1123. *The Colour, Isomerism, and Structure of Some Copper Co-ordination Compounds. Part V.*[1] *The Crystal Structure of* NN'-*Ethylenebis(acetylacetoneiminato)copper*(II).

By D. Hall, A. D. Rae, and T. N. Waters.

A two-dimensional *X*-ray analysis of *NN'*-ethylenebis(acetylacetoneiminato)copper(II) has shown the copper to be quadricovalent, as predicted from the colour of the compound. Pairs of centrically related molecules appear to be bound together by polarisation-type bonds.

Crystal-structure determinations of the green complexes of copper with *NN'*-disalicylidenepropane-1,2-diamine and *NN'*-disalicylidene-ethylenediamine have shown the metal atom to be quinqueco-ordinate.[1] These observations, together with spectral evidence, prompted the suggestion that a green colour in complexes of this type indicated a co-ordination number greater than four. That this is not generally true has been demonstrated for bis(salicyclaldiminato) copper,[2] and it is necessary to study the spectral transitions to make an exact correlation between colour properties and structure. Nevertheless, the " colour rule " often applies, for reasons which are qualitatively obvious from spectra,[3,4] and it still seems reasonable to assume that where " colour isomerism " occurs extra co-ordination is shown by the green isomer. The purple complex, *NN'*-ethylenebis(acetylacetoneiminate)copper(II), and its green hydrate present such a situation. Their crystal structures have therefore been determined as a further test of this assumption and to provide evidence towards an eventual quantitative explanation of the colour effects. This paper describes the structure of the anhydrous form.

Experimental

The compound was prepared as previously described,[5] and crystallised from hot light petroleum (b. p. 40—60°) as violet plates, tabular on (100) with (011) well developed. The crystal data were: $C_{12}H_{18}O_2N_2Cu$, $M = 285{\cdot}5$, monoclinic, $a = 11{\cdot}02 \pm 0{\cdot}04$, $b = 8{\cdot}97 \pm 0{\cdot}03$, $c = 13{\cdot}10 \pm 0{\cdot}04$ Å, $\beta = 94{\cdot}0°$, $U = 1290{\cdot}8$ Å^3. $D_m = 1{\cdot}46$ g. cm.$^{-3}$ by flotation, $Z = 4$, $D_c = 1{\cdot}47$ g. cm.$^{-3}$, $F(000) = 596$. Space group $P2_1/c(C_{2h}^5$, no. 14). Cu-K_α radiation, single-crystal Weissenberg photographs. Intensity data were collected for the *hk*0, *h*0*l*, and 0*kl* zones by the multiple-film method. Relative intensities were estimated by visual comparison against a standard scale. Small crystals were used, and no absorption correction was made.

The copper–copper vectors were easily recognisable on the Patterson projection $P(u,w)$, and the copper–light atom vectors were resolved by application of the minimum function.[6] The resulting map was interpreted with the help of a model of the expected molecule and the atomic positions were refined by successive Fourier and difference Fourier syntheses. Analysis of the data, as described by Pinnock, Taylor, and Lipson,[7] showed the intensities to be suffering from extinction, and the eleven largest were corrected accordingly. An overall isotropic temperature factor for the light atoms and a separate isotropic temperature factor for the copper atom were determined by least-squares methods. The final reliability factor was 0·108 for 186 observed reflections, and the final electron density map is shown in Fig. 1.

Analysis of the [100] projection was attempted by the same procedure, but no recognisable picture was obtained from the minimum function or from a Fourier synthesis based on the heavy atom. It was seen that although the 022 amplitude was the largest in this zone it received only a very small contribution from the copper atom. On its inclusion in the Fourier synthesis with negative sign (arbitrarily chosen) the electron density map could be interpreted as a heavily

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[1] Parts III and IV, *J.*, 1960, 2639, 2644.
[2] Stewart and Lingafelter, *Acta Cryst.*, 1959, **12**, 842.
[3] Part I, *J.*, 1959, 1200.
[4] Piper and Belford, *Mol. Phys.*, 1962, **5**, 169.
[5] McCarthy, Hovey, Ueno, and Martell, *J. Amer. Chem. Soc.*, 1955, **77**, 5820.
[6] Buerger, *Acta Cryst.*, 1951, **4**, 531.
[7] Pinnock, Taylor, and Lipson, *Acta Cryst.*, 1956, **9**, 175.

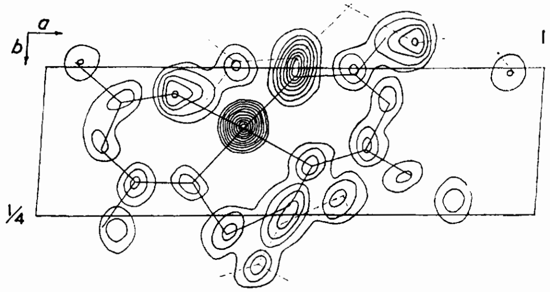

FIG. 1. Electron density projected along the [b] axis. The lowest contour is at 4 eÅ^{-2}; contour interval 4 eÅ^{-2} on the copper atom; and 2 eÅ^{-2} elsewhere.

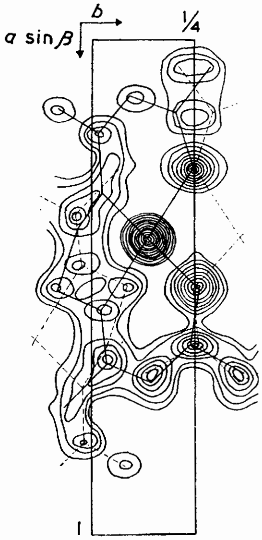

FIG. 2. Electron density projected along the [c] axis. Contours as in Fig. 1.

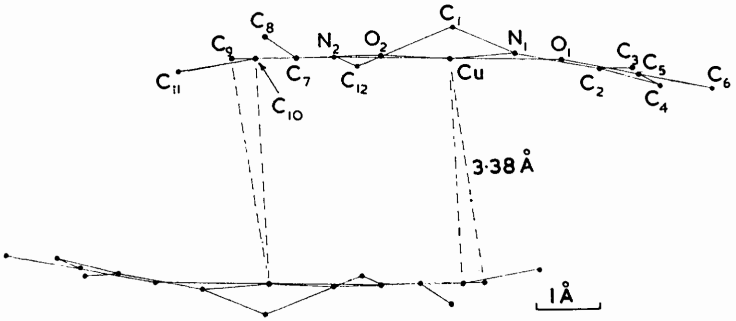

FIG. 3. The two molecules centrically related through (½,0,0) projected parallel to the mean plane through Cu, N(2), C(10), C(9), C(7), O(2).

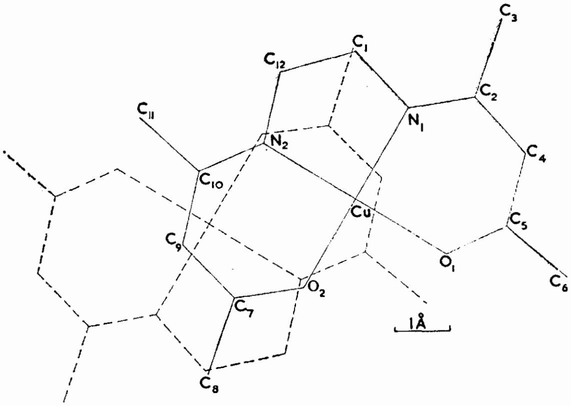

FIG. 4. The two molecules centrically related through (½,0,0) projected normal to the mean plane through Cu, N(2), C(10), C(9), C(7), O(2).

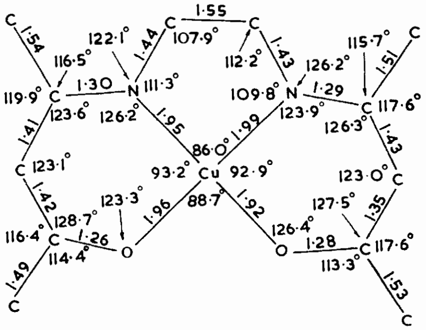

FIG. 5. Bond lengths (A) and bond angles.

overlapped projection of the molecule. It was not feasible to refine this, but the approximate y co-ordinates thus obtained were used, together with the x co-ordinates from the [010] projection, to provide an initial model for the [001] projection. This was also overlapped to some extent but could be refined by means of difference syntheses. With 3 of 135 observed reflections corrected for extinction, the final reliability factor was 0·124. The electron-density map is shown in Fig. 2. A problem in interpretation was posed by atoms O(1), O(2), and C(7) which lay very close to the apparent mirror plane at $y = \frac{1}{4}$, and the choice between (x,y) and $(x,\frac{1}{2} - y)$ was made on bond-length considerations.

TABLE 1.

Atom	x/a	y/b	z/c
Cu	0·4040	0·1376	0·1007
N(1)	0·0393	0·0270	0·1954
N(2)	0·5463	0·0233	0·1604
O(1)	0·2615	0·2465	0·0415
O(2)	0·5024	0·2530	0·0148
C(1)	0·3858	−0·0395	0·2760
C(2)	0·1912	0·0191	0·1929
C(3)	0·1375	−0·0840	0·2726
C(4)	0·1128	0·0970	0·1217
C(5)	0·1539	0·2099	0·0563
C(6)	0·0590	0·2910	−0·0083
C(7)	0·6166	0·2369	0·0055
C(8)	0·6727	0·3650	−0·0527
C(9)	0·6937	0·1421	0·0578
C(10)	0·6552	0·0400	0·1332
C(11)	0·7476	−0·0705	0·1780
C(12)	0·5070	−0·0845	0·2313

TABLE 2.

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

(Planes corrected for secondary extinction are marked with an asterisk.)

Plane	F_o	F_c
	$h0l$ zone	
002	42·9 *	+55·6
4	3·8	−0·4
6	23·0	−20·0
8	12·2	+14·3
10	31·0	+34·8
12	<6·4	+1·0
14	11·4	−12·7
16	<3·6	−3·1
100	‡	−176·6
2	83·3 *	−91·1
4	32·2	−28·3
6	21·6	+22·4
8	11·8	+2·0
10	26·1	−24·9
12	29·7	−32·0
14	12·4	+16·1
16	10·7	+14·6
$\bar{2}$	48·3 *	+50·4
$\bar{4}$	90·1 *	+92·8
$\bar{6}$	24·6	+28·7
$\bar{8}$	43·3	−41·7
$\bar{10}$	33·3	−29·6
$\bar{12}$	11·5	+12·1
$\bar{14}$	<5·8	+3·9
$\bar{16}$	4·9	+5·9
200	5·6	+2·5
2	49·8 *	+48·3
4	46·6	+41·6
6	30·1	−25·8
8	<5·6	+1·2
10	13·9	+19·4
12	39·4	+44·4
14	<5·8	+13·0
16	11·5	−14·2
$\bar{2}$	21·1	−16·9
$\bar{4}$	40·2	−48·9
$\bar{6}$	21·4	+16·2
$\bar{8}$	89·1 *	+102·8
$\bar{10}$	25·3	+24·0
$\bar{12}$	13·3	−11·4
$\bar{14}$	12·7	−11·9
$\bar{16}$	<4·1	+0·2
300	18·1	+11·0
2	27·6	−31·6
4	75·9 *	−76·4
6	49·8	+52·8
8	42·5	+40·8
10	19·2	+16·2
12	29·0	−28·4
14	<5·6	−4·1
16	6·9	+8·6
$\bar{2}$	101·1 *	+103·0
$\bar{4}$	21·4	+23·4
$\bar{6}$	76·5 *	−81·6
$\bar{8}$	48·1	−57·1
$\bar{10}$	<6·2	−2·8
$\bar{12}$	19·4	+21·4
$\bar{14}$	<5·8	+2·3
$\bar{16}$	5·5	−8·1
400	58·7 *	−57·7
2	38·8	+37·3
4	106·3 *	+100·0
6	27·7	+25·2
8	53·0	−48·6
10	24·7	−24·6
12	15·2	+15·9
14	<5·2	+5·1
$\bar{2}$	37·6	−45·8
$\bar{4}$	19·0	+13·5
$\bar{6}$	75·7 *	+85·2
$\bar{8}$	5·5	+2·9
$\bar{10}$	25·5	−26·3
$\bar{12}$	16·1	−15·7
$\bar{14}$	<5·6	+0·6
$\bar{16}$	6·7	+5·8
500	16·0	+16·1
2	16·9	+10·4
4	70·3	−68·5
6	31·8	−29·5
8	23·8	+23·7
10	19·9	+19·4
12	6·6	+11·0
14	10·7	−12·0
$\bar{2}$	11·5	−8·8
$\bar{4}$	42·8	−41·6
$\bar{6}$	37·5	−46·4
$\bar{8}$	6·1	−0·5
$\bar{10}$	43·6	+53·7
$\bar{12}$	11·0	+8·7
$\bar{14}$	10·0	−9·6
$\bar{16}$	6·5	−10·2
600	24·8	−25·2
2	38·6	−37·9
4	42·2	+41·4
6	42·1	+32·2
8	<6·3	+1·2
10	14·5	−16·6
12	11·7	−12·0
14	6·8	+6·7
$\bar{2}$	6·0	+2·9
$\bar{4}$	46·8	+52·9
$\bar{6}$	13·8	+9·4
$\bar{8}$	25·7	−28·8
$\bar{10}$	32·3	−37·6
$\bar{12}$	<6·2	−3·6
$\bar{14}$	17·5	+22·0
700	19·7	+17·7
2	48·2	+42·6
4	12·7	+10·3
6	59·1	−58·6
8	25·6	−25·0
10	7·5	+8·4
12	9·2	+8·4
14	<4·2	−0·3
$\bar{2}$	49·8	−46·3
$\bar{4}$	69·7	−70·9
$\bar{6}$	13·7	+11·3
$\bar{8}$	<6·4	+2·7
$\bar{10}$	<6·6	−5·5
$\bar{12}$	10·8	−14·4
$\bar{14}$	13·4	−16·1
800	25·4	+18·1
2	45·0	−41·3
4	14·6	−12·5
6	17·7	+14·3
8	29·9	+30·1
10	<5·8	+2·6
12	9·7	−10·6
$\bar{2}$	55·3	+49·8
$\bar{4}$	35·6	+33·6
$\bar{6}$	25·0	−28·3
$\bar{8}$	6·6	+0·6
$\bar{10}$	<6·3	+0·9
$\bar{12}$	16·1	+15·3
$\bar{14}$	3·9	+3·4
900	37·0	−36·2
2	15·0	+15·7
4	23·4	−20·4
6	<6·6	+0·9
8	26·5	−26·8
10	15·3	−14·1
12	7·2	+5·1
$\bar{2}$	51·9	−50·7
$\bar{4}$	<6·6	+0·1
$\bar{6}$	18·7	+22·7
$\bar{8}$	11·7	+11·5
$\bar{10}$	17·4	−18·9
$\bar{12}$	17·7	−19·3
10,0,0	29·4	+27·2
2	7·5	−3·8
4	9·7	−13·2
6	16·9	−14·9
8	14·8	+11·7
10	15·6	+16·3
$\bar{2}$	17·7	+14·4
$\bar{4}$	15·8	−11·9
$\bar{6}$	23·4	−24·2
$\bar{8}$	<6·0	+3·1
$\bar{10}$	23·5	+24·9
$\bar{12}$	4·8	+5·0
11,0,0	28·6	−28·9
2	20·5	−18·7
4	12·5	+12·0
6	30·3	+27·5
8	<4·5	−1·4
$\bar{2}$	<6·2	+1·7
$\bar{4}$	<6·2	−1·7
$\bar{6}$	5·4	+5·1
$\bar{8}$	11·7	−12·3
$\bar{10}$	12·5	−13·5
12,0,0	15·6	+13·1
2	20·4	+19·2
4	<5·0	+0·8
6	20·1	−16·7
$\bar{2}$	5·8	−4·8
$\bar{4}$	14·7	−12·9
$\bar{6}$	<5·3	+4·5
$\bar{8}$	8·9	+8·1
13,0,0	<4·7	+0·2
2	15·3	−15·0
4	7·9	−7·0
$\bar{2}$	14·9	+14·8
$\bar{4}$	12·5	+13·0
$\bar{6}$	6·4	−5·8
14,0,0	9·0	−8·9
$\bar{2}$	9·1	−11·1
$\bar{4}$	<2·3	+1·0
	$0kl$ zone	
002	43·8 *	+55·9
4	4·7	−1·7
6	26·3	−21·2
8	14·0	+14·4
10	38·8	+37·8
12	+5·9	+0·8
14	11·3	−15·0
16	4·1	−4·6
011	127·7 *	+119·9
012	115·6 *	−127·3
3	95·3 *	−107·9
4	65·9 *	−76·9
5	38·5	−37·7
6	<3·5	+4·9
7	<3·9	+0·6
8	23·9	+24·2
9	14·7	+12·0
10	18·2	+13·8
11	25·6	+25·2
12	26·1	−21·6
13	13·1	−14·6
14	9·4	−5·9
15	6·0	−6·6
16	4·0	+7·1
020	9·5	+4·4
1	46·4 *	−55·7
2	180·8 *	−174·4
3	160·1 *	−161·7
4	44·0	−48·6
5	7·7	+2·6
6	10·2	+2·4
7	37·2	+39·1
8	19·0	−15·7
9	31·5	+22·2
10	7·3	−4·2
11	20·2	−21·6
12	6·7	−5·0
13	13·2	−13·9
14	<4·5	+1·2
15	4·4	+6·9
16	<2·8	−0·1
031	36·9	−39·5
2	52·8	−50·5
3	17·8	−16·6
4	25·9	+19·6
5	70·8 *	+81·7
6	44·4	+50·3
7	26·5	+26·1
8	41·7	+45·0
9	36·5	−33·3
10	<5·2	−4·2
11	12·9	−11·7
12	7·7	−8·8
13	<4·9	+3·5
14	<4·5	−2·7
15	13·9	+16·2
16	3·0	+2·0
040	14·9	−10·1
1	27·3	+25·8
2	3·9	+0·8
3	12·6	+6·2
4	72·8 *	+74·7
5	40·6	+39·2
6	68·7 *	+79·6
7	23·2	−12·0
8	13·1	−11·1
9	<5·1	−4·6
10	20·6	−20·3
11	<5·2	−0·1
12	6·3	−2·8
13	6·2	+6·9
14	15·4	+15·8
15	<3·0	+0·6
051	17·0	−11·7
2	22·0	+22·6
3	6·3	−2·5
4	32·1	+27·8
5	28·5	+25·9
6	42·4	+44·5

TABLE 2. (*Continued.*)

Plane	F_o	F_o
7	<4·9	−5·4
8	39·7	−41·2
9	19·4	−22·3
10	10·4	−11·7
11	8·6	−8·9
12	16·9	+18·7
13	<4·2	+0·6
14	5·3	+8·1
15	5·4	+6·7
060	4·3	−5·6
1	18·9	+17·7
2	9·2	−6·7
3	37·2	+39·1
4	38·4	−37·5
5	14·5	+10·5
6	17·9	−16·1
7	37·1	−37·3
8	11·4	−11·1
9	15·6	−14·0
10	10·5	+10·0
11	9·6	+9·6
12	<4·2	+1·5
13	10·6	+11·9
14	3·4	−4·3
102	9·7	−8·4
3	<3·9	+3·8
4	24·4	+24·1
5	5·6	+4·9
6	11·9	−14·5
7	11·9	+8·7
8	32·5	−35·7
9	11·2	−11·1

Plane	F_o	F_c
10	25·7	−26·3
11	<4·2	−1·2
200	6·4	+3·0
1	16·8	−5·9
2	25·0	−24·9
3	33·0	+39·2
4	21·8	−18·3
5	55·2	−63·7
6	8·8	+0·7
7	17·8	−15·1
8	9·3	+7·6
9	15·8	+16·3
10	<6·0	−0·3
11	6·6	−7·1
300	18·3	+12·0
1	41·6	−44·6
2	<3·9	+3·9
3	33·8	−36·3
4	26·6	−26·2
5	83·7 *	+95·0
6	24·3	+25·2
7	15·8	+12·6
8	11·1	+7·9
9	12·3	−13·6
10	13·4	−13·5
11	<3·5	−2·3
400	52·8 *	−59·1
1	41·2	+41·5
2	22·7	−15·6
3	36·8	+34·2

Plane	F_o	F_c
4	57·5	+63·1
5	49·6	−56·2
6	31·0	−26·4
7	10·3	−7·2
8	15·1	−11·7
9	17·3	+19·3
10	9·3	+5·9
11	<2·6	−2·7
500	16·0	+16·4
1	48·8	−43·8
2	7·0	−0·7
3	8·4	−8·4
4	39·9	−41·5
5	6·6	−7·9
6	28·7	+32·5
7	11·4	+10·0
8	18·5	+17·2
9	6·3	−3·3
10	13·5	−12·1
600	29·0	−28·7
1	12·4	−15·4
2	20·3	+17·6
3	23·2	−19·2
4	41·5	+40·1
5	30·6	+33·5
6	15·9	−9·8
7	9·8	−0·7
8	14·7	−15·1
9	12·1	−9·0
10	11·2	+10·3
700	21·4	+19·8

Plane	F_o	F_c
1	48·9	+48·0
2	<6·2	+1·9
3	33·9	+31·8
4	31·3	−29·1
5	38·4	−38·6
6	13·0	+11·9
7	11·0	−14·8
8	8·4	+8·0
9	20·2	+19·6
10	3·5	−2·9
800	27·1	+20·9
1	50·8	−44·9
2	23·1	−17·6
3	19·0	−12·9
4	<7·0	+0·7
5	25·4	+26·4
6	25·7	−29·0
7	<6·6	+1·4
8	<5·6	+0·6
9	20·1	−22·4
900	42·9	−42·2
1	18·4	+15·2
2	34·4	+28·3
3	23·1	+21·2
4	<7·1	+3·8
5	14·0	−12·9
6	8·6	+4·2
7	8·9	+4·5
8	13·2	−10·6
10,0,0	34·7	+34·1
1	<7·2	+0

Plane	F_o	F_c
2	<7·2	−2·8
3	7·0	−3·2
4	27·2	−28·8
5	<6·6	+2·4
6	9·9	+10·6
7	<4·9	−0·9
8	14·3	+18·5
11,0,0	36·2	−36·7
1	<7·0	+3·2
2	10·4	+9·3
3	16·8	−17·5
4	29·6	+28·3
5	14·5	+11·6
6	6·1	−4·0
7	<3·2	−1·0
12,0,0	16·7	+17·4
1	11·4	+10·3
2	11·4	−9·3
3	11·2	+7·3
4	13·5	−11·0
5	13·3	−13·5
6	<3·5	−1·1
13,0,0	<5·2	−0·7
1	16·1	−15·9
2	<4·9	+1·3
3	14·3	−14·1
4	<3·5	+0·2
14,0,0	13·5	−13·0
1	14·0	+14·5

‡ Denotes not observable through masking by the beam stop.

TABLE 3.

Intermolecular approaches (Å) less than 3·6 Å. The indices refer to molecules as follows: $1 = x,y,z$; $2 = \bar{x},\bar{y},\bar{z}$; $3 = \bar{x},\tfrac{1}{2} + y,\tfrac{1}{2} - z$.

Cu^1–C(9)^2	3·38	C(11)^1–O(1)^2	3·28	O(2)^1–C(1)^3	3·46
Cu^1–C(10)^2	3·38	C(7)^1–C(12)^2	3·57	C(7)^1–C(1)^3	3·50
O(2)^1–N(2)^2	3·40	Cu^1–C(12)^3	3·49		

Co-ordinates for the [100] projection were taken from the other two. With 11 of 153 observed reflections corrected for extinction, the reliability factor was 0·121.

The atom co-ordinates are listed in Table 1 and the observed amplitudes and calculated structure factors in Table 2. The numbering system for the atoms, and the calculated bond lengths and angles, are shown in Figs. 3 and 5, respectively. The closer intermolecular approaches are listed in Table 3. The standard deviations in atomic co-ordinates for resolved atoms are 0·003 Å for the copper atom and 0·02 Å for the light atoms.[8] A number of the co-ordinates were, however, obtained from unresolved maxima, and the standard deviation in individual bond lengths and angles may be higher than the above would imply.

DISCUSSION

Figs. 3 and 4 show the two molecules related through the centre at ($\tfrac{1}{2}$,0,0), projected normal and parallel, respectively, to a plane through the ring Cu, N(2), C(10), C(9), C(7), O(2). Mean planes through various groups of atoms were calculated by the least-squares procedure of Schomaker *et al.*,[9] and the displacements of various atoms from these planes are displayed in Table 4. It may be seen that the copper atom is essentially coplanar with the four atoms co-ordinated to it, that each of the co-ordinated rings is planar, but that the molecule as a whole is distinctly bent. The two mean planes of the conjugated rings make an angle of 15·5°, the bend in the molecule occurring mainly at atoms N(1) and O(1). The methyl groups are displaced from the planes of their attached ring, presumably owing to strain introduced at the nitrogen atom by the ethylene bridge. The bridge is in

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[8] Cruickshank, *Acta Cryst.*, 1949, **2**, 65.

[9] Schomaker, Waser, Marsh, and Bergman, *Acta Cryst.*, 1959, **12**, 600.

TABLE 4.

Atoms defining plane	Max. displacement (Å) from mean plane	Displacement (Å) of other atoms from plane
N(1), O(1), N(2), O(2)	0·036	Cu = −0·022, C(1) = +0·437, C(12) = −0·115
N(1), C(2), C(4), C(5), O(1) ...	0·040	Cu = −0·300, C(3) = +0·184, C(6) = +0·194
N(2), C(10), C(9), C(7), O(2)...	0·009	Cu = −0·064, C(8) = +0·333, C(11) = −0·222

Displacement away from the centre at ($\frac{1}{2}$,0,0) is taken as positive.

the *gauche* conformation, and is unsymmetrical in that C(1) is displaced considerably further from the plane of the co-ordinated atoms than is C(12). This asymmetry appears related to the bent shape of the molecule, but it is not obvious which is cause and which effect. A similarly asymmetric bridge has been reported for an unsubstituted copper–ethylenediamine complex.[10]

The closest approaches to the copper atom, normal to the co-ordination square, are atoms C(9) in the centrically related molecule at 3·38 Å, and at 3·49 Å in the other octahedral location, C(12) in the molecule with the equivalent position $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$. The absence of any close approach is in accord with the prediction made above.

Figs. 3 and 4 show that the molecules are stacked in pairs such that two rings Cu, N(2), C(10), C(9), C(7), O(2) overlay one another with a normal separation of 3·36 Å. This is comparable with that observed in aromatic compounds in which polarisation bonding is thought to occur,[11] and with the conjugated bond system and the copper atom available as donor and acceptor, respectively, it is likely that such bonding stabilises the crystal structure, and possible that it may be the cause of the concave bending of the molecule.

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CHEMISTRY DEPARTMENT,
UNIVERSITY OF AUCKLAND, NEW ZEALAND.

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[10] Komiyama, Stewart, and Lingafelter, Paper G.3; Ann. Meeting, Amer. Cryst. Assoc., August 1961.

[11] Wallwork, *J.*, 1961, 494.