ture de T_0 impliqués dans ce trièdre soient 'responsables': seuls le sont nécessairement ij, ik, jk dont le fusionnement dans les calculs vient de provoquer l'arrêt des opérations. En effet n'ont été testés au cours de la condensation que les trièdres composés ayant des sommets notés par des indices en succession naturelle sans lacunes (**1234**, **12345**, ...), et il se peut que **125**,ijk ($i, j, k \neq 3, 4$), par exemple, dont on ne sait rien, soit la seule cause de l'inconstructibilité de **1**...α,ijk. Il importe donc d'y remonter par le biais d'un sous-programme. Deux chemins sont possibles.

Le plus systématique consiste à intervertir les lignes-colonnes de la partie utile de T_0 de façon à y faire apparaître i, j, k en tête, puis à condenser dans l'ordre i, j, k, 1, 2, ... jusqu'à rencontre d'une inconstructibilité mettant en cause m, n, p. On reclasse alors le tableau des ijk, ...m...n...p... (troisième condensation – donc privée de lignes-colonnes i, j, k) en y faisant apparaître les lignes-colonnes m, n, p en tête, et ainsi de suite jusqu'à ce que l'inconstructibilité se produise au contact du domaine reclassé.

Le second procédé, moins sûr mais souvent plus rapide, consiste à reprendre la condensation des tableaux $T_{\alpha-1}$, $T_{\alpha-2}$, ... déjà calculés, en y supprimant la première colonne, puis en opérant de même, si nécessaire, sur les nouveaux tableaux dérivés.

7. Rectification des hypothèses de signes

Un groupe de signes ayant été reconnu incompatible avec une densité électronique positive, il convient de le modifier. Cette modification, opérée sur T_0, rend caduque une partie des calculs de condensation déjà effectués, qu'il convient alors de recommencer. De la sorte, l'inversion du 'signe' de ij ($i < j$) oblige à recalculer:

(1) l'élément ji dans les tableaux T_1 à T_{i-1},
(2) la ligne-colonne j dans les tableaux T_i à T_{j-1},
(3) la totalité des tableaux d'indice supérieur à $j-1$.

Outil pratique: un cache en rhodoïde permettant de gommer un seul terme et une seule ligne.

8. Stockage des incompatibilités

Le stockage des incompatibilités est effectué sur un tableau en tête duquel figurent les indices cristallographiques des angles ij dans l'ordre de leur intervention dans les calculs. Les signes relatifs à chaque incompatibilité sont inscrits dans les colonnes correspondantes; en regard, les indices tensoriels qui caractérisent le sous-espace inconstructible.

Lors du changement d'hypothèse, il convient évidemment de vérifier que l'on ne va pas reproduire une hypothèse déjà essayée.

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The Crystal Structure of Copper(II)*bis*(Benzene Azo-β-Naphthol)

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The monoclinic unit cell has dimensions:

$$a = 17.34, \quad b = 3.90, \quad c = 17.46 \text{ Å}; \quad \beta = 96.9° .$$

The space group is $P2_1/n$ and the cell contains 2 Cu (at symmetry centres) and four molecules of $C_{16}H_{11}N_2O$. The structure was determined from the intensities of 1807 hkl reflexions by least-squares refinement on Pegasus; $R = 16\%$.

The copper atoms have square planar coordination, with two oxygen atoms at 1.93 Å and two nitrogen atoms at 2.01 Å. The next nearest neighbours are oxygen atoms of two adjacent molecules (Cu–O = 3.00 Å) which complete a distorted octahedral coordination group. The structure shows that only one nitrogen atom of each azo group is bonded to the metal atom.

Introduction

Although the aromatic azo compounds are extremely numerous and of considerable technical importance and theoretical interest, very few have been subjected to structural studies. The crystal structures of the two isomers of azobenzene have been determined (de Lange, Robertson & Woodward, 1939, Hampson & Robertson, 1941), and more recently benzene diazonium chloride has been studied (Rømming, 1959). Stable metal derivatives are formed by compounds

R_1–N $=$ N–R_2 in which R_1 and R_2 are aromatic systems having substituents in one or more of the ortho positions which are capable of bonding to a metal atom. It is supposed that in these chelate compounds the ortho substituent and the azo group are bonded to the metal atom, but it was not known whether the bond to the azo group involves one or both of the nitrogen atoms. The structure of the copper derivative of benzene azo-β-naphthol has been studied to distinguish between these two possibilities.

Experimental

The complex was obtained in the form of acicular crystals which appeared a dark metallic green by reflected light. By transmitted light the thinnest crystals appeared deep red when the electric vector was parallel to the needle axis and opaque when the light was polarized at right angles to the needle axis.

X-ray photographs showed that the crystals are monoclinic, the needle axis is the symmetry axis, and the cell dimensions are:

$$a = 17\cdot34, \ b = 3\cdot90, \ c = 17\cdot46 \ \text{Å}; \ \beta = 96\cdot9° \ .$$

With this choice of axes the only systematic absences are $h0l$ for $h + l = 2n + 1$, and $0k0$ for $k = 2n + 1$. The space group is therefore $P2_1/n$. The measured density is $1\cdot577$ g.cm.$^{-3}$, the density calculated for two molecules of $\text{Cu}(\text{C}_{16}\text{H}_{11}\text{N}_2\text{O})_2$ is $1\cdot581$ g.cm.$^{-3}$. The copper atoms must therefore lie at centres of symmetry at $0, 0, 0$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.

Weissenberg photographs of zero, first, second and third layers about [*b*] were taken; the usual multiple-film and visual-estimation techniques were used to obtain observed intensities, which were then corrected for polarization and rotation factors in order to obtain values of $F^2(hkl)$ and hence $F(hkl)$ on an arbitrary scale. There are 312 $F(h0l)$, 570 $F(h1l)$, 550 $F(h2l)$, and 385 $F(h3l)$ measured structure factors.

The extreme acicular habit of the crystals made it impracticable to obtain reliable intensity data except for rotation about [*b*]. The separate layers were brought to an approximately absolute scale by comparison with calculated structure factors during the refinement.

The photographs of the first, second and third layers were taken with a different crystal from that used for the zero layer; it was not until the higher layers came to be estimated that it was noticed that this crystal was twinned, one component having a and c axes interchanged with respect to the other. Because of the near equality of the two axes, reflexions hkl from one component and lkh from the other overlap accurately except for large values of h or l. Intensities of separated high-angle reflexions indicated a ratio of 5 : 1 for the intensities of the two components.

If $I(hkl)$, $I(lkh)$ are actual intensities from the stronger component, and $I'(hkl)$, $I'(lkh)$ intensities measured on the film,

$$I'(hkl) = I(hkl) + 0\cdot2I(lkh)$$
$$I'(lkh) = I(lkh) + 0\cdot2I(hkl) \ .$$

Thus

$$I(hkl) = 1\cdot04 \ \{I'(hkl) - 0\cdot2I'(lkh)\}$$
$$= I'(hkl) - 0\cdot2I'(lkh) \ \text{to the usual}$$

accuracy of visual estimation. This correction was applied to $I'(hkl)$ if $I'(lkh) > \frac{1}{4}I'(hkl)$.

X-ray structure analysis

Since the copper atoms must lie at centres of symmetry, and thus give a maximum positive contribution to all $h0l$ structure factors, it may be assumed that most of these will have positive signs. A projection in which all observed $F(h0l)$ were included with positive signs showed peaks from which the positions of all atoms in the benzene azo-β-naphthol molecule could be deduced. Coordinates were assigned and structure factors calculated. These indicated that several moderately large terms were negative. The projection was accordingly corrected, fresh coordinates were assigned, and the structure factors were recalculated. It was then possible to incorporate all the observed $F(h0l)$, of which all but 20 were positive, in a final electron-density projection.

Recalculation of the $F(h0l)$ with coordinates derived from this synthesis gave good agreement and no indication of further sign changes.

A first approximation to the y-coordinates was obtained by computing the generalized projection.

$$C(1) \equiv \sum_h \sum_l{}^{\!\!\!\!h+l \ \text{odd}} F(h1l) \cos 2\pi(hx + lz) \ .$$

Copper makes a maximum contribution to all $F(hkl)$ for which $h + k + l$ is even; hence those $F(h1l)$ for which $h + l$ is odd may be assumed positive. The height of a peak at (x, z) in $C(1)$ is proportional to the value for $\cos 2\pi y$ for the atom at that position, and thus enables an estimate of y to be made. This estimate was checked by comparing bond lengths measured in projection with those expected for regular benzene and naphthalene rings.

Since the y-coordinates of the two nitrogen atoms of the azo link are both close to zero there is an ambiguity in the sign of the y-coordinates of the phenyl group, which may be tilted either up or down with respect to the β-naphthol group. The terms $F(h1l)$ for which $h + k + l$ is even are of the form

$$F(h1l) \ (\text{even}) = 2f_{\text{Cu}} + 2\sum_{i=1}^{19} f_i \cos 2\pi(hx_i + lz_i) \cos 2\pi y_i$$

and are unaffected by the sign of y_i; calculated structure factors showed reasonable agreement with experimental values.

The ambiguity was resolved by calculating structure factors $F(h1l)$ for which $h + k + l$ is odd; for these, there is no copper contribution, so that:

$$F(h1l) \text{ (odd)} = \sum_{i=1}^{19} f_i \sin 2\pi(hx_i + lz_i) \sin 2\pi y_i \,.$$

It was soon seen that one of the alternative sets of y-coordinates gave better agreement than the other. These y-coordinates were refined by computing generalized projections, of both C and S terms, first for the $F(h1l)$, and later for $F(h2l)$ and $F(h3l)$.

This process was continued until the signs of all but a few small structure factors were settled, when the individual layers were scaled by multiplying by $\Sigma|F_c|/\Sigma|F_o|$.

The refinement was completed by a three-dimensional least-squares method on a Ferranti 'Pegasus' computer. The programmes used were supplied by Dr D. W. J. Cruickshank. The weighting factor w was given by $1/w = F + F^2/80$.

Three positional parameters and one isotropic temperature parameter were refined for each carbon, nitrogen and oxygen atom, and one isotropic temperature parameter for the copper atom. The overall scale factor for the F_o was also refined. Hydrogen atoms were included in the structure-factor calculations but were not refined by the least-squares programme. Each hydrogen atom was placed 1·00 Å from its carbon atom, along the extension of the diagonal of the corresponding six-membered ring. The scales of the individual layers were adjusted separately in order to make $\Sigma F_o = \Sigma F_c$ when these sums differed by more than 5% for any particular layer.

The final agreement factor is $R = 16·0\%$, calculated for 1807 reflexions; 10 reflexions with small indices were omitted as they were obviously affected by extinction. The accuracy of the structure determination is limited by the inadequate intensity data—in particular by the twinning and omission of $F(hkl)$ for $k > 3$.

Description of the structure

Positional and temperature parameters of all the atoms

Table 1. *Atomic parameters*

|	x (Å)	y (Å)	z (Å)	B (Å^2)
Cu	0·000	0·000	0·000	3·25
C_1	3·095	0·320	−0·313	2·63
C_2	2·130	0·984	−1·255	2·40
C_3	2·523	1·432	−2·512	2·93
C_4	3·820	1·193	−2·810	2·96
C_5	6·117	0·360	−2·276	3·19
C_6	7·047	−0·281	−1·360	3·62
C_7	6·713	−0·739	−0·147	3·19
C_8	5·410	−0·521	0·212	3·18
C_9	4·435	0·129	−0·665	2·51
C_{10}	4·799	0·551	−1·913	3·16
C_{11}	1·691	−0·321	2·704	2·38
C_{12}	0·632	0·209	3·283	3·05
C_{13}	0·598	−0·004	4·684	3·83
C_{14}	1·658	−0·668	5·416	3·60
C_{15}	2·713	−1·186	4·838	3·09
C_{16}	2·748	−0·996	3·444	2·71
N_{17}	1·688	−0·083	1·309	2·52
N_{18}	2·904	−0·036	0·935	2·57
O_{19}	0·914	1·275	−1·013	3·02
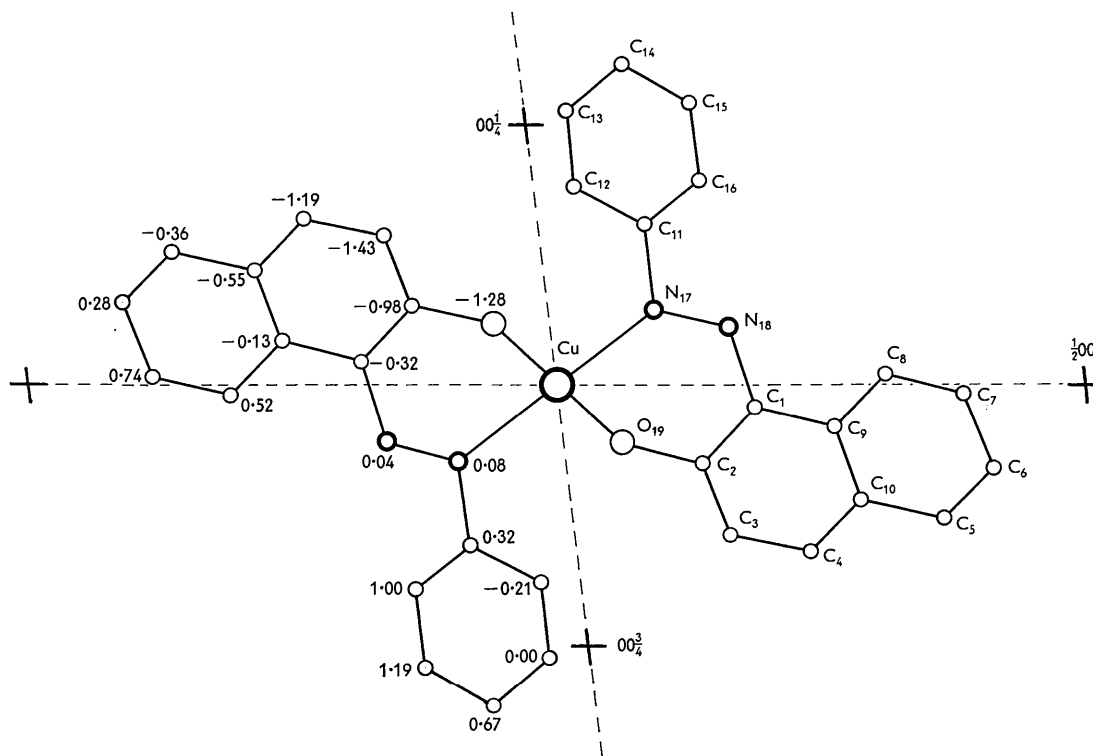
Fig. 1. Molecule of Cu(II)bis(benzene-azo-β-naphthol) projected down b-axis: figures on left are y-coordinates in Å.
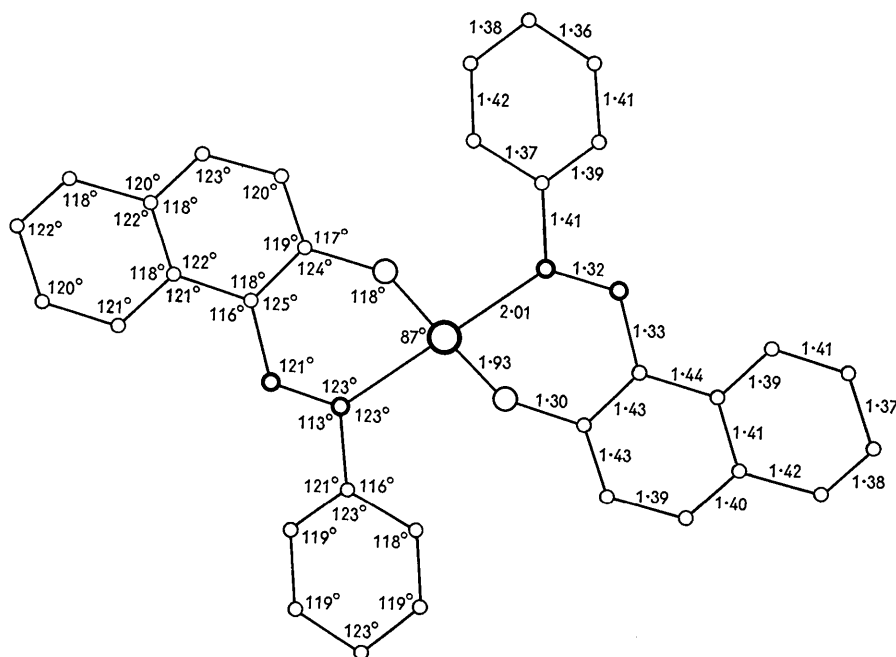
Fig. 2. Cu(II)*bis*(benzene-azo-β-naphthol): bond lengths (in Å) and bond angles.

are given in Table 1. The estimated standard deviation of the carbon atoms is about 0·015 Å, and of the nitrogen and oxygen atoms about 0·010 Å.

Bond-lengths and bond-angles are given in Fig. 2, which also indicates the direction of tilt of the various planar groups of atoms. The copper atoms are spaced at intervals of 3·90 Å (*b*) along the *b*-axis, and have square planar coordination, with two oxygen atoms at 1·93 Å and two nitrogen atoms (N_{17}) at 2·01 Å. This square is tilted about its N–Cu–N diagonal by $41\frac{1}{2}°$, so that the next-nearest neighbours of any copper atom, in a direction roughly perpendicular to the square, are two oxygen atoms (one from each adjacent molecule), which complete a distorted octahedral coordination group (Cu–O = 3·00 Å).

As can be seen from Figs. 1 and 2, only one nitrogen atom (N_{17}) of the azo-group is bonded to copper. The situation is similar to that in the cuprous chloride azomethane complex (Brown & Dunitz, 1960) where it is concluded that interaction between copper and the azo group is due to a dative σ-bond formed by the unshared pair of electrons on one nitrogen atom.

The ten carbon atoms of the naphthalene group are all within the estimated standard deviation of their mean plane (0·015 Å). The oxygen atom (no. 19) is 0.06 Å out of the plane and the two nitrogen atoms

(nos. 17 and 18) are 0·07 and 0·11 Å respectively out of the plane. The mean plane of the naphthalene group is tilted by 28° from the *a–c* plane, so that the perpendicular distance between parallel groups related by the *b*-translation is 3·43 Å.

The six carbon atoms C_{11} to C_{16}, and nitrogen N_{17}, are coplanar to within the estimated standard deviation, and the tilt of 31° relative to the *a–c* plane results in a perpendicular spacing of 3·35 Å between these groups along the *b*-axis. The angle between the plane of the six-membered ring and that of the naphthalene group is 19°.

The bond lengths and bond angles in the ring systems are within the range of values usually obtained in comparable organic structures but the accuracy of the structure would not justify detailed discussion of the significance of particular bond lengths.

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