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Structure of Copper–Dimethylglyoxime at Low Temperature

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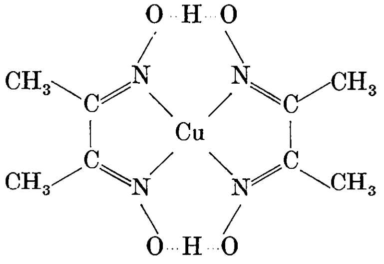
The crystal structure of copper–dimethylglyoxime has been examined at liquid-nitrogen temperatures and refined by two-dimensional Fourier syntheses. The unit cell is monoclinic with $a = 9{\cdot}71$, $b = 16{\cdot}88$, $c = 7{\cdot}08$ Å, $\beta = 108°\ 26'$. The space group is $P2_1/n$ and the unit cell contains 4 molecules of copper–dimethylglyoxime.

The two organic radicals bonded to the copper atom do not lie in the same plane, but form an angle of 180°–21° 44′. The copper is bonded with four N atoms (Cu–N = 1·94 Å) and with an O atom in a nearby molecule (Cu–O = 2·43 Å) forming a dimer. There are two hydrogen bonds between pairs of oxygen atoms; when one of these oxygen atoms is bonded to a copper atom the hydrogen bond is very weak.

Introduction

In a preliminary note, Bezzi, Bua & Schiavinato (1951) reported the crystallographic characteristics and some structural properties of Cu–dimethylglyoxime; this compound belongs to the monoclinic system space group C^5_{2h}–$P2_1/n$ with 4 molecules in the unit cell (Bua & Schiavinato, 1951). The copper atoms were located by a Patterson projection, and then a Fourier projection was calculated by attributing to the F_o the signs of the copper contribution; Bezzi, Bua & Schiavinato (1951) thus found planar coordination for the Cu in this molecule.



The well known differences of properties between Cu and Ni–dimethylglyoxime have been interpreted by the recent work of Godycki & Rundle (1953). The Ni–dimethylglyoxime was seen to belong to the orthorhombic system with space group *Ibam* and two molecules in the elementary cell. But, besides crystallographic differences, fundamental structural differences distinguish the compound of Ni from that of Cu. The existence of two weak bonds of 3·25 Å was noticed, normal to the plane of the Ni–N bonds between Nickel atoms in overlying molecules. An octahedral structure of this type is impossible for the Cu–dimethylglyoxime because of the considerable distance between Cu atoms in overlying molecules and also because of the interposition between them of the organic part of another molecule. This fundamental difference between the structures of the two compounds of dimethylglyoxime, which is not easy to interpret, rendered the completion of the structure of the Cu–dimethylglyoxime highly interesting.

The diffraction pattern was recorded at room temperature and at −140 °C. using the technique described by Post, Schwartz & Fankuchen (1951). With the low-temperature technique, we have attempted to obtain the maximum possible resolution of the atoms in the projections, and to reach a low standard error in the final coordinates. The influence of the temperature factor on the precision obtainable for the final coordinates has in fact been demonstrated by Burbank (1953) as well as by Hirschfeld & Schmidt (1956).

Experimental and diffraction data

The Cu–dimethylglyoxime compound was prepared by reaction between dimethylglyoxime in alcoholic solution and copper acetate. By re-crystallization of the precipitate from alcoholic solution, long needles of small cross section were obtained having an intense wine-red colour.

At the low temperature we obtained a set of cell constants slightly different from those determined at room temperature by Bua & Schiavinato (1951), which are also given here for comparison.

$t = -140$ °C.	$t = +20$ °C.
$a = 9{\cdot}71 \pm 0{\cdot}04$ Å	$a = 9{\cdot}80 \pm 0{\cdot}04$ Å
$b = 16{\cdot}88 \pm 0{\cdot}06$	$b = 17{\cdot}10 \pm 0{\cdot}06$
$c = 7{\cdot}08 \pm 0{\cdot}03$	$c = 7{\cdot}12 \pm 0{\cdot}03$
$\beta = 108°\ 26' \pm 20'$	$\beta = 107°\ 20' \pm 20'$

The $hk0$ and $0kl$ diffractions were measured by the multiple-film technique in a Weissenberg camera having an apparatus for linear integration. Intensities were evaluated by means of photometric integration

Table 1. *Observed and calculated structure factors for the hk*0 *and* 0*kl reflexions*

hkl	F_o	F_c
020	55·5	+53·8
040	14·4	−28·9
060	78·2	−85·8
080	40·9	+40·9
0,10,0	36·8	+40·9
0,12,0	31·6	+35·8
0,14,0	19·7	−15·6
0,16,0	16·1	−19·4
0,18,0	5·9	+8·5
0,20,0	36·0	+42·7
110	141·6	+143·3
120	9·4	+7·6
130	4·2	−5·4
140	10·8	+15·6
150	96·6	−95·0
160	30·3	−36·3
170	58·1	−58·9
180	5·8	+5·6
190	65·9	+57·9
1,10,0	24·3	−20·1
1,11,0	43;8	+47·0
1,12,0	2·6	+5·3
1,13,0	21·4	−22·2
1,14,0	32·5	+35·6
1,15,0	31·4	−32·2
1,16,0	15·5	+16·7
1,17,0	17·1	−13·9
1,18,0	19·8	−20·8
1,19,0	16·2	−18·5
1,20,0	4·6	−4·5
1,21,0	21·3	+25·0
200	27·9	+41·2
210	8·5	+7·7
2,22,0	16·5	+19·6
230	3·6	−7·8
240	28·1	−29·4
250	110·4	+96·0
260	44·1	−46·2
270	30·7	−31·2
280	16·4	+19·4
290	50·6	−44·8
2,10,0	59·8	+62·5
2,11,0	9·4	−0·8
2,12,0	20·2	+20·6
2,13,0	13·4	+18·2
2,14,0	25·3	−30·2
2,15,0	19·5	+18·5
2,16,0	38·3	−40·3
2,17,0	7·8	−8·4
2,18,0	7·3	−9·8
2,19,0	3·5	−4·9
2,20,0	23·2	+26·8
2,21,0	9·1	+10·2
310	74·1	+73·5
320	56·6	+56·4
330	12·6	−8·4
340	20·9	+26·3
350	4·7	−5·4
360	7·7	+9·2
370	12·3	−13·1
380	44·6	−40·8
390	45·2	+47·3
3,10,0	45·1	−35·5
3,11,0	27·0	+31·4
3,12,0	6·9	−5·1
3,13,0	33·6	+32·2
3,14,0	—	+0·1
3,15,0	23·4	−29·6
3,16,0	11·5	−12·7
3,17,0	21·6	−22·8
3,18,0	23·5	−27·5
3,19,0	22·7	+26·6
400	13·9	+15·5
410	32·8	+30·6
420	46·9	+45·6
430	73·8	+72·1
440	32·3	−32·2
450	33·7	−37·6
460	19·2	−28·6
470	23·5	−23·3
480	13·4	−14·3
490	43·5	−40·6
4,10,0	59·2	+65·2
4,11,0	34·6	+32·2
4,12,0	20·1	+23·0
4,13,0	3·0	+5·7
4,14,0	3·0	−1·4
4,15,0	11·6	+9·2
4,16,0	30·2	−31·0
4,17,0	23·9	−23·4
4,18,0	12·3	−11·5
4,19,0	18·6	−21·3
4,20,0	12·7	+12·1
510	23·0	+19·1
520	74·2	+74·4
530	12·4	−6·6
540	24·6	+27·9
550	2·4	−1·0
560	13·3	−13·9
570	3·6	−1·5
580	65·8	−65·3
590	46·9	+46·5
5,10,0	15·6	+17·5
5,11,0	59·1	+60·6
5,12,0	42·6	+43·0
5,13,0	4·2	+3·9
5,14,0	27·9	+31·9
5,15,0	20·8	−20·8
5,16,0	6·2	−7·0
5,17,0	13·6	−18·0
5,18,0	25·3	−26·1
600	21·6	+18·2
610	34·6	+34·1
620	19·2	−19·5
630	75·0	+78·7
640	14·2	−9·1
650	18·3	+13·2
660	5·4	−2·4
670	47·4	−46·3
680	35·2	+33·5
690	42·9	−43·6
6,10,0	24·7	+25·4
6,11,0	17·1	+21·1
6,12,0	3·0	+2·5
6,13,0	31·1	+29·9
6,14,0	—	−0·0
6,15,0	11·3	+10·7
6,16,0	15·8	−12·0
6,17,0	36·7	−38·3
710	2·8	+2·8
720	49·0	+50·4
730	3·9	+2·2
740	27·8	+32·3
750	13·1	−18·3
760	26·4	−32·5
770	12·1	+14·8
780	44·3	−45·0
790	16·3	−11·7
7,10,0	4·2	−3·1
7,11,0	7·1	−7·1
7,12,0	21·9	+23·1
7,13,0	6·7	−6·8
7,14,0	19·2	+17·3
800	2·9	+0·1
810	44·2	+47·2
820	32·5	+30·2
830	2·9	+0·0
840	25·0	+27·0
850	—	−0·2
860	16·9	+13·8
870	45·8	−43·0
880	2·9	+1·8
890	18·7	−18·5
8,10,0	2·7	+1·2
8,11,0	15·4	+17·4
8,12,0	2·5	+1·7
8,13,0	38·7	+38·8
910	2·9	+1·9
920	24·1	+24·2
930	11·6	+11·9
940	18·8	+13·6
950	17·0	+16·5
960	14·2	−16·4
970	5·4	+4·4
980	37·6	−43·0
990	2·5	−1·9
9,10,0	2·4	−1·8
9,11,0	13·1	−8·3
9,12,0	33·8	+37·8
10,0,0	5·2	−11·3
10,1,0	26·3	+27·5
10,2,0	6·2	+4·7
10,3,0	38·7	+34·4
10,4,0	3·6	−3·8
10,5,0	2·4	+2·3
10,6,0	18·5	+22·9
10,7,0	25·0	−27·7
10,8,0	14·3	−16·0
10,9,0	17·1	−16·4
10,10,0	17·0	−21·5
10,11,0	4·6	+4·6
11,1,0	9·8	−10·6
11,2,0	22·8	+25·1
11,3,0	18·2	+19·6
11,4,0	9·8	+9·3
11,5,0	17·6	+17·4
11,6,0	14·4	−14·9
020	53·0	+53·4
040	17·3	26·8
060	70·1	83·0
080	40·9	40·4
0,10,0	35·7	37·8
0,12,0	31·6	32·9
0,14,0	19·7	13·2
0,16,0	19·0	13·6
0,18,0	2·9	7·0
0,20,0	34·2	34·3
0,11,1	94·0	94·7
021	79·9	97·6
031	34·1	34·3
041	8·1	5·9
051	40·5	47·5
061	27·8	33·4
071	56·1	57·9
081	72·9	83·1
091	43·0	40·0
0,10,1	12·0	8·7
0,11,1	27·5	31·3
0,12,1	23·2	23·4
0,13,1	2·9	0·1
0,14,1	23·3	23·3
0,15,1	15·8	15·9
0,16,1	8·6	8·4
0,17,1	21·8	21·2
0,18,1	24·9	23·3
0,19,1	15·6	12·7
0,20,1	13·5	12·0
0,21,1	20·4	16·2
012	186·0	205·3
022	95·3	101·2
032	61·7	72·1
042	18·5	19·4
052	10·2	6·4
062	22·9	20·4
072	77·1	89·5
082	8·4	8·2
092	26·0	23·8
0,10,2	3·3	2·5
0,11,2	16·3	13·4
0,12,2	3·7	1·4
0,13,2	39·3	39·7
0,14,2	14·2	15·4
0,15,2	3·1	5·2
0,16,2	12·1	13·7
0,17,2	22·6	21·4
0,18,2	7·2	9·1
0,19,2	29·2	25·2
013	90·0	91·7
023	61·1	64·3
033	25·8	26·1
043	23·9	34·2
053	48·4	45·1
063	12·1	8·6
073	37·8	41·1
083	52·0	47·9
093	15·5	18·0
0,10,3	2·8	2·9
0,11,3	18·3	16·8
0,12,3	23·3	24·6
0,13,3	4·0	6·4
0,14,3	12·9	12·6
0,15,3	5·6	4·4
0,16,3	3·9	5·1
0,17,3	11·3	12·9
0,18,3	31·4	26·6
0,19,3	9·4	5·9
0,20,3	4·5	3·6
014	9·1	2·1
024	49·2	46·8
034	29·5	27·4
044	62·1	65·0
054	15·0	18·2
064	59·0	59·2
074	6·1	9·6
084	16·3	19·1
094	5·4	2·6
0,10,4	38·9	35·1
0,11,4	3·1	0·8
0,12,4	16·1	14·7
0,13,4	13·8	14·3
0,14,4	25·2	24·9
0,15,4	2·9	0·8
0,16,4	24·1	27·7
015	13·2	11·4
025	51·2	47·6
035	21·7	15·3
045	18·9	17·8
055	15·5	18·7
065	3·0	2·0
075	17·9	13·8
085	20·9	23·6
095	42·8	38·4
0,10,5	4·0	1·7
0,11,5	21·3	23·4

Table 1 (*cont.*)

hkl	F_o	F_c
0,12,5	5·5	4·3
0,13,5	7·5	7·9
0,14,5	5·0	4·0
0,15,5	24·3	23·7
0,16,5	4·0	1·2
0,17,5	26·6	18·5
016	43·1	44·9
026	4·0	0·5
036	24·1	25·1
046	23·9	24·4
056	3·1	0·2
066	3·1	8·6
076	28·9	31·4
086	4·0	9·2
096	17·8	16·0
0,10,6	3·8	4·8
0,11,6	14·5	13·1
0,12,6	9·5	10·8
0,13,6	21·2	23·8
0,14,6	8·4	8·9
017	8·6	10·3
027	11·2	13·1
037	6·8	6·3
047	3·8	9·3
057	5·3	5·5
067	2·8	5·7
077	2·7	2·8
087	18·5	27·4
097	9·0	12·5
0,10,7	4·2	5·3
0,11,7	5·4	6·0
0,12,7	15·5	21·6
002	105·6	114·1
004	86·9	97·3
006	13·9	5·4

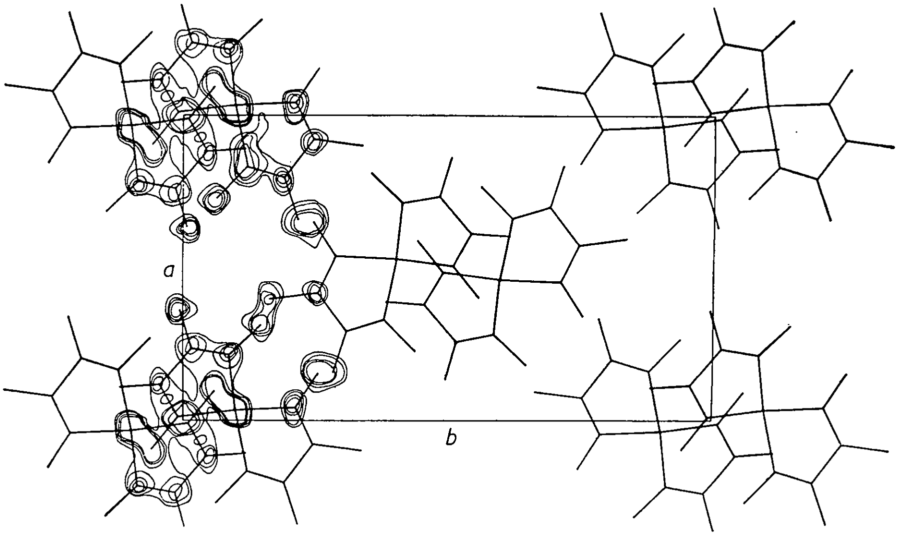


Fig. 1. Arrangement of the molecules projected on (001). Contours from electron-density projection are also shown (3, 5, 7, 9 e.Å^{-2}).

in the other direction with a photometer fitted with a potentiometric recorder.

Experimental intensities were corrected by means of the usual Lorentz and polarization factors, while correction coefficients for absorption were rapidly determined by a method elaborated by some of us (E. Frasson and S. Bezzi, to be published). The *hk*0 intensities were found to be free from secondary extinction errors, while for the 0*kl* intensity data, secondary extinction coefficients have been calculated using the method proposed by Housty & Clastre (1957) on the basis of the slope of the graph:

$$F_o/F_c = \exp(\varphi I_c)\ .$$

F_c have been calculated using the atomic scattering factors given by Berghuis *et al.* (1955). Table 1 gives the Fourier coefficients F_o and F_c for the *hk*0 and 0*kl* reflections.

Refinement of the (001) projection

The plane of the molecule is approximately parallel to (001). In spite of this, the exact location of the maxima in the electron-density projections is very uncertain, since practically every maximum contains the contribution of a nearby atom (see Fig. 1). To overcome this difficulty, a number of Fourier difference maps were calculated and for each one the contribution of any atom which disturbed the location of a nearby atom was subtracted. The Fourier differences successively calculated were as follows:

$$F_o-F_{\mathrm{Cu}}$$
$$F_o-F_{\mathrm{O}_2}$$
$$F_o-F_{\mathrm{Cu}}-F_{\mathrm{N}_3}$$
$$F_o-F_{\mathrm{Cu}}-F_{\mathrm{C}_4}$$
$$F_o-F_{\mathrm{Cu}}-F_{\mathrm{O}_1}$$
$$F_o-F_{\mathrm{Cu}}-F_{\mathrm{C}_8}$$
$$F_o-F_{\mathrm{Cu}}-F_{\mathrm{O}_3}$$
$$F_o-F_{\mathrm{Cu}}-F_{\mathrm{C}_6}$$

From the first two we determined the position of the Cu atom. The subtraction of the contribution of the Cu atom was aimed at eliminating one of the major causes of diffraction ripples. This subtraction did not increase the lack of precision in the Fourier coefficients since the Cu coordinates were assumed to be very close to the final value. For each pair of overlapping atoms the subtraction of the heavier atom was first carried out, for which the calculated contribution to the structure factor could be considered closer to the real contribution. This procedure was repeated three times and led to a reliability index $R = 0{\cdot}16$. Then two Fourier differences F_o-F_c were calculated; these suggested some displacements which led to a reduction of R to 0·12. A third Fourier difference F_o-F_c contained maxima which were interpreted as hydrogen atoms belonging to methyl groups. No indication was found for the hydrogen of the two hydrogen bonds.

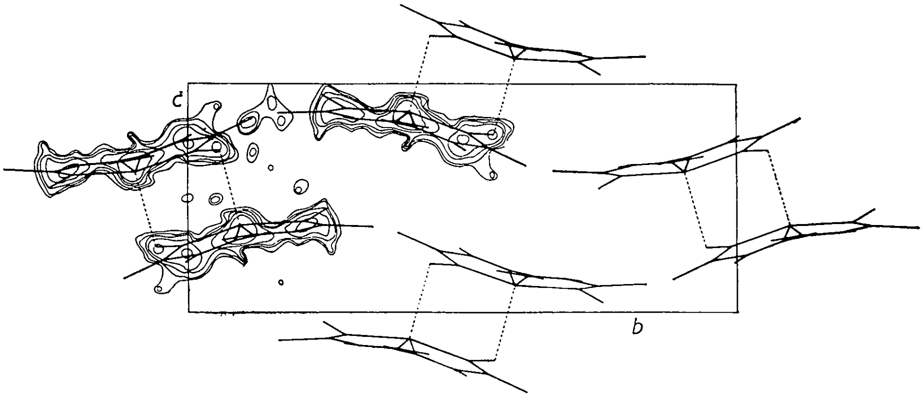


Fig. 2. Arrangement of the molecules projected on (100). Contours from electron-density projection are also shown (5, 6, 7, 10, 16 e.Å^{-2}).

Introduction of hydrogen atoms led to a lowering of R to a final value of 0·10.

On the basis of atomic coordinates for this projection it has been possible to deduce the non co-planarity of the two organic rings bonded to copper, thus enabling us to make a model of the molecule on the basis of the approximate angle between the two rings.

Refinement of the (100) projection

In the (100) electron-density projection, the molecule of Cu–dimethylglyoxime appears in profile (see Fig. 2) and therefore there is no possibility at all of locating the maxima.

Table 2. *Atomic coordinates for copper–dimethylglyoxime*

	x/a	y/b	z/c
Cu	0·034	0·097	0·382
C_1	0·231	0·018	0·248
C_2	0·636	0·006	0·783
C_3	0·897	0·040	0·772
C_4	0·893	0·118	0·856
N_1	0·216	0·086	0·312
N_2	0·989	0·011	0·711
O_1	0·314	0·146	0·345
O_2	0·095	0·059	0·711
H_1	0·927	0·159	0·806
H_2	0·868	0·157	0·955
H_3	0·837	0·127	0·906
H_4	0·625	0·034	0·787
H_5	0·597	0·014	0·761
H_6	0·399	0·012	0·707
C_5	0·797	0·191	0·352
C_6	0·658	0·217	0·365
C_7	0·923	0·246	0·386
C_8	0·401	0·163	0·876
N_3	0·835	0·121	0·339
N_4	0·042	0·212	0·400
O_3	0·655	0·246	0·912
O_4	0·728	0·061	0·316
H_7	0·667	0·250	0·318
H_8	0·635	0·233	0·422
H_9	0·625	0·185	0·422
H_{10}	0·465	0·139	0·955
H_{11}	0·403	0·133	0·904
H_{12}	0·365	0·137	0·806

From the y atomic coordinates and from approximate values of the z coordinates derived from a model of the molecule, values for F_c were obtained which gave $R = 0{\cdot}25$. The satisfactory initial value of R and the lack of information from the electron-density map, induced us to proceed to the refinement by means of several Fourier $F_o - F_c$ syntheses. Such a procedure made the calculation of twelve syntheses necessary. The improvement of R obtained by each Fourier synthesis was always very slight. After carrying out these procedures and introducing the contribution of hydrogen atoms located on the twelfth Fourier $F_o - F_c$ and aided by the molecular model, R was brought to a final value of 0·12.

Table 2 lists the final coordinates of the atoms of Cu–dimethylglyoxime.

Estimation of accuracy

In both projections, calculation of standard errors by Cruickshank's method (1949) has been rendered impossible by the overlapping of the maxima which are present in this structure. Therefore, in order to have an indication of the accuracy of the proposed coordinates, we have used the method elaborated by Luzzati (1952). The mean error for $hk0$ reflections is 0·025 Å, while for $(0kl)$ reflections, the mean error is 0·035 Å.

Description of the structure

Bond lengths and angles are given in Table 3.

In order to evaluate the lack of co-planarity of the two organic rings of the molecule, the mean planes of the two radicals were calculated. The angle between these mean planes is 21° 44′. Within experimental error each dimethylglyoxime radical is planar. The deviation of the atoms from the mean plane is ±0·03 Å, which is of the same order as the mean error.

The molecule is shown in Fig. 3. Bond lengths and angles are also given. The dotted lines indicate the organic radical which forms an angle of 21° 44′ with the plane of the paper.

Table 3. *Bond lengths and angles in copper–dimethylglyoxime*

	Cu–N	N–O	N=C	C–C	C–CH_3
Radical I	1·96 Å	1·34 Å	1·27 Å	1·53 Å	1·44 Å
	1·93	1·33	1·22		1·45
Radical II	1·91	1·39	1·25	1·50	1·46
	1·95	1·32	1·27		1·52

Hydrogen bonds O_1–O_3 = 2·53 Å
O_2–O_4 = 2·70
Mean error = 0·04 Å

Radical I		Radical II	
N_1–Cu–N_2	81° 0′	N_4–Cu–N_3	79° 30′
Cu–N_1–O_1	121° 30′	Cu–N_4–O_3	125° 0′
Cu–N_1–C_1	113° 0′	Cu–N_4–C_7	115° 30′
O_1–N_1–C_1	125° 30′	O_3–N_4–C_7	119° 30′
N_1–C_1–C_3	115° 20′	N_4–C_7–C_5	114° 30′
N_1–C_1–C_2	123° 30′	N_4–C_7–C_8	124° 30′
C_2–C_1–C_3	121° 10′	C_5–C_7–C_8	121° 0′
C_1–C_3–N_2	111° 0′	C_7–C_5–N_3	110° 30′
C_1–C_3–C_4	124° 30′	C_7–C_5–C_6	122° 30′
C_4–C_3–N_2	124° 30′	C_6–C_5–N_3	127° 0′
C_3–N_2–Cu	118° 0′	C_5–N_3–O_4	117° 30′
C_3–N_2–O_2	115° 30′	C_5–N_3–Cu	120° 30′
Cu–N_2–O_2	126° 30′	Cu–N_3–O_4	122° 0′

Mean error ±70′

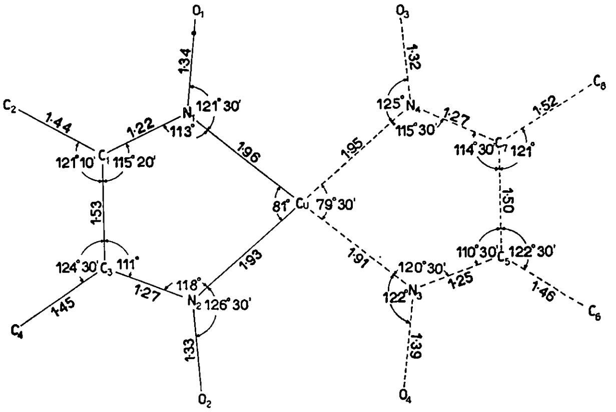


Fig. 3. Bond lengths and angles in copper–dimethylglyoxime. The organic radical that forms an angle of 21° 44′ with the plane of the paper is dotted.

Discussion of the structure

Orgel & Dunitz (1957) have pointed out that three types of environment are encountered for cupric compounds: (1) octahedral distorted, with four short bonds and two long ones, (2) square coplanar, (3) tetrahedral.

In this structure the Cu^{++} gives rise to the formation of an unusual type of molecular structure. The Cu atom is surrounded by four N atoms at a mean distance of 1·94 Å. The Cu is displaced from the plane of the four N atoms in the direction of an oxygen O_2 in a nearby molecule. There is therefore a fifth coordinating Cu–O_2 bond of length 2·43 Å lying on the extension of the axis of the pyramid formed by the Cu and the four N atoms. Fig. 4 represents the dimer formed between a pair of overlapping molecules with two Cu–O bonds. On the prolongation of the O–Cu bond a methyl group of another molecule is found 3·76 Å beyond the copper.

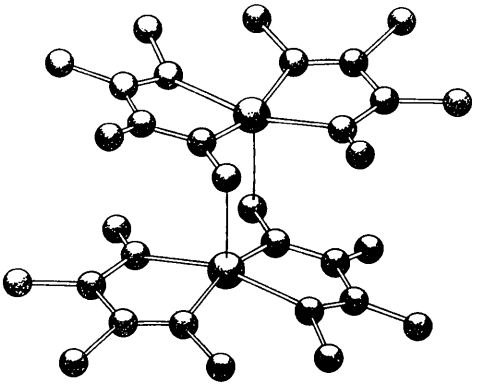


Fig. 4. A perspective view of a couple of copper–dimethylglyoxime molecules.

The Cu has therefore an electronic structure $d^9s^np^{3-n}d^2 (0 \leq n \leq 1)$. The formation of Me–Me chains similar to those in Ni–dimethylglyoxime, is extremely improbable for Cu^{++} since this would lead to a structure which is less stable energetically, due to the promotion of an electron to a 4*d* orbital.

Hydrogen bonds in Cu- and Ni–dimethylglyoxime should be of equal lengths, as the lengthening due to the bigger atomic radius of copper should compensate the shortening due to the distortion of the molecule. In fact, the O_1–O_3 bond of 2·53 Å is a little longer than that of the hydrogen bond in the Ni–dimethylglyoxime of 2·44 Å. The O_2–O_4 bond on the contrary is very much weaker and its lengthening to 2·70 Å is attributable to the Cu–O_2 coordinating bond.

We are working on other metal complexes of dimethylglyoxime and on the methyl–ethyl–glyoximes of nickel and copper.

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