900. *Molecular Complexes. Part IV.* Observations on the Structure of the* 1 : 1 *Molecular Compound of Bis*-8-*hydroxyquinolinatocopper*(II) *and Benzotrifuroxan*

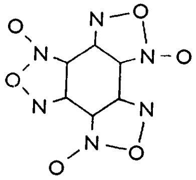
By C. K. Prout and H. M. Powell

Copper bis-8-hydroxyquinolinate and benzotrifuroxan form a 1 : 1 crystalline complex. A three-dimensional *X*-ray analysis has been attempted. The general form of this complex and the detail of the copper complex have been determined. The benzotrifuroxan molecules are disordered.

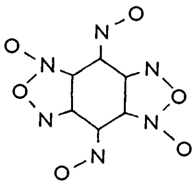
If hot solutions of copper bis-8-hydroxyquinolinate and benzotrifuroxan, $C_6N_6O_6$ (previously known as hexanitrosobenzene) are mixed, dark brown crystals of a 1 : 1 complex separate out.[1] It was prepared as a heavy-atom derivative of benzotrifuroxan, the structure of which was at that time unknown. The reflection spectrum of this complex has an intense band at 21,500 cm.$^{-1}$ given by neither constituent. This band has been assigned to charge transfer between the 8-hydroxyquinolinatocopper(II) and the benzotrifuroxan and it is suggested that the compound is of the π-complex type.

Crystal Data.—$C_{24}H_{12}CuN_8O_8$, $M = 604{\cdot}17$. Monoclinic prismatic, $a = 9{\cdot}28 \pm 0{\cdot}02$, $b = 9{\cdot}11 \pm 0{\cdot}02$, $c = 14{\cdot}17 \pm 0{\cdot}03$ Å, $\gamma = 104{\cdot}33 \pm 0{\cdot}2$; $U = 1160{\cdot}6$ Å^3, $D_m = 1{\cdot}719 \pm 0{\cdot}003$ (by flotation); $Z = 2$; $D_c = 1{\cdot}725$, $F(000) = 610$; space group $P2_1/b$ (C_{2h}^5, No. 14); Cu-K_α radiation, $\mu = 30{\cdot}8$ cm.$^{-1}$, single-crystal oscillation and Weissenberg photographs. Optically biaxial.

If the space group is $P2_1/b$ as suggested by the systematic absences then the bis-8-hydroxyquinolinatocopper(II) molecules and the other component must occupy centres of symmetry. The copper complex presents no difficulties in this respect since a planar centrosymmetric form of this molecule has been reported by Kanamaru *et al.*[2] in one form of bis-8-hydroxyquinolatocopper(II) crystals. However, the accepted[3] benzotrifuroxan structure (I) does not possess a centre of symmetry. Three possibilities must be considered,



(I)



(II)

(i) some centrosymmetric alternative to the benzotrifuroxan form, (ii) that the non-centrosymmetric benzotrifuroxan form is randomly distributed over the centric sites, (iii) that the space group is not that suggested by the systematic absences but is one of the two related non-centrosymmetric groups $P2_1$ and Pb.

A three-dimensional Patterson function "sharpened to point atoms at rest" was computed from 842 independent reflections. Eleven prominent, well-resolved, independent maxima were consistent with the presence of two planar centro-symmetric bis-8-hydroxyquinolinatocopper(II) molecules centred at 0,0,0, and $0,\frac{1}{2},\frac{1}{2}$, and related to one another as required by the space group $P2_1/b$. From two intersecting planes of diffuse vector density corresponding to the copper complex, suggestions of carbon and nitrogen atom sites could be made for the benzotrifuroxan molecule. There was nothing that suggested definite oxygen positions.

In the absence of more certain information a three-dimensional electron-density distribution was computed with phases based on contributions of the atoms of the copper

* Part III, A. S. Bailey and C. K. Prout, preceding Paper.

[1] A. S. Bailey, R. J. P. Williams, and J. D. Wright, *J.*, 1965, 2579.

[2] F. Kanamaru, K. Ogawa, and I. Nitta, *Bull. Chem. Soc. Japan*, 1963, **36**, 422.

[3] B. Kamenar and C. K. Prout, *J.*, 1965, 4838.

complex only. The electron density in a plane approximately parallel to the plane of the metal complex is shown in Figure 1. The centre of symmetry is at $\frac{1}{2}$,0,0, and the equation to the plane is

$$0{\cdot}662x + 0{\cdot}488y + 0{\cdot}335z - 3{\cdot}07 = 0$$

The angle between this plane and the best plane of the metal complex is 10°. In Figure 1 the atoms of the benzene nucleus are clearly visible and the nitrogen less clearly so. The nitrogen atoms N(13)′ complete the copper co-ordination octahedra and are only 3·0—3·1 Å from the metal atom. It is possible to assign the electron density to the atoms of a centrosymmetric variant of hexanitrosobenzene [Figure (1a)]. The *p*-dinitrosobenzotrifuroxan model (II) has some appeal. It presents no space-group difficulties, it is no more difficult to suggest an electronic structure for it than for the benzotrifuroxan form itself, and finally the two nitrogen atoms of the isolated nitroso-group are chemically different from the other nitrogen atoms in the molecule and are those that complete the copper co-ordination octahedron. This model of the structure was refined first by difference maps, then by " isotropic " and " anisotropic " least-squares methods in the belief that this might prove to be the correct and unexpected structure. A reliability index of 0·148 resulted. However, the interatomic distances and angles (Figure 2) are not in good agreement with acceptable values. The thermal parameters of the oxygen atoms O(11), O(12), and O(13) are impossibly high for atoms oscillating about a fixed site, even allowing for a large molecular libration. This raised doubts as to whether this model was acceptable. Meanwhile the molecule was shown to have the benzotrifuroxan structure in the complex with 13,14-dithiatricyclo[8,2,1,$1^{4,7}$]tetradeca-4,6,10,12-tetraene.

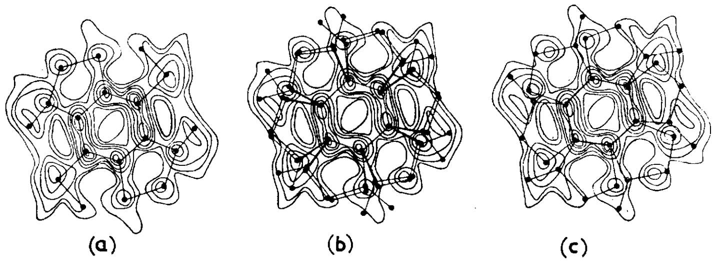


FIGURE 1. The electron density in a plane approximately parallel to the plane of the metal complex. In (a) the centrosymmetric form resulting from the attempted refinement is superimposed on the electron density. In (b) four and in (c) only two equally occupied sites are assigned to the benzotrifuroxan molecules

Non-centrosymmetric benzotrifuroxan molecules may occupy two or four sites [Figure 1 (b and c)] in a disordered array to give a structure that will satisfy the systematic absence conditions. A refinement of the space and thermal parameters of all atoms of the benzotrifuroxan has been carried out for these models [Figure 1 (b and c)] on the assumption of equal occupation numbers for all sites and exact superposition of benzene nuclei, both somewhat unlikely assumptions. Reliability indexes of about 0·195 were obtained. These are greater than the final value obtained in the attempted refinement of the ordered

The atomic co-ordinates (× 10^4) of the atoms of the bis-8-hydroxyquinolinatocopper(II) molecule and the benzene-ring carbon atoms of the benzotrifuroxan system

	x/a	y/b	z/c		x/a	y/b	z/c
Cu	0	0	0	C(6)	2978	−3680	−1153
N(1)	391	−1762	685	C(7)	2493	−2407	−1385
O(1)	1224	−520	−955	C(8)	1584	−1715	−7341
C(1)	−75	−2279	1568	C(9)	1173	2386	114
C(2)	363	−3483	1857				
C(3)	1246	−4283	1330	C(11)	4445	−219	897
C(4)	1665	−3732	461	C(12)	5320	−1150	553
C(5)	2496	−4324	−221	C(13)	5989	−892	−355

structure with centrosymmetric molecules. The difference is, however, not such as to eliminate the possibility that further refinement of the alternative structures would produce R values as good as, or better than, that of the ordered structure. Such refinements, which for completeness would require that there be no restraint on position or occupation number, are considered impracticable at the present time.

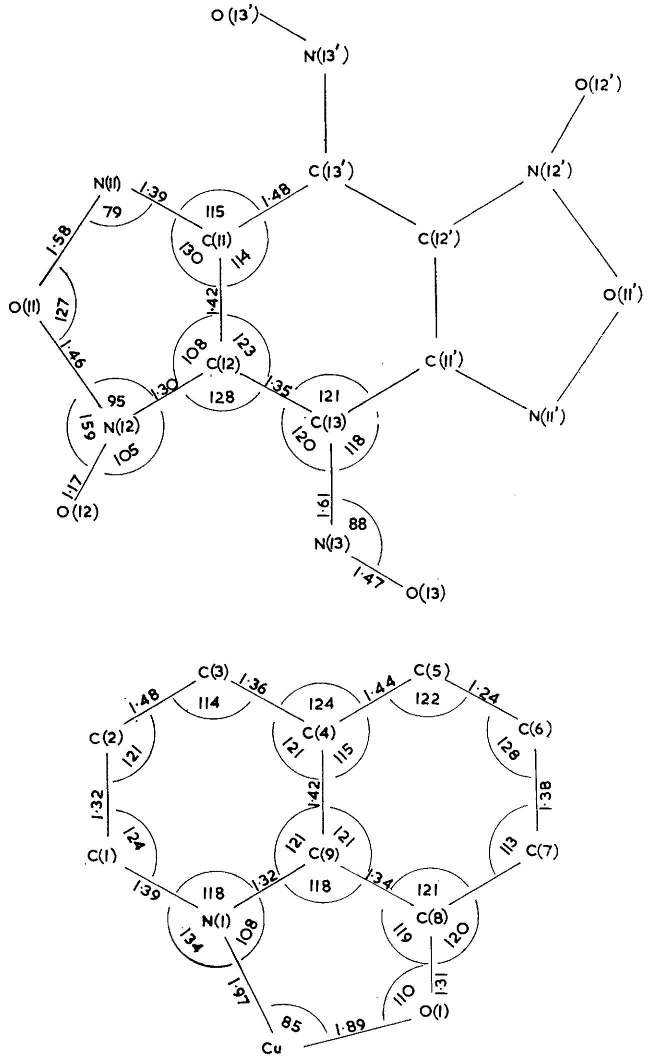


FIGURE 2. Interatomic distances (in Å) and angles resulting from the attempted refinement of the centrosymmetric model

There is some experimental evidence for the disordered structures. Different crystals from the same sample of about equal size and similar in external appearance gave Bragg scattering of greatly differing intensity. Crystals that were good " Bragg scatterers " at room temperature retained the same sharp single crystal diffraction pattern at liquid-air temperature but the intensity was greatly diminished and not restored at room temperature. Crystals of the palladium analogue which might be expected to be similar, were examined. The *X*-ray diffraction patterns of these crystals, which appeared to be of at least three distinct types, all showed characteristics associated with disordered lattices.

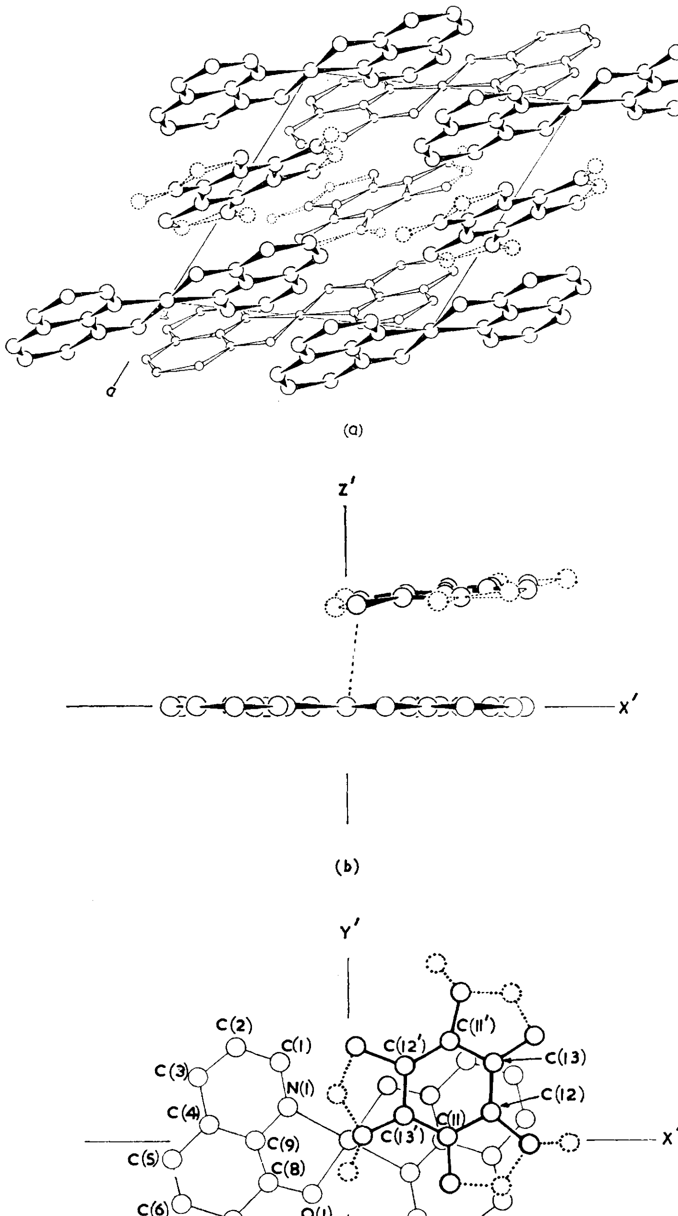


FIGURE 3. The molecular packing in the crystals. In (a) the crystal structure is projected perpendicular to the (100) planes of the crystal. In (b) and (c), respectively, the benzotrifuroxan molecule is projected on to, and perpendicular to, the plane of the bis-8-hydroxyquinolinatocopper(II) molecule. In all cases the oxygen atom sites (broken lines) must be regarded as undetermined

One of them corresponds to a unit cell closely related to that of the copper bis-8-hydroxyquinolinate compound, if account is taken only of the observed sharp diffraction spots. However, there are a number of weak diffuse reflections which are indicative of a partly disordered structure which has the *c* dimension doubled.

If the true space group was $P2_1$ or Pb an ordered structure can be formed in which there is a near centrosymmetric arrangement of oxygen atoms. The carbon and nitrogen positions would be similar to those discussed in previous models. Such an ordered model implies that each copper atom is attached to one type of furoxan nitrogen (*e.g.*, the N-oxide nitrogen atom) at one octahedral site and to the other type of nitrogen at the opposite position. This arrangement would have to be maintained systematically throughout the structure. This seems unlikely in view of the pseudo-centrosymmetric state of the copper atom. Further, the Patterson function showed no evidence for the ordered model and none of the additional reflections required by either space group could be observed even on over-exposed films.

Conclusions.—Limited but useful conclusions about the general form of the complex may be drawn. The crystals of this 1 : 1 complex contain planar bis-8-hydroxyquinolinatocopper(II) molecules and planar benzotrifuroxan molecules in what are to the first approximation plane-to-plane stacks of the π-complex type (Figure 3). The best plane of the benzotrifuroxan molecule makes an angle of about 10° to that of the metal complex. The co-ordination of the copper atom is square-planar but a distorted octahedral co-ordination sphere is completed by two nitrogen atoms of benzotrifuroxan molecules. The general relative disposition of the molecules differs greatly from that in the 1 : 2 complex of bis-8-hydoxyquinolinatocopper(II) and picryl azide,[4] but is similar to that in the 1 : 1 complex of bis-8-hydroxyquinolinatopalladium(II) and chloranil.[5] The benzotrifuroxan molecules are mostly probably disordered. However, in any postulated structure, the nitrogen and carbon atom sites will remain approximately the same and only the oxygen atom sites will differ greatly. The carbon and nitrogen atom sites are such that the electron donor and acceptor groups are far removed from the best positions derived from the " overlap and orientation principle " [6] and some of the contact distances between atoms of the donor and acceptor are slightly shorter than those normally found in π-complexes. Both these anomalies result from the copper–nitrogen interaction.

In view of the conclusions reached the intensity data are not published. They can be obtained from the authors.

EXPERIMENTAL

Preparation.—The bis-8-hydroxyquinolinatocopper(II)–benzofuroxan complex was prepared by the method of Bailey, Williams, and Wright.[1]

X-*Ray Photography.*—The unit-cell dimensions were obtained from zero-layer Weissenberg films about the *b*- and *c*-axes calibrated with the powder diffraction pattern of copper wire. The *X*-ray intensities were estimated visually from sets of multiple film equi-inclination Weissenberg photographs taken about the *c*-axis and the similar zero- and first-layer films about the *b*-axis. These were placed on a common scale after the application of Lorentz and polarisation corrections by the method of Rollett and Sparks.[7] No absorption or extinction corrections were applied.

Calculations.—Calculations were carried out on a Ferranti Mercury computer. Structure factors and cycles of least-squares refinement were calculated using the SFLS programme of Rollett.[8] The atomic scattering factors used were those of Berghuis *et al.*[9] (for carbon,

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[4] A. S. Bailey and C. K. Prout, *J.*, 1965, 4867.

[5] B. Kamenar, C. K. Prout, and J. D. Wright, *J.*, 1965, 4851.

[6] A. S. Mulliken, *Rec. Trav. chim.*, 1956, **75**, 845.

[7] J. S. Rollett and R. Sparks, *Acta Cryst.*, 1960, **13**, 273.

[8] O. S. Mills and J. S. Rollett in " Computing Methods and the Phase Problem in X-ray Crystal Analysis," Pergamon, London, 1961, p. 107.

[9] J. Berghuis, I. M. Hannapel, M. Potters, B. O. Loopstra, C. H. MacGillarry, and A. L. Veenendal, *Acta Cryst.*, 1955, **8**, 478.

nitrogen, and oxygen), Thomas and Umeda [10] (for copper), and McWeeny [11] (for hydrogen). The general Fourier programme of Mills [8] was used and the interatomic-distances programme of Sparks.[8]

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CHEMICAL CRYSTALLOGRAPHY LABORATORY,
SOUTH PARKS ROAD, OXFORD.

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[10] L. H. Thomas and K. Umeda, *J. Chem. Phys.*, 1957, **26**, 293.
[11] R. McWeeney, *Acta Cryst.*, 1951, **4**, 513.