7	−22	20
−6	−12	13
−5	11	13
−4	28	29
−3	12	13
−2	−5	4
−1	−3	6
0	6	10
2	23	25
3	21	23
4	8	10
5	6	7
6	−2	5
7	5	7
8	12	13
	4, 4, l	
−14	−13	13
−13	−9	8
−11	−2	4
−9	−10	12
−8	−13	14
−7	−5	5
−6	4	4
−5	13	14
−4	20	20
−3	6	10
−2	−6	8
−1	4	4
0	17	20
1	25	28
2	23	25
3	10	14
4	−3	5
5	3	5
6	9	10
7	9	11
8	5	6
	4, 5, l	
−14	−8	6
−13	−3	4
−9	−8	10
−8	−9	10
−7	6	8
−6	12	15
−5	19	20
−4	17	20
−3	8	11
−2	6	8
−1	15	20
0	19	25
1	22	26
2	7	11
3	−8	10
4	−8	10
6	4	5
	4, 6, l	
−9	−5	6
−6	17	17
−5	16	18
−4	13	15
−3	−3	4
−2	6	9
−1	9	13
0	5	6
1	5	4
2	−6	8
3	−12	16
4	−3	5
	4, 7, l	
−8	5	8
−7	8	10
−6	8	9

l	F_o	$\|F_o\|$
	4, 7, l	
−5	1	3
−4	−2	3
−3	−5	8
0	4	5
1	−5	6
2	−12	17
3	−7	12
	4, 8, l	
−9	3	3
−8	7	8
−7	7	8
−6	5	9
−5	−10	14
−4	−18	19
0	−7	10
1	−19	24
2	−14	18
3	−4	5
	4, 9, l	
−9	4	5
−8	6	7
−6	−6	9
−5	−17	20
−4	−16	19
−3	−2	4
−2	−1	3
−1	−6	9
0	−13	20
1	−16	19
2	−7	9
	4, 10, l	
−8	0	3
−7	−7	9
−6	−14	18
−5	−13	16
−4	−3	5
−2	−14	6
−1	−8	14
1	−8	11
	4, 11, l	
−8	−5	8
−7	−11	12
−6	−14	17
−5	−4	9
−4	4	6
−3	3	6
−2	−3	5
−1	−8	12
	5, −10, l	
0	−10	7
1	−6	6
4	−9	7
5	−11	7
	5, −9, l	
−4	6	5
−2	−7	6
0	−10	8
3	−9	8
4	−11	8
5	−11	9
6	−6	4
	5, −8, l	
−3	−8	8
−2	−18	13
1	11	11
4	−8	6
5	−7	6
	5, −7, l	
−4	−7	7
−3	−16	14
−2	−19	15
0	14	12
1	16	14
6	10	7
	5, −6, l	
−4	−16	13
−3	−12	11
−2	−8	7
0	12	10

l	F_c	$\|F_o\|$
	5, −6, l	
1	5	5
4	4	4
5	12	10
6	16	13
	5, −5, l	
−5	−11	11
−4	−12	12
−2	7	6
0	16	17
1	5	4
2	8	7
3	6	5
4	11	9
5	20	18
6	11	10
	5, −4, l	
−11	−9	12
−10	−5	7
−9	−4	5
−8	6	7
−7	14	13
−6	8	9
−4	3	5
−3	13	12
−2	23	20
−1	31	29
0	17	16
1	7	8
2	5	4
3	11	10
4	15	13
5	14	12
	5, −3, l	
−12	−5	6
−11	−11	11
−10	−7	8
−9	7	8
−8	14	14
−7	8	11
−6	2	6
−5	15	17
−4	12	13
−3	13	13
−2	16	15
−1	6	5
0	9	9
1	7	10
2	4	6
3	16	13
4	17	13
7	−6	5
	5, −2, l	
−9	17	17
−8	17	17
−7	6	8
−5	12	11
−4	16	14
−3	16	14
−2	24	23
−1	−11	14
0	−15	16
1	−4	6
2	3	5
3	12	10
4	2	4
5	−15	14
6	−18	15
7	−10	8
	5, −1, l	
−12	2	5
−11	10	10
−10	16	16
−9	16	17
−8	19	21
−7	6	10
−6	−3	4
−5	5	6
−4	17	17
−3	27	26
−2	13	16
−1	−19	18
0	−30	27
1	−13	14
2	−6	8
4	−6	7

l	F_c	$\|F_o\|$
	5, −1, l	
5	−20	17
6	−19	17
7	−8	7
	5, 0, l	
−12	5	7
−11	9	11
−10	4	5
−9	13	14
−8	5	11
−7	−7	8
−6	−2	5
−5	3	5
−4	18	17
−3	20	20
−2	−19	19
−1	−25	23
0	−21	20
1	−21	20
1	−8	9
2	0	3
3	−2	4
4	−12	14
5	−20	19
6	−9	9
7	−2	4
8	3	4
	5, 1, l	
−12	6	7
−11	5	7
−10	−2	6
−8	−21	17
−7	−17	17
−6	−3	5
−5	−2	5
−4	0	3
−3	−28	27
−2	−42	36
−1	−36	34
0	−13	14
1	6	7
2	7	9
3	−12	13
4	−20	19
5	−11	13
7	7	6
	5, 2, l	
−12	6	5
−11	8	9
−10	−6	8
−9	−37	31
−8	−32	29
−7	−13	15
−4	−27	25
−3	−40	40
−2	−30	26
−1	−15	16
0	−3	3
1	6	9
2	2	3
3	−14	15
4	−10	12
7	9	9
	5, 3, l	
−11	3	5
−10	−11	14
−9	28	25
−8	−13	14
−7	−3	5
−4	−17	19
−3	−21	21
−2	−17	19
−1	9	9
0	8	9
2	−3	8
3	−8	12
4	7	9
5	13	13
6	8	9
	5, 4, l	
−11	−5	7
−10	−11	14
−9	−12	14
−8	−12	13
−5	−5	8
−4	−16	18

l	F_c	$\|F_o\|$
	5, 4, l	
−3	−17	18
−2	15	15
−1	26	30
0	16	18
3	9	12
4	17	20
5	14	15
6	8	9
	5, 5, l	
−11	−12	13
−10	−16	15
−9	−14	15
−7	7	12
−5	−7	8
−4	−14	15
−3	3	4
−1	10	14
0	5	7
3	10	13
4	8	9
5	7	7
	5, 6, l	
−11	−9	6
−10	−5	10
−9	4	7
−8	10	12
−4	3	6
−3	6	8
0	2	3
3	4	5
4	6	7
6	−4	6
	5, 7, l	
−10	10	10
−9	19	19
−8	7	7
−5	7	10
−4	21	22
−3	12	15
−1	6	10
0	−4	6
1	−4	6
	5, 8, l	
−11	6	8
−10	15	15
−9	17	17
−8	6	9
−5	7	10
−4	20	22
−3	15	16
−2	4	7
−1	−7	10
0	−10	15
1	−3	7
	5, 9, l	
−5	5	8
−4	9	11
−3	4	7
−2	−9	10
−1	−12	17
0	−8	11
	5, 10, l	
−3	−7	12
−2	−14	18
−1	−11	14
0	−5	8
	6, −10, i	
0	8	5
	6, −9, l	
1	2	5
4	−10	6
	6, −8, l	
−4	−12	11
2	−10	8
3	−8	6
	6, −7, l	
−4	−15	12
1	−22	18

TABLE 1 (*Continued*)

l	F_c	$\|F_o\|$
	6, −7, *l*	
2	−19	14
3	−6	6
	6, −6, *l*	
−4	−16	13
0	−21	18
1	−18	18
2	−5	8
3	6	7
4	14	10
	6, −5, *l*	
−4	−4	6
0	−10	9
1	6	8
2	11	9
3	14	10
4	12	9
5	2	5
	6, −4, *l*	
−10	−2	5
−9	0	2
−8	−2	7
−7	−11	12
−6	−10	11
−5	2	5
−4	7	8
−3	12	13
−2	1	3
−1	−4	4
0	13	15
1	5	5
2	12	9
3	16	11
4	6	6
	6, −3, *l*	
−12	−9	10
−11	−6	9
−9	1	4
−8	−4	5
−7	−13	13
−6	3	7
−5	12	13
−4	15	15
−3	17	18
−2	−3	4
−1	−4	4
0	12	11
1	18	15
2	18	15
3	9	8
4	−5	6
5	−6	7
	6, −2, *l*	
−9	−3	5
−8	−13	13
−7	−6	8
−6	12	12
−5	22	22
−4	16	15
−3	6	8
−2	−7	8
−1	−5	8
0	14	13
1	25	20
2	7	5
3	−6	6
4	−13	11
5	−8	9
7	−6	6
8	−5	5
	6, −1, *l*	
−12	10	13
−11	10	14
−9	−10	11
−8	−15	15
−7	12	12
−6	21	20
−5	18	17
	6, −1, *l*	
−4	7	6
−3	−11	12
−2	−5	6
−1	4	6
0	15	15
1	9	9
3	−10	7
4	−14	12
5	−6	7
	6, 0, *l*	
−13	10	10
−12	12	14
−11	7	9
−10	3	5
−9	−2	4
−8	7	10
−7	21	22
−6	24	24
−5	12	12
−3	−19	16
−2	−10	10
−1	6	8
0	5	8
1	3	4
2	−8	7
3	−18	17
4	−14	13
5	−6	3
	6, 1, *l*	
−13	13	14
−12	11	12
−11	5	6
−9	5	8
−8	16	18
−7	13	14
0	−7	8
2	−17	5
3	−16	16
4	−6	6
5	−5	5
	6, 2, *l*	
−13	10	8
−10	−10	11
−8	6	9
−6	−6	6
−5	−13	16
−4	−23	23
−3	−13	14
0	−14	15
1	−19	21
2	−18	6
3	−8	11
4	4	4
	6, 3, *l*	
−6	−12	14
−5	−16	19
−4	−19	20
−3	−15	19
0	−14	18
1	−18	21
2	−6	8
3	7	8
4	10	11
5	5	6
6	−3	5
	6, 4, *l*	
−11	−9	10
−10	−4	6
−6	−16	20
−5	−12	15
−4	−6	8
−3	4	5
2	6	7
3	12	14
4	5	6
	6, 5, *l*	
−6	−8	8
−4	8	8
	6, 5, *l*	
−3	13	13
3	14	15
3	10	11
4	4	4
	6, 6, *l*	
−6	−5	8
−5	10	13
−4	21	22
−3	8	11
1	16	18
2	16	17
3	7	7
	6, 7, *l*	
−6	6	9
−5	20	22
−4	21	22
−3	4	5
0	8	13
2	8	8
	6, 8, *l*	
−6	15	18
−5	17	19
−4	8	11
1	8	11
	6, 9, *l*	
−6	16	18
	7, −9, *l*	
0	−6	5
1	−9	7
	7, −8, *l*	
0	−8	5
	7, −7, *l*	
0	−13	10
1	−6	6
	7, −6, *l*	
0	−10	7
4	−8	6
5	−9	6
	7, −5, *l*	
3	−6	5
4	−10	8
5	−3	6
	7, −4, *l*	
−10	−5	5
−9	−15	15
−8	−16	17
−7	−8	9
−5	−4	7
−4	−8	9
−3	−12	12
−2	−16	15
−1	4	5
0	12	11
1	10	9
2	6	6
	7, −3, *l*	
−11	−7	11
−10	−11	12
−9	−11	13
−8	−15	16
−7	−6	10
−6	5	7
−5	4	6
−4	−7	7
−3	−18	16
−2	−14	15
−1	9	9
0	23	18
1	14	12
	7, −3, *l*	
2	6	6
5	9	7
6	11	6
	7, −2, *l*	
−11	−7	9
−10	−4	4
−9	−6	4
−7	7	7
−6	7	9
−5	5	5
−4	−7	8
−3	−11	12
−2	9	9
−1	14	14
0	18	16
1	10	8
3	−2	4
5	9	8
	7, −1, *l*	
−8	20	19
−7	20	19
−6	9	10
−5	5	7
−3	14	15
−2	27	23
−1	23	20
0	11	11
2	−9	8
4	10	9
5	6	7
	7, 0, *l*	
−11	−5	7
−9	24	25
−8	27	25
−7	16	18
−6	5	7
−4	10	10
−3	20	19
−2	15	14
−1	9	9
1	−7	7
2	−6	6
3	6	5
4	6	7
5	−2	6
	7, 1, *l*	
0	−11	12
1	−6	6
3	3	5
4	−7	7
	7, 2, *l*	
0	−20	19
1	−5	7
3	−4	5
4	−12	11
5	−13	10
	7, 3, *l*	
0	−7	6
2	5	4
3	−4	5
5	−5	10
	7, 4, *l*	
2	4	4
	7, 5, *l*	
1	8	13
	7, 6, *l*	
0	12	17
1	8	12
	7, 7, *l*	
0	11	15
1	5	7
	7, 8, *l*	
0	6	11
	8, −8, *l*	
0	7	6
1	8	6
	8, −7, *l*	
1	−3	4
	8. −6, *l*	
0	−5	6
1	−3	3
2	−7	8
3	−10	6
	8, −5, *l*	
1	−8	5
3	−8	6
	8, −4, *l*	
−8	8	9
−7	8	10
−6	−5	7
−5	15	13
−4	−15	13
−3	−6	7
−2	5	7
−1	8	10
1	−13	11
2	−6	5
3	2	4
	8, −3, *l*	
−11	−11	10
−10	−6	6
−9	4	5
−8	11	11
−6	−10	11
−5	−14	13
−4	−8	8
−3	5	5
−2	6	5
−1	4	4
1	−4	4
	8, −2, *l*	
−11	−9	9
−10	−5	7
−8	−2	5
−7	−11	12
−6	−13	12
−5	−9	9
−3	13	11
−2	9	9
4	8	6
5	4	3
	8, −1, *l*	
−8	−5	8
−7	−4	6
−5	5	6
−4	16	15
−3	16	15
−2	8	7
2	11	7
3	11	8
	8, 0, *l*	
−10	11	13
−9	7	10
−5	12	11
−4	18	15
−3	12	11
−2	5	6
−1	6	5
0	9	9
1	11	11
2	12	11
3	6	7
	8, 1, *l*	
0	9	11
1	12	12
2	5	6
3	−5	8
	8, 2, *l*	
3	−9	6
	8, 3, *l*	
2	−10	9
3	−10	5
	8, 4, *l*	
1	−9	13
2	−11	13
3	−6	3
	8, 5, *l*	
1	−8	11
3	1	3
	9, −6, *l*	
0	−6	3
	9, −5, *l*	
0	−12	10
1	−10	7
	9, −4, *l*	
−7	−5	5
−6	−7	8
−5	−7	7
−3	5	5
−1	−7	7
0	−11	10
1	−8	7
	9, −3, *l*	
−8	−12	13
−7	−14	15
−6	−8	9
−5	−5	6
−3	−6	8
−2	−14	14
−1	−10	9
0	−6	5
1	−1	3
	9, −2, *l*	
−9	−11	12
−8	−17	16
−7	−12	13
−6	−4	5
−4	−2	8
−3	−7	5
1	7	6
3	−1	6
4	−4	4
	9, −1, *l*	
0	12	10
1	9	7
	9, 0, *l*	
−7	−2	8
−3	−9	8
−1	17	14
0	17	16
1	7	7
	10, −3, *l*	
−5	−4	4
−4	−11	9
−3	−12	10
−2	−7	6

co-ordinates so obtained, a set of structure factors was calculated using an arbitrarily chosen overall isotropic temperature factor with $B = 3{\cdot}0$ Å^2; the discrepancy factor, *R*, was 0·39.

The positions of the atoms were confirmed from a three-dimensional electron-density distribution which was computed using all the data except those planes of doubtful sign (11% of the total data).

The refinement was carried out by successive differential syntheses and structure factor calculations. Changes in the overall scale factor and the individual temperature factors for each atom were made by trial and error according to the criteria $\rho_o - \rho_c = 0$, and $\partial^2(\rho_o - \rho_c)/\partial r^2 = 0$, respectively, where $\partial^2(\rho_o - \rho_c)/\partial r^2$ is the mean of the three principal second derivatives $\partial^2(\rho_o - \rho_c)/\partial x,^2$ etc. When there were no further significant changes in either scale factor or any of the temperature factors, the average observed shift was somewhat less than 0·003 Å (excluding copper atoms) and the maximum shift was 0·007 Å. As the shifts for every atom were now less than half the estimated standard deviations, the refinement was stopped and back-shift corrections were applied to all the atoms. The final set of structure factors $R = 0{\cdot}15$, is listed in Table 1.

The final co-ordinates of the atoms, their estimated standard deviations, and temperature factors are listed in Table 2. The orthogonal axes are orientated as follows: *B* coincides with the orginal triclinic axis *b*; *A* is the projection of the triclinic axis *a* on the plane perpendicular to *B*; *C* is perpendicular to *A* and *B*.

Confirmation that the space group is $P\bar{1}$ comes from the absence of spurious peaks in the electron density map (the maximum electron density apart from atomic centres was less than 1 eÅ^{-3}) and the good agreement between electron densities and curvatures for the calculated and observed syntheses. The calculated and observed electron densities are listed in Table 2.

TABLE 2

Final electron densities, atomic co-ordinates, and thermal parameters

	Electron density (eÅ^{-3})		Fractional co-ordinates			Orthogonal co-ordinates			R.M.S. e.s.d.	*B*
Atom	obs.	calc.	*x*/*a*	*y*/*b*	*z*/*c*	*X* (Å)	*Y* (Å)	*Z* (Å)	(Å)	(Å^2)
Cu(1)	60·1	60·7	0·3371	0·1119	0·1673	2·2935	0·6467	1·7884	0·002	1·7
O(1_1)	11·2	11·4	0·4095	0·1617	0·3429	2·1953	0·7276	3·6643	0·012	2·9
O(2_1)	13·1	13·4	0·2601	0·0510	−0·0096	2·3568	0·4550	−0·1025	0·009	2·4
N(1)	10·9	11·1	0·4895	0·2353	0·1418	3·7590	1·9408	1·5159	0·011	2·3
C(1_1)	6·3	5·9	0·5422	0·3010	0·5440	2·5262	1·6624	5·8140	0·025	5·2
C(2_1)	7·4	7·1	0·5075	0·2699	0·4062	2·8001	1·6747	4·3408	0·017	3·7
C(3_1)	6·0	6·5	0·5863	0·3574	0·3512	3·7348	2·6905	3·7531	0·021	5·2
C(4_1)	8·0	8·1	0·5736	0·3392	0·2326	4·1237	2·7833	2·4853	0·016	3·0
C(5_1)	5·6	5·6	0·6562	0·4518	0·2098	4·9559	3·9847	2·2425	0·027	5·0
C(6_1)	9·0	9·0	0·4772	0·2046	0·0139	4·1905	1·9248	0·1490	0·012	3·0
C(7_1)	8·8	9·3	0·5806	0·2573	−0·0360	5·3227	2·5541	−0·3844	0·013	2·0
C(8_1)	7·2	7·5	0·5508	0·2106	−0·1599	5·5820	2·3677	−1·7086	0·018	3·5
C(9_1)	7·4	7·3	0·4307	0·1102	−0·2378	4·8421	1·5458	−2·5418	0·018	3·4
C(10_1)	7·3	7·3	0·3368	0·0598	−0·1832	3·7746	0·9258	−1·9577	0·019	3·5
C(11_1)	10·3	10·3	0·3529	0·0967	−0·0624	3·4075	1·0216	−0·6672	0·010	2·0
Cu(2)	61·0	59·6	0·1145	−0·1081	−0·0331	1·1595	−1·1009	−0·3542	0·002	1·9
O(1_2)	11·9	12·1	0·0878	−0·1953	−0·1987	1·6229	−1·6147	−2·1237	0·010	3·0
O(2_2)	13·1	12·7	0·1368	−0·0118	0·1342	0·6506	−0·4932	1·4337	0·009	2·3
N(2)	11·2	11·3	−0·0037	−0·2508	0·0051	−0·0541	−2·6398	0·0541	0·010	2·3
C(1_2)	5·9	5·6	−0·0536	−0·3294	−0·3979	1·2066	−2·4962	−4·2529	0·027	5·0
C(2_2)	8·2	8·4	−0·0231	−0·2936	−0·2594	0·8924	−2·4584	−2·7722	0·014	2·6
C(3_2)	7·2	6·8	−0·1086	−0·3706	−0·2036	−0·1061	−3·3639	−2·1755	0·016	4·0
C(4_2)	9·2	9·1	−0·1019	−0·3465	−0·0884	−0·5337	−3·3846	−0·9451	0·013	2·8
C(5_2)	6·9	7·1	−0·2102	−0·4405	−0·0612	−1·6128	−4·3915	−0·6545	0·018	4·0
C(6_2)	7·8	7·7	0·0247	−0·2214	0·1345	−0·3494	−2·6475	1·4369	0·017	3·0
C(7_2)	7·5	7·5	0·0004	−0·3055	0·2053	−0·8656	−3·6868	2·1939	0·018	3·4
C(8_2)	6·8	7·0	0·0216	−0·2653	0·3252	−1·1841	−3·5560	3·4755	0·020	3·7
C(9_2)	7·4	7·1	0·0940	−0·1347	0·3904	−0·8151	−2·3681	4·1724	0·019	3·4
C(10_2)	6·8	6·5	0·1297	−0·0515	0·3259	−0·2249	−1·3581	3·4834	0·022	4·4
C(11_2)	9·7	9·5	0·1063	−0·0930	0·2021	0·0912	−1·4925	2·1596	0·012	2·6

The scattering factors of Berghuis *et al.*[6] were used for copper, oxygen, nitrogen, and carbon. An anomalous dispersion correction[7] (−2·1 electrons uniformly over the range) was applied to the copper values.

[6] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.
[7] Dauben and Templeton, *Acta Cryst.*, 1955, **8**, 841.

Three-dimensional Fourier series and structure factors were calculated on UTECOM (a DEUCE electronic digital computer) with programmes written by Dr. J. S. Rollett. The interatomic distances and bond angles were calculated using programmes written by Drs. J. G. Sime and J. C. Speakman, respectively. The differential synthesis programme was written by one of us (G. A. B.).

DISCUSSION

The atomic arrangement in the crystal of acetylacetone-mono-(*o*-hydroxyanil)copper(II) is shown in Figure 1. The structure is made up of dimeric molecules (Figure 2) arranged in layers parallel to the $(1\bar{1}0)$ plane and separated by a distance of 3·50 Å, which is of the order expected for van der Waals forces. However, these molecules are associated in pairs due to a weak bond between the copper atom of one molecule and an oxygen atom of another. The intermolecular distances are listed in Table 3. The bond lengths and angles in the dimer (together with their estimated standard deviations) are in Table 4.

TABLE 3

Intermolecular distances *

Contact	Distance (Å)	Contact	Distance (Å)	Contact	Distance (Å)
Cu(1)–Cu(2a)	3·77	C(11_1)–C(6_2a)	3·55	C(8_1)–C(11_2b)	3·50
Cu(1)–C(4_2a)	3·36	C(5_2)–N(1a)	3·37	C(11_1)–C(11_1b)	3·48
Cu(2)–Cu(2a)	3·27	Cu(1)–C(8_1b)	3·22	C(1_1)–C(8_1c)	3·76
Cu(2)–O(2_2a)	2·64	Cu(2)–C(7_1b)	3·13	C(1_1)–C(9_1c)	3·90
O(2_1)–O(2_2a)	3·29	O(1_1)–C(9_1b)	3·44	C(8_2)–C(1_1c)	3·72
O(2_1)–C(5_2a)	3·26	O(1_2)–C(7_1b)	3·45	C(9_2)–C(1_2c)	4·02
O(2_1)–C(11_2a)	3·36	O(1_2)–C(4_1b)	3·54	C(1_1)–C(8_2d)	3·71
O(2_2)–O(1_2a)	3·18	N(1)–C(10_1b)	3·56	C(1_1)–C(9_2d)	3·66
O(2_2)–O(2_2a)	3·30	N(2)–C(6_2b)	3·66	C(5_1)–C(5_2e)	4·10
N(2)–O(2_2a)	3·17	C(5_1)–C(1_2b)	3·89	C(5_1)–C(7_2e)	3·92
C(1_1)–C(1_2a)	4·13	C(5_1)–C(2_2b)	3·65	C(5_1)–C(8_2e)	3·96
C(4_1)–C(5_2a)	3·50	C(6_1)–C(7_2b)	3·62	C(7_1)–C(5_2e)	3·72
C(5_1)–C(5_2a)	3·72	C(8_1)–C(6_2b)	3·68	C(8_1)–C(5_2e)	3·89
C(6_1)–C(5_2a)	3·60				

* The co-ordinates of the atoms marked a, b, c, d, and e are related to those in Table 1 as follows: *a*, $(\bar{x},\bar{y},\bar{z})$; *b*, $(1-x,\bar{y},\bar{z})$; *c*, $(x,y,z+1)$; *d*, $(1-x,\bar{y},1-z)$; *e*, $(x+1,y+1,z)$.

The Ligand.—There are no significant differences between corresponding bond lengths and angles in the two independent ligand molecules. The average values for the bond lengths and angles in the ligand molecules are shown in Figure 2 which also indicates the system used in the numbering of the atoms; the subscripts 1 and 2 refer to the ligand molecules attached to Cu(1) and Cu(2), respectively.

The carbon–carbon distances and bond angles are consistent with sp^3 hybridisation of C(1) and C(5), with sp^2 hybridisation of C(2), C(3), and C(4), and with the aromatic nature of C(6), C(7), C(8), C(9), C(10), and C(11) [$C_{sp}(3)$–$C_{sp}(2)$, 1·500; $C_{sp}(2)$–$C_{sp}(2)$, 1·487; C=C, 1·316; C–C (aromatic), 1·384 Å].[8,9] The average carbon–nitrogen and carbon–oxygen bond lengths in the acetylacetone component of the ligand are similar to those found respectively in amides,[8] in which the carbon atom has sp^2 hybridisation, and in copper(II) ethylacetoacetate,[10] in which the ester–carbonyl bond length is 1·27 Å. It seems probable, therefore, that there is no delocalisation of the π-electrons in this portion of the ligand or in the chelate ring containing it.

The distances from the aromatic ring to its substituent atoms [C(6) to N and C(11) to O(2)] do not differ significantly from values obtained for similar bonds in other structures; 1·426 and 1·36 Å, respectively.[9]

Although the aromatic system [C(6) to C(11), N, O(2)] and the acetylacetone-imine component of the ligand, [C(1) to C(5), N, O(1)] are both planar, neither of the ligand

[8] Ham, *Rev. Pure Appl. Chem.*, 1961, **11**, 159.

[9] Sutton *et al.*, " Interatomic Distances and Configuration in Molecules and Ions," Chem. Soc. Special Publ. No. 11, London, 1958.

[10] Barclay and Cooper, unpublished observations.

TABLE 4

Interatomic distances and bond angles in acetylacetone-mono-(*o*-hydroxyanil)copper(II)

Bond	Length (Å)	e.s.d. (Å)	Angle	Value	e.s.d.	Angle	Value	e.s.d.
$Cu(1)-Cu(2)$	2·989	0·003	$O(1_1)-Cu(1)-O(2_2)$	99·0°	0·5°	$Cu(2)-O(2_1)-C(11_1)$	139·8	0·6
$Cu(1)-O(1_1)$	1·880	0·012	$O(1_2)-Cu(2)-O(2_1)$	100·5	0·4	$C(1_1)-C(2_1)-C(3_1)$	120·3	1·9
$Cu(2)-O(1_2)$	1·900	0·010	$O(1_1)-Cu(1)-N(1)$	98·5	0·5	$C(1_2)-C(2_2)-C(3_2)$	121·4	1·7
$Cu(1)-O(2_1)$	1·902	0·009	$O(1_2)-Cu(2)-N(2)$	97·5	0·4	$C(1_1)-C(2_1)-O(1_1)$	114·6	1·7
$Cu(2)-O(2_2)$	1·956	0·009	$O(2_1)-Cu(1)-N(1)$	84·5	0·5	$C(1_2)-C(2_2)-O(1_2)$	113·0	1·6
$Cu(1)-O(2_2)$	2·031	0·009	$O(2_2)-Cu(2)-N(2)$	84·0	0·4	$O(1_1)-C(2_1)-C(3)_1$	125·0	1·6
$Cu(2)-O(2_1)$	1·979	0·009	$O(2_2)-Cu(1)-O(2_1)$	78·3	0·4	$O(1_2)-C(2_2)-C(3_2)$	125·6	1·3
			$O(2_2)-Cu(2)-O(2_1)$	78·3	0·4			
$Cu(1)-N(1)$	1·974	0·011	$Cu(1)-O(2_1)-Cu(2)$	100·7	0·4	$C(2_1)-C(3_1)-C(4_1)$	127·1	1·9
$Cu(2)-N(2)$	2·002	0·009	$Cu(1)-O(2_2)-Cu(2)$	97·1	0·4	$C(2_2)-C(3_2)-C(4_2)$	127·9	1·4
$C(1_1)-C(2_1)$	1·499	0·030	$Cu(1)-O(1_1)-C(2_1)$	121·5	1·1	$C(3_1)-C(4_1)-C(5_1)$	112·2	1·9
$C(1_2)-C(2_2)$	1·514	0·031	$Cu(2)-O(1_2)-C(2_2)$	120·3	1·0	$C(3_2)-C(4_2)-C(5_2)$	115·4	1·5
$C(2_1)-O(1_1)$	1·312	0·020	$Cu(1)-N(1)-C(4_1)$	121·1	1·0	$C(3_1)-C(4_1)-N(1)$	124·7	1·6
$C(2_2)-O(1_2)$	1·291	0·017	$Cu(2)-N(2)-C(4_2)$	119·6	0·9	$C(3_1)-C(4_1)-N(2)$	125·5	1·4
$C(2_1)-C(3_1)$	1·500	0·027	$Cu(1)-N(1)-C(6_1)$	110·4	1·0	$N(1)-C(4_1)-C(5_1)$	123·1	1·7
$C(2_2)-C(3_2)$	1·474	0·021	$Cu(2)-N(2)-C(6_2)$	109·3	0·9	$N(2)-C(4_2)-C(5_2)$	119·1	1·4
$C(3_1)-C(4_1)$	1·329	0·026	$Cu(1)-O(2_1)-C(11_1)$	114·1	0·6	$C(4_1)-N(1)-C(6_1)$	128·1	1·2
$C(3_2)-C(4_2)$	1·303	0·021	$Cu(2)-O(2_2)-C(11_2)$	111·6	0·7	$C(4_2)-N(2)-C(6_2)$	130·8	1·2
$C(4_1)-N(1)$	1·335	0·019	$Cu(1)-O(2_2)-C(11_2)$	130·8	0·6	$N(1)-C(6_1)-C(7_1)$	127·0	1·1
$C(4_2)-N(2)$	1·335	0·016				$N(2)-C(6_2)-C(7_2)$	128·0	1·5
$C(4_1)-C(5_1)$	1·482	0·031	$N(1)-C(6_1)-C(11_1)$	112·5	1·0			
$C(4_2)-C(5_2)$	1·504	0·022	$N(2)-C(6_2)-C(11_2)$	115·2	1·4			
$N(1)-C(6_1)$	1·434	0·016	$C(11_1)-C(6_1)-C(7_1)$	120·2	1·1			
$N(2)-C(6_2)$	1·414	0·019	$C(11_2)-C(6_2)-C(7_2)$	116·4	1·5			
$C(6_1)-C(7_1)$	1·401	0·018	$C(6_1)-C(7_1)-C(8_1)$	117·6	1·3			
$C(6_2)-C(7_2)$	1·386	0·024	$C(6_2)-C(7_2)-C(8_2)$	122·9	1·7			
$C(7_1)-C(8_1)$	1·362	0·024	$C(7_1)-C(8_1)-C(9_1)$	124·4	1·5			
$C(7_2)-C(8_2)$	1·327	0·027	$C(7_2)-C(8_2)-C(9_2)$	119·5	1·8			
$C(8_1)-C(9_1)$	1·388	0·025	$C(8_1)-C(9_1)-C(10_1)$	115·5	1·6			
$C(8_2)-C(9_2)$	1·426	0·028	$C(8_2)-C(9_2)-C(10_2)$	119·0	1·8			
$C(9_1)-C(10_1)$	1·365	0·026	$C(9_1)-C(10_1)-C(11_1)$	126·3	1·6			
$C(9_2)-C(10_2)$	1·358	0·029	$C(9_2)-C(10_2)-C(11_2)$	121·2	1·8			
$C(10_1)-C(11_1)$	1·352	0·021	$C(10_1)-C(11_1)-C(6_1)$	116·0	1·2			
$C(10_2)-C(11_2)$	1·368	0·025	$C(10_2)-C(11_2)-C(6_2)$	119·8	1·4			
$C(11_1)-C(6_1)$	1·447	0·016	$C(6_1)-C(11_1)-O(2_1)$	117·2	1·0			
$C(11_2)-C(6_2)$	1·432	0·021	$C(6_2)-C(11_2)-O(2_2)$	116·8	1·1			
$C(11_1)-O(2_1)$	1·321	0·013	$C(10_1)-C(11_1)-O(2_1)$	126·7	1·2			
$C(11_2)-O(2_2)$	1·356	0·015	$C(10_2)-C(11_2)-O(2_2)$	122·8	1·2			

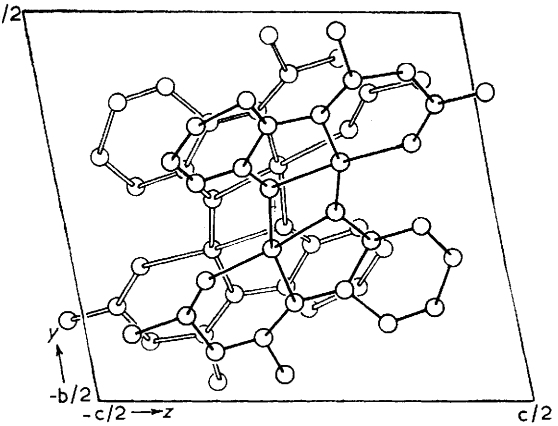


FIGURE 1. The arrangement of the atoms in the unit cell of acetylacetone-mono-(*o*-hydroxyanil)copper(II)

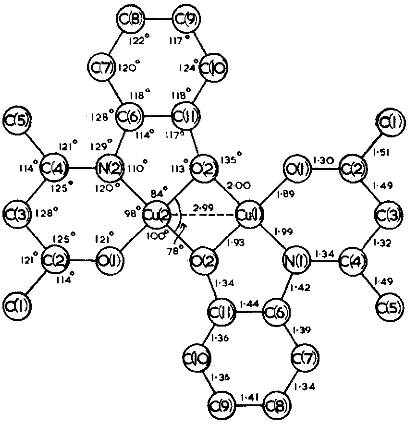


FIGURE 2. Mean bond lengths and bond angles in the molecule of acetylacetone-mono-(*o*-hydroxyanil)-copper(II)

molecules as a whole is planar. Table 5 lists the equations of the mean planes for each ligand and the deviations of the atoms from them. The dihedral angle between the two planes describing each ligand is approximately 16°. Catalin models suggest that this deviation from planarity is probably due to steric hindrance between the hydrogen atom attached to C(7) and the methyl group represented by C(5). Another contributing factor to the non planarity of the ligand molecule is the close copper–oxygen approach between centrosymmetrically related molecules.

The Environment of the Copper Atoms.—The two copper atoms in the asymmetric unit are bridged together by the phenolic oxygen atoms of the ligand, the copper–copper distance being 2·99 Å. Each copper atom is surrounded by four near neighbours at the corners of a very distorted square; the average deviations of the copper atom and the atoms bonded to it from the mean plane are about 0·04 and 0·08 Å, respectively (see Table 5). The dihedral angle between the two planes is 24°.

TABLE 5

Equations of least-squares planes [deviations of the atoms from the plane]

Ligand molecule 1.

Acetylacetone-imine component:

$0{\cdot}7898X - 0{\cdot}5846Y + 0{\cdot}1854Z - 2{\cdot}0581 = 0$ .... Plane 1

[$C(1_1)$, 0·043; $C(2_1)$, 0·021; $C(3_1)$, 0·015; $C(4_1)$, 0·032; $C(5_1)$, 0·058; $O(1_1)$, 0·070; N(1), 0·057 Å]

Aromatic component:

$0{\cdot}5816X - 0{\cdot}7788Y + 0{\cdot}2349Z - 1{\cdot}0092 = 0$ .... Plane 2

[$C(6_1)$, 0·036; $C(7_1)$, 0·007; $C(8_1)$, 0·008; $C(9_1)$, 0·006; $C(10_1)$, 0·005; $C(11_1)$, 0·020; N(1), 0·022; $O(2_1)$, 0·017 Å]

Dihedral angle between planes 1 and 2: 16·6°.

Ligand molecule 2.

Acetylacetone-imine component:

$0{\cdot}6911X - 0{\cdot}6997Y + 0{\cdot}1807Z - 1{\cdot}8416 = 0$ .... Plane 3

[$C(1_2)$, 0·030; $C(2_2)$, 0·006; $C(3_2)$, 0·046; $C(4_2)$, 0·013; $C(5_2)$, 0·002; N(2), 0·022; $C(1_2)$, 0·026 Å]

Aromatic component:

$0{\cdot}8971X - 0{\cdot}3954Y + 0{\cdot}1968Z - 1{\cdot}0457 = 0$ .... Plane 4

[$C(1_2)$, 0·031; $C(7_2)$, 0·067; $C(8_2)$, 0·018; $C(9_2)$, 0·019; $C(10_2)$, 0·025; $C(11_2)$, 0·051; N(2), 0·040; O(2), 0·015 Å]

Dihedral angle between planes 3 and 4: 14·7°.

Copper atom 1 *environment.*

$0{\cdot}6178X - 0{\cdot}7827Y + 0{\cdot}0756Z - 0{\cdot}9925 = 0$ .... Plane 5

[$O(1_1)$, 0·071; $O(2_1)$, 0·100; $O(2_2)$, 0·096; N(1), 0·074 Å]

Deviation of Cu(1) from this plane: 0·053 Å

Copper atom 2 *environment.*

$0{\cdot}7647X - 0{\cdot}5278Y + 0{\cdot}3697Z - 1{\cdot}3730 = 0$ .... Plane 6

[$O(2_1)$, 0·151; $O(1_2)$, 0·065; $O(2_2)$, 0·085; N(2), 0·001 Å]

Deviation of Cu(2) from this plane: 0·036 Å.

Dihedral angle between planes 5 and 6: 24·0°.

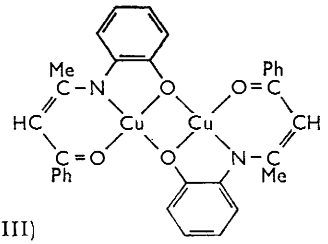
Although each of the copper atoms of the dimer has an identical arrangement of atoms for its four near neighbours, they have different environments. One of them, Cu(2), forms a distorted square pyramid with an oxygen atom [$O(2_2')$] of the centrosymmetrically related dimer. This oxygen atom lies at a distance of 2·64 Å along a line pasing through the copper atom and making an angle of 6·6° with the normal to the plane of best fit through its four neighbours. The nearest atom in the sixth octahedral position, at 3·13 Å, of this copper atom is a carbon atom [$C(7_1)$] of a molecule in an adjacent unit cell. The other copper atom, Cu(1), has essentially square co-ordination; $C(4_2)$ of the centrosymmetrically related molecule and $C(8_1)$ of a molecule in an adjacent cell occupy approximately octahedral sites at distances of 3·36 and 3·22 Å, respectively.

The interatomic distances between the atoms bonded to the copper atom are almost identical for each of the copper atoms in the dimer (the mean values are shown in Figure 2). The deviations from the values expected (and found in other compounds) indicate the considerable distortion of the square which probably arises from the same steric hindrances as cause the non-planarity of the ligands.

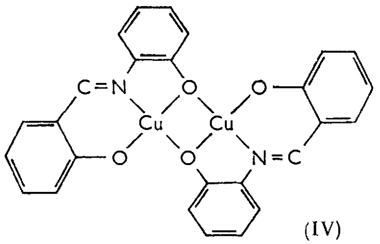
In general the copper–oxygen and copper–nitrogen bond lengths are in good agreement with previously reported values.[9,11] The bonds from the two copper atoms to $O(2_1)$ are about 0·05 Å shorter than the corresponding ones to $O(2_2)$. This is probably due to the weak bond between the Cu(2′) and $O(2_2)$ atoms which also leads to significantly different values of the corresponding bond angles around $O(2_2)$ and $O(2_1)$.

General Discussion.—The structure analysis of acetylacetone-mono(*o*-hydroxyanil)-copper(II) has shown that the copper atom is not three-covalent as originally thought. Although the two copper atoms in the asymmetric unit have different environments, each has a stereochemistry commonly found in copper(II) compounds.[12]

In the formation of acetylacetone-mono-(*o*-hydroxyanil)copper(II), the ligand must function as a monobasic acid. The structure proposed for (I) by Kishita *et al.* assumed that the acid hydrogen was produced by the formation of an acid enol group, that is, the ligand reacted in its enol-imine form as suggested in (I). However, the results of the structure analysis strongly suggest that the complex formation takes place through the keto-amine form as suggested in (III). Other examples of this type of tautomerism are known, for example, bis(acetylacetone)ethylenediamine and related Schiff's bases.[13] Unsaturated amino-ketones are known also to exist in the keto-amine form.[14]



(III)



(IV)

Using the known structure of acetylacetone-mono-(*o*-hydroxyanol)copper(II), it is reasonable to propose structures for the other magnetically anomalous complexes related to it. Structures (III) and (IV) were suggested for the two other compounds studied by Harris and Kokot. All these compounds form monopyridine complexes which have normal magnetic moments at room temperature; the pyridine complex of (I) obeys the Curie–Weiss law down to the temperature of liquid nitrogen.[15] It is probable that pyridine becomes co-ordinated to the copper atom and destroys the binuclear arrangement of the magnetically anomalous complex.

Since it is not obvious that a delta-bond between copper atoms could form in acetylacetone-mono-(*o*-hydroxyanil)copper(II), Harris and Kokot[2] postulated that the electron exchange in this compound takes place *via* the intermediate oxygen atoms in an essentially similar fashion to that proposed in copper(II) formate tetrahydrate.[16] However, because

[11] Barclay and Kennard, *J.*, 1961, 3289.

[12] Orgel and Dunitz, *Nature*, 1957, **179**, 462; Orgel, "An Introduction to Transition-Metal Chemistry Ligand Field Theory," Methuen, 1960, p. 60.

[13] Dudek and Holm, *J. Amer. Chem. Soc.*, 1961, **83**, 2099.

[14] Cromwell, Miller, Johnson, Frank, and Wallace, *J. Amer. Chem. Soc.*, 1949, **71**, 3337.

[15] Kokot, personal communication.

[16] Martin and Waterman, *J.*, 1959, 1359.

of the close approach of the two copper atoms (3·0 Å which is only 0·35 Å greater than the Cu–Cu single-bond distance) the possibility of direct electron exchange between them cannot be ignored.

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