Colour, Isomerism, and Structure of Some Copper Co-ordination Compounds. Part XXI.[1] Crystal and Molecular Structure of the 2:1 Adduct between 1,3,5-Trinitrobenzene and Bis-(*N*-methylsalicylaldiminato)-copper(II)

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An *X*-ray structural analysis by the heavy-atom method of the title compound has revealed a donor–acceptor interaction between trinitrobenzene and the salicylidene residues. The monoclinic cell has dimensions a = 11·726(4), b = 9·327(2), c = 14·10(1) Å, β = 93·55(5)°, Z = 2, space group $P2_1/c$. Diffractometer data (1972 observations) were refined by block-diagonal least-squares to R 0·072. The two species are arranged alternately in stacks so that each donor interacts with two acceptors and *vice versa*. Their molecular planes are not parallel, but make dihedral angles of 5·8 and 26·4° with one another, the interactions at *ca.* 3·2 Å being between specific regions of each. The complex shows the familiar stepping feature and the copper atom completes a distorted but centrosymmetric octahedral stereochemistry by interaction with an oxygen atom of two symmetry related nitro-groups at 3·08 Å.

SOME years ago we undertook preliminary experiments to see what adducts could be prepared between supposedly square-planar complexes of copper(II) and aromatic molecules with a known donor or acceptor capacity. The implications of one of our observations have recently become apparent since it now seems clear that the co-ordination of further donor atoms to square-planar complexes is related to the in-plane ligand-field or to the amount of back-bonding achieved.[2,3]

Having found that hydrogen bonding to the in-plane donors seems to influence the need for 'extra' co-ordination [3,4] we considered the possibility that a suitable interaction with other regions of the ligand would prove equally effective. In particular the possibility of increasing back-donation from the central metal-atom by depleting the electronic charge on the chelate groups led us to examine the crystal structure of the 1 : 2 adduct formed between bis-(*N*-methylsalicylaldiminato)copper(II) and 1,3,5-trinitrobenzene. The complex itself is known to be five- [5] or six-co-ordinate [6] in the solid state in contrast to the four-co-ordinate state of the analogous bis(salicylaldiminato)copper(II).[7] This distinction is correlated with the decreased ligand-field effect in the former consequent upon the lengthening of the copper to nitrogen bonds by steric pressure from the methyl groups.[6] We hoped to elucidate the mode of interaction between the trinitrobenzene and the complex and if, as we suspected, a donor–acceptor situation existed, to observe the co-ordination behaviour of the metal.

EXPERIMENTAL

Slow evaporation of a chloroform solution containing bis-(*N*-methylsalicylaldiminato)copper(II) and 1,3,5-trinitrobenzene yielded dark brown prismatic crystals.

Crystal Data.—$C_{28}H_{22}CuN_8O_{14}$, M = 758·06, Monoclinic, a = 11·726(4), b = 9·327(2), c = 14·10(1) Å, β = 93·55(5)° (standard deviations from least-squares fit to the diffractometer co-ordinates of 7 reflexions), U = 1540·9 Å^3, D_m = 1·627, Z = 2 (formula units), D_c = 1·633. Mo-K_α radiation, λ = 0·7107 Å; μ(Mo-K_α) = 8·67 cm^{-1}. Space group $P2_1/c$.

A crystal of dimensions 0·30 × 0·25 × 0·20 mm was used for intensity measurements with zirconium-filtered Mo-K_α radiation. Data were collected on a Hilger and Watts Y290 four-circle diffractometer by the ω-scan procedure, by use of a 70-step scan at the step-rate of 0·01° s^{-1}. After correction for background, intensities having $I_{\text{corr.}} < 2{\cdot}5\sigma(I_{\text{corr.}})$ were regarded as unobserved leaving 1972 independent values of $|F_o|$. Absorption corrections were not applied.

The presence of two molecules per unit cell implied that the copper atoms were placed on centres of symmetry with half the formula unit in the asymmetric unit. The structure was solved by the conventional heavy-atom method the approximate atomic parameters then being adjusted by a least-squares block-diagonal calculation. The observations were weighted by the relation $w = 1/[1 + (F_o - b)^2/a^2]$, the values of a and b being adjusted at appropriate stages to maintain $\langle w\{|F_o| - |F_c|\}^2\rangle$ reasonably constant over $|F_o|$ ranges. Final values are listed in Table 1. Initial refinement with isotropic temperature factors reduced R to 0·118, anisotropic temperature factors then being assigned. When R was 0·093 a difference-Fourier synthesis was computed, and enabled location of all

TABLE 1

Final weighting analysis

$\lvert F_o\rvert$ ranges	$\langle w\Delta^2\rangle$	No. of data
88·37—29·34	0·305	51
29·34—13·78	0·484	252
13·78—9·99	0·334	231
9·99—8·00	0·235	208
8·00—6·31	0·486	217
6·31—5·30	0·311	221
5·30—4·63	0·303	206
4·05—3·62	0·505	195
3·62—1·89	0·477	196

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[1] Part XX, C. A. Bear, J. M. Waters, and T. N. Waters, *J. Chem. Soc.* (*A*), 1970, 2494.

[2] H. C. Freeman, 'The Biochemistry of Copper,' eds. J. Peisach, P. Aisen, and W. E. Blumberg, Academic Press, New York, 1966, p. 104.

[3] E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc.* (*A*), 1970, 406.

[4] E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc.* (*A*), 1970, 400.

[5] D. Hall, S. V. Sheat, and T. N. Waters, *J. Chem. Soc.* (*A*), 1968, 460.

[6] E. C. Lingafelter, G. L. Simmons, B. Morosin, C. Scheringer, and C. Freiburg, *Acta Cryst.*, 1961, **14**, 1222.

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hydrogen atoms which were positioned at idealised geometries. These atomic parameters and estimated isotropic temperature factors (5·0 Å^2) were then kept constant during subsequent calculations. Final convergence was reached at R 0·073.

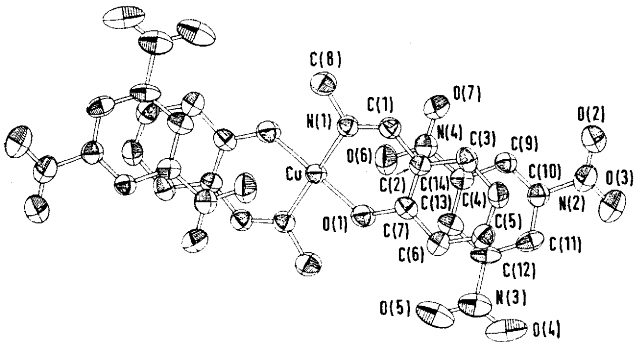

FIGURE 1 An ORTEP diagram showing the atom numbering system used

TABLE 2

Atom positions with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Cu	0·0000	0·0000	0·5000
O(1)	0·1545(4)	−0·0557(4)	0·5085(3)
O(2)	−0·0058(4)	−0·3848(5)	0·6903(3)
O(3)	0·0348(4)	−0·1609(5)	0·6900(3)
O(4)	0·4176(4)	−0·0129(7)	0·7712(4)
O(5)	0·5396(5)	−0·1639(8)	0·8346(4)
O(6)	0·4112(5)	−0·6334(7)	0·9173(5)
O(7)	0·2541(4)	−0·7136(5)	0·8535(4)
N(1)	−0·0454(4)	−0·1839(5)	0·4380(3)
N(2)	0·0588(4)	−0·2861(5)	0·7074(3)
N(3)	0·4479(5)	−0·1289(7)	0·8018(4)
N(4)	0·3233(4)	−0·6208(7)	0·8679(4)
C(1)	0·0181(5)	−0·2959(6)	0·4377(4)
C(2)	0·1333(5)	−0·3050(6)	0·4739(4)
C(3)	0·1881(5)	−0·4422(6)	0·4716(4)
C(4)	0·3016(5)	−0·4586(6)	0·5049(4)
C(5)	0·3616(5)	−0·3402(8)	0·5391(4)
C(6)	0·3135(5)	−0·2052(7)	0·5401(4)
C(7)	0·1984(5)	−0·1862(6)	0·5083(4)
C(8)	−0·1610(6)	−0·2018(8)	0·3918(5)
C(9)	0·1935(5)	−0·4545(6)	0·7841(4)
C(10)	0·1723(5)	−0·3186(6)	0·7497(4)
C(11)	0·2516(5)	−0·2090(7)	0·7564(4)
C(12)	0·3574(5)	−0·2428(8)	0·7977(4)
C(13)	0·3850(5)	−0·3756(8)	0·8347(4)
C(14)	0·3006(5)	−0·4768(6)	0·8259(4)
H(1) *	−0·039	−0·390	0·414
H(3)	0·139	−0·533	0·499
H(4)	0·342	−0·566	0·506
H(5)	0·451	−0·340	0·542
H(6)	0·363	0·114	0·566
H(8a)	−0·218	−0·197	0·438
H(8b)	−0·180	−0·296	0·362
H(8c)	−0·162	−0·170	0·348
H(9)	0·128	−0·537	0·780
H(11)	0·233	−0·102	0·729
H(13)	0·469	−0·378	0·837

* Hydrogen atoms are numbered according to the atom to which they are bonded.

Atom positions are listed in Table 2 and temperature parameters in Table 3. Calculated bond lengths and angles are in Tables 4 and 5 and structure factor data are listed in Supplementary Publication No. SUP 20664 (2 pp., 1 microfiche).* The atom numbering scheme is shown in Figure 1.

TABLE 3

Temperature parameters * (× 10^4)

Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
Cu	62	95	52	−28	23	−9
O(1)	80	119	78	−45	28	−9
O(2)	83	176	100	−9	−31	−8
O(3)	123	150	94	19	31	82
O(4)	191	226	123	23	74	−186
O(5)	115	363	125	−56	1	−189
O(6)	130	265	161	75	−84	68
O(7)	136	140	146	32	−54	−1
N(1)	76	107	51	−11	10	−6
N(2)	90	132	54	−15	19	19
N(3)	123	219	76	−28	45	−102
N(4)	92	188	91	9	−16	50
C(1)	73	112	53	−2	21	−6
C(2)	69	115	43	5	21	−9
C(3)	103	112	52	30	36	12
C(4)	99	123	68	20	16	39
C(5)	82	161	54	41	15	20
C(6)	80	148	44	0	15	22
C(7)	83	109	43	8	50	−9
C(8)	97	142	85	−60	−19	−18
C(9)	71	103	50	−30	14	−8
C(10)	74	123	39	−26	19	−19
C(11)	95	130	47	−17	38	−41
C(12)	80	173	50	−41	46	−105
C(13)	58	193	58	−37	35	−18
C(14)	78	121	58	−24	22	18

* The scattering factor for an atom is expressed as:

$$= f_0 \exp(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{23}kl + b_{13}hl + b_{12}hk).$$

TABLE 4

Bond lengths (Å) with standard deviations in parentheses

Cu–O(1)	1·881(4)	N(2)–O(2)	1·207(7)
Cu–N(1)	1·983(5)	N(2)–O(3)	1·223(8)
N(1)–C(1)	1·283(8)	N(2)–C(10)	1·455(8)
N(1)–C(8)	1·477(9)	N(3)–O(4)	1·210(10)
C(1)–C(2)	1·418(8)	N(3)–O(5)	1·190(9)
C(2)–C(3)	1·433(9)	N(3)–C(12)	1·530(9)
C(2)–C(7)	1·414(9)	N(4)–O(6)	1·214(9)
C(3)–C(4)	1·392(10)	N(4)–O(7)	1·195(8)
C(4)–C(5)	1·380(10)	N(4)–C(14)	1·485(9)
C(5)–C(6)	1·380(10)	C(9)–C(10)	1·375(9)
C(6)–C(7)	1·407(9)	C(10)–C(11)	1·383(9)
C(7)–O(1)	1·322(7)	C(11)–C(12)	1·374(9)
		C(12)–C(13)	1·374(10)
		C(13)–C(14)	1·367(9)
		C(14)–C(9)	1·370(8)

TABLE 5

Bond angles (°) with standard deviations in parentheses

O(1)–Cu–N(1)	91·2(2)	O(2)–N(2)–O(3)	123·7(6)
Cu–O(1)–C(7)	128·9(4)	O(2)–N(2)–C(10)	118·0(5)
Cu–N(1)–C(1)	124·4(4)	O(3)–N(2)–C(10)	118·3(5)
Cu–N(1)–C(8)	120·4(4)	O(4)–N(3)–O(5)	128·5(8)
C(1)–N(1)–C(8)	115·1(5)	O(4)–N(3)–C(12)	114·8(6)
N(1)–C(1)–C(2)	126·0(6)	O(5)–N(3)–C(12)	115·6(7)
C(1)–C(2)–C(7)	124·0(6)	O(6)–N(4)–O(7)	124·8(7)
C(1)–C(2)–C(3)	117·6(6)	O(6)–N(4)–C(14)	116·2(6)
C(3)–C(2)–C(7)	118·4(5)	O(7)–N(4)–C(14)	119·0(6)
C(2)–C(3)–C(4)	120·7(6)	C(10)–C(9)–C(14)	115·7(5)
C(3)–C(4)–C(5)	119·1(6)	N(2)–C(10)–C(9)	118·5(5)
C(4)–C(5)–C(6)	122·2(6)	N(2)–C(10)–C(11)	118·0(6)
C(5)–C(6)–C(7)	119·8(6)	C(9)–C(10)–C(11)	123·5(6)
O(1)–C(7)–C(2)	121·4(5)	C(10)–C(11)–C(12)	116·5(6)
O(1)–C(7)–C(6)	118·8(6)	N(3)–C(12)–C(11)	117·6(6)
C(2)–C(7)–C(6)	119·8(6)	N(3)–C(12)–C(13)	117·7(6)
		C(11)–C(12)–C(13)	123·5(6)
		C(12)–C(13)–C(14)	115·9(6)
		N(4)–C(14)–C(9)	116·5(5)
		N(4)–C(14)–C(13)	118·6(6)
		C(9)–C(14)–C(13)	124·9(6)

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are sent as full-sized copies.)

DISCUSSION

TABLE 6

Comparison of standard deviations calculated from deviations in atom positions and from the spread of values for chemically identical situations

Atoms	σ from positions/Å	σ from spread/Å
C–C	0·009	0·03
C–N	0·009	0·023
N–O	0·009	0·005
C–H		0·06
C–C–C	0·59°	0·48°
N–C–C	0·55	0·33
O–N–C	0·59	0·54
O–N–O	0·68	0·97

A comparison between the standard deviations derived from the least-squares variances and those obtained from the internal consistency of bonds and angles of known equality (here the aromatic ring of trinitrobenzene since the equivalence of bonds in the salicylidene ring is unlikely [8]) can be made from Table 6. The quoted σ values, taken from the least-squares approximation, are seen to be reliable.

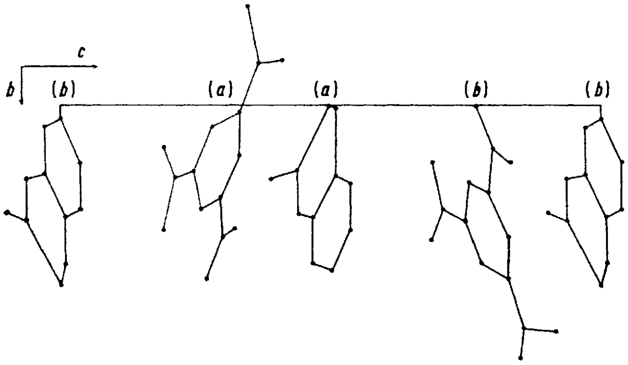

FIGURE 2 The molecular arrangement along *c*

The crystal structure reveals discrete trinitrobenzene and complex molecules in a 2 : 1 ratio. Molecular planes are approximately parallel with one another and with (001), the two species being arranged alternately so that the nitrobenzenes can be roughly described as being sandwiched between salicylaldiminato-residues. This relationship is indicated diagrammatically in Figure 2 in which the two half complex-molecules and two nitrobenzene molecules are labelled as (*a*) and (*b*). The planes of the molecules are slightly tipped with respect to one another so that the angle between complex (*a*) and trinitrobenzene (*a*) is 5·8°, between complex (*a*) and trinitrobenzene (*b*) 26·4°. Overlap between complex (*a*) and trinitrobenzene (*a*) is in the staggered mode expected of a charge-transfer interaction at distances (3·1—3·4 Å) again typical. (Atom-to-plane distances are listed in Table 7 which also includes other data pertaining to planes of best fit, and atom-to-atom distances in Table 8 which details intermolecular approaches less than the sum of van der Waals radii.) Trinitrobenzene (*b*) also approaches the aromatic ring of complex (*a*) quite closely but on the opposite side from molecule (*a*) and only to a small region: the 'edge' C(6)–C(7) (Tables 7 and 8).

TABLE 7

(*a*) Equations of specified planes and, in square brackets, deviations (Å) therefrom. Equations are in the form $lX + mY + nZ = P$ where X, Y, and Z are orthogonal axes and $X = x + z\cos\beta$, $Y = y$, $Z = z\sin\beta$. Only the defining atom (asterisked) showing the largest deviation is listed for each plane

Plane (1): C(1), O(1), N(1)

$$0{\cdot}176X + 0{\cdot}407Y - 0{\cdot}896Z = 6{\cdot}383$$

[C(1) −0·291, C(2) −0·550, C(7) −0·404, C(8) 0·283]

Plane (2): C(2)—(7)

$$0{\cdot}345X + 0{\cdot}182Y - 0{\cdot}921Z = 6{\cdot}254$$

[Cu(1) −0·377, O(1) 0·041, N(1) −0·049, C(1) 0·021, C(6)* 0·011, C(8) 0·065]

Plane (3): C(9)—(14)

$$0{\cdot}375X - 0{\cdot}273Y - 0{\cdot}886Z = 8{\cdot}030$$

[C(11)* −0·012, O(2) 0·150, O(3) −0·237, O(4) 0·029, O(5) 0·140, O(6) −0·289, O(7) 0·040, N(2) −0·035, N(3) 0·006, N(4) −0·075]

(*b*) Interplanar angles/deg.

(1)–(2) 16·3 (1)–(3) 41·5

(2)–(3), *i.e.* between complex (*a*) and trinitrobenzene (*b*), 26·4
Plane (2) and benzene ring C(9′)–C(14′), *i.e.* between complex (*a*) and trinitrobenzene (*a*), 5·8

TABLE 8

Intermolecular distances (Å)

$C(2) \cdots C(9^{I})$	3·71	$C(6) \cdots C(12^{I})$	3·52
$C(2) \cdots C(10^{I})$	3·42	$C(6) \cdots C(13^{I})$	3·16
$C(2) \cdots C(11^{I})$	3·45	$C(6) \cdots C(14^{I})$	3·46
$C(3) \cdots C(11^{I})$	3·47	$C(7) \cdots C(9^{I})$	3·42
$C(5) \cdots C(12^{I})$	3·49	$C(7) \cdots C(13^{I})$	3·43
$C(6) \cdots C(11)$	3·18	$Cu \cdots O(3)$	3·08

Roman numeral superscripts refer to the following equivalent position relative to x, y, z: $x, -\frac{1}{2} - y, -\frac{1}{2} + z$.

A view of the cell contents projected down *c* is given in Figure 3. It should be realised that a 2 : 1 ratio of adduct to salicylidene residue is not implied, these constituents being stacked alternately so that the same

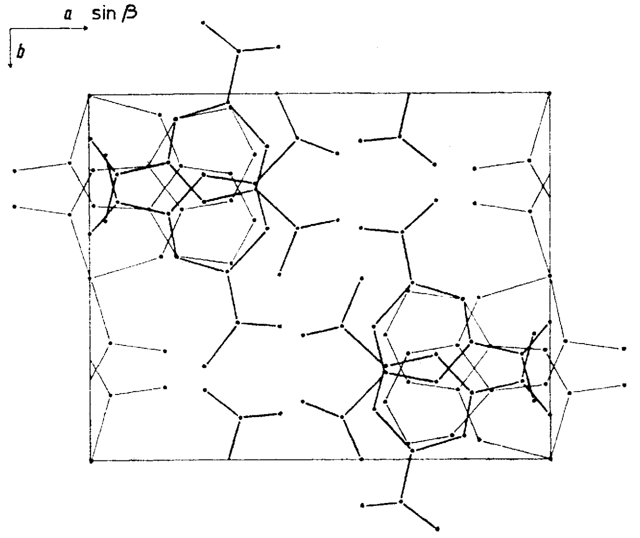

FIGURE 3 A view of the cell contents projected down *c*

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[8] K. Iijima, I. Oonishi, F. Muto, A. Nakahara, and Y. Komiyama, *Bull. Chem. Soc. Japan*, 1970, **43**, 1040.

data could be presented with respect to a ' central ' trinitrobenzene.

We interpret this arrangement as revealing the presence of a charge-transfer interaction between a salicylidene donor and trinitrobenzene acceptor. It is more difficult to decide whether or not the association is strictly monomeric [between complex (*a*) and adduct (*a*)] or whether a polymeric charge transfer donor–acceptor ' stack ' is present. It is likely that the true situation lies between these extremes. The association thus differs from that in the 1 : 1 complexes formed between trinitrobenzene and bis-(*N*-t-butylsalicylaldiminato)copper(II),[9] where the interaction is unambiguously monomeric, and between bis-(quinolin-8-olato)copper(II) and 7,7,8,8-tetracyanoquinodimethane,[10] and bis-(quinolin-8-olato)copper(II)–benzotrifuran,[11] where discrete donor–acceptor pairs also occur even though the components are interleaved.

The arrangement in the present structure is probably most like that seen in the 1 : 2 complex formed between bis-(quinolin-8-olato)copper(II) and tetracyanobenzene [12] where the copper atoms also complete a distorted octahedral co-ordination sphere with donors from the adducts. Bis-(quinolino-8-olato)copper(II) and picryl azide [13] similarly form a 1 : 2 complex with alternate stacking of ligands and acceptor molecules but the interactions with the metal atoms are absent.

The bond lengths and angles in both molecules of the crystal are as expected. The complex has the ' stepped ' conformation (Table 7) often seen in planar copper(II) compounds of this type, the rise of the step being 0·75 Å. The nitro-groups are not coplanar with their aromatic ring, a distortion to be expected. The angle of twist is respectively 7·5, 6·7, and 8·6° for the nitro-groups based on N(2), N(3), and N(4).

Intermolecular distances (Table 8) reveal that the copper atom is *quasi*-six-co-ordinate, apparently interacting with the oxygens, O(3), of centrosymmetrically related nitro-groups. The Cu–O(3) (3·08 Å) distance approaches the limit of values indicative of bonding. That the interaction occurs equally on both sides of the co-ordination plane is consistent with other situations with ' bonds ' of this length.[14,15]

Details of the bonding geometry are given in Table 9 from which it can be seen that the atoms, O(3), do not lie on an axis perpendicular to the main co-ordination square. It could then be argued that the interaction is much more of the ' polarisation ' type seen in isomers of bis(salicylaldehydato)copper(II) [14] and bis-(*N*-methyl-2-hydroxy-1-naphthaldiminato)copper(II) [15] rather than being weakly covalent. It is perhaps also significant in this context that the nitro-group which is involved makes the same sort of angle with its benzene ring as do its two non-interacting partners.

There are no other intermolecular approaches less than the sum of van der Waals radii, including those involving hydrogen atoms, other than the charge-transfer interactions already discussed. The crystal structure can thus be interpreted in terms of the associations between electron-donor and electron-acceptor aromatic systems and between copper and oxygen atoms. The tenuous nature of these interactions is perhaps suggested, however, by a comparison with the trinitrobenzene adduct of the tetrahedrally distorted complex bis-(*N*-t-butylsalicylaldiminato)copper(II).[9] That only a 1 : 1 adduct is found with this compound undoubtedly reflects packing problems in assembling two salicylidene–trinitrobenzene ' stacks ' per complex molecule when the salicylidene planes intersect at *ca.* 66°. Conversely the 2 : 1 adduct here reported reflects the ease of packing parallel stacks, two per molecule, when the salicylidene residues are themselves parallel.

TABLE 9

Co-ordination geometry at copper

(*a*) Distances (Å)

Cu–N(1)	1·98	Cu–O(3)	3·08
Cu–O(1)	1·88		

(*b*) Angles (deg.)

N(1)–Cu–O(1)	91·2	O(1)–Cu–O(3)	74·6
N(1)–Cu–O(1$^{\text{I}}$)	88·8	Cu–O(3)–N(2)	131·1
N(1)–Cu–O(3)	88·9		

We see no strong structural evidence for an increase in ligand-field strength consequent upon adduct formation. Certainly the molecular ' step ' has not been reduced from common values in the manner seen in hydrogen-bonded adducts. The very weak axial interaction with the copper atom does contrast with the strong dimeric association found in the γ-isomer of this complex [5] but is similar to that seen in the α-isomer.[6] Two of the bis-(quinolin-8-olato)copper(II) adducts mentioned earlier do contain four-co-ordinate copper,[10,13] the ' fifth ' donor-atom, 2·83 Å from the metal in the β-isomer of the parent complex,[16] being absent. On the other hand, interactions with copper atoms are present in the other adducts of this complex and the evidence remains inconclusive.

[2/2352 *Received*, 16*th October*, 1972]

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