Crystal and Molecular Structures of Bis[2-hydroxy-*N*-3-hydroxypropyl-5-nitrobenzylideneaminato-(μ-*O*)-copper(II)] and Bis[2-hydroxy-*N*-3-hydroxypropyl-α-methylbenzylideneaminato-(μ-*O*)-copper(II)] and Relation of Structural and Magnetic Properties

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The crystal structures of the title complexes (Ia) $Cu_2O_8N_4C_{20}H_{20}$ and (Ib) $Cu_2O_4N_2C_{22}H_{26}$ have been studied by single crystal *X*-ray diffraction, from counter data. Crystal data: (Ia), space group $P2_1/c$, $Z = 2$, $a = 10.988(5)$, $b = 5.444(5)$, $c = 17.455(7)$ Å, $\beta = 96.49°$, R 0.098, 506 reflections; (Ib), space group $C2/c$, $Z = 8$, $a = 20.700(9)$, $b = 9.555(6)$, $c = 21.64(1)$ Å, $\beta = 92.49(4)°$, R 0.034, 1 649 reflections. The structures were solved by the heavy-atom method.

Complex (Ia) has the closest intermolecular Cu · · · Cu distance for any complex of this type [3.6 Å *vs.* Cu · · · Cu (intramolecular) 3.0 Å], a property probably responsible for the high degree of cohesion in the lattice; it is also the closest to being completely coplanar. Complex (Ib) differs from others of this type in space group, and in the inequivalence of the two copper atoms in the binuclear molecule. The structures and magnetic properties of both complexes support a general correlation between decreasing strength of antiferromagnetic interaction and increasing distortion towards tetrahedral metal environment in binuclear copper(II) complexes.

A WIDE range of complexes of type (I) have been prepared [1-3] and their structural formulae were established from magnetic and i.r. data. The strength of their antiferromagnetic interactions may be expressed in terms of the singlet–triplet separation $-2J$. The $-2J$ values in these and other complexes increase as the copper(II) stereochemistry approaches square planar.[3-5] Accurate

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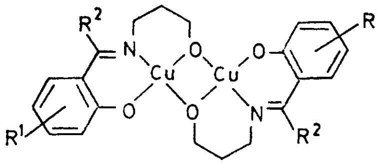
crystal structures of three of these complexes [(I); c—e] have been determined. All showed great structural similarity: space group $P2_1/c$, $Z = 2$, the centre of symmetry being in the molecule, and the Cu_2O_2 groups well isolated. In addition, the mass spectra showed the molecular ion in addition to the $M/2$ peak. Two complexes, (Ia) and (Ib), differ significantly from the others, suggesting possible structural differences. Complex (Ia) is far less soluble in any solvent than the others, and only half the dimeric unit is observed in the mass spectrum. An X-ray crystallographic investigation was undertaken to investigate the possibility of a polymeric structure linking neighbouring dimers. Complex (Ib) has $Z = 8$ in $C2/c$, which excludes an intramolecular centre of symmetry, so that the two copper atoms cannot be in equivalent environments. The crystal structure of this complex is also presented here.



	R^1	R^2
(I) a;	5-NO_2	H
b;	H	Me
c;	Cl	H
d;	3-NO_2	H
e;	5,6-benzo	H

EXPERIMENTAL

The complexes were synthesised by literature methods,[1–3] (Ia) as a powder, and (Ib) as fine black crystals. Magnetic and spectroscopic properties were determined as previously described.[2,4,5] Suitable crystals of (Ib) were grown by heating the solid in dimethylformamide under reflux at 90 °C for 3 days. The crystal selected for data collection was ground to an approximately spherical shape. Complex (Ia) appears to be nearly insoluble in any solvent except under conditions which destroy it. However, it is very slightly soluble in dimethylformamide and small crystals grew slowly on heating in this solvent for 2 years at 80—100 °C. Cell parameters for the crystals were determined and refined in each case from 28 independent reflections, and intensity data collected on an Enraf–Nonius CAD 4 diffractometer as described previously.[6] The 1 687 intensities for (Ia) and 2 315 for (Ib) in the ranges $0 < 2\theta < 46°$ and $0 < 2\theta < 50°$ respectively were measured and corrected for Lorentz polarisation effects and absorption. The final refinement of structure parameters was based on the 506 (Ia) and 1 649 (Ib) intensities which had $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics as detailed in ref. 7.

Crystal Data.—(Ia), $C_{20}H_{20}Cu_2N_4O_8$, $M = 571.5$, Monoclinic, $a = 10.988(5)$, $b = 5.444(5)$, $c = 17.455(7)$ Å, $\beta = 96.49(5)°$, $U = 1\ 038$ Å^3, $D_m = 1.80$, $Z = 2$, $D_c = 1.85$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) = 22.2 cm^{-1}. Space group $P2_1/c$.

(Ib), $C_{22}H_{26}Cu_2N_2O_4$, $M = 509.5$, Monoclinic, $a = 20.700(9)$, $b = 9.555(6)$, $c = 21.64(1)$ Å, $\beta = 92.49(4)°$, $U = 4\ 141$ Å^3, $D_m = 1.62$, $Z = 8$, $D_c = 1.65$ g cm^{-3}. μ(Mo-K_α) = 21.8 cm^{-1}. Space group $C2/c$.

Refinement of the Structure.—Full-matrix least-squares refinement was based on F, and the function minimised was $\Sigma w(|F_o| - |F_c|)^2$. Weights w were taken as $[2F_o/\sigma(F_o^2)]^2$. Atomic scattering factors for non-hydrogen atoms were taken from ref. 8, and those for hydrogen from ref. 9. The effects of anomalous dispersion were included ($\Delta f'$ and $\Delta f''$) from ref. 10 for copper.

Patterson functions located the Cu and O(1) positions in (Ia) and those of two independent copper atoms and O(1) for 1(b). The remaining atoms were located from Fourier difference maps. Anisotropic temperature factors were introduced for all the atoms in (Ib), though this was not possible for (Ia) owing to the sparsity of the data set. Hydrogen atoms were introduced as fixed atoms in the tetrahedral positions of the methylene carbons and at the trigonal positions for the unsubstituted phenyl ring carbons, with isotropic temperature factors of 5.0 assuming C–H 1.00 Å, except that no hydrogen atoms were inserted on atoms C(9′), C(10′) of (Ib) which evidenced positional disorder. After convergence, hydrogen atoms were inserted at their new calculated positions. The models converged with R 9.8, R' 11.1% for (Ia), and R 3.4, R' 4.5% for (Ib) $\{R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$. A final Fourier difference map was featureless. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21555 (11 pp., 1 microfiche).*

RESULTS AND DISCUSSION

Final positional and thermal parameters for the atoms are given in Table 1. Tables 2 and 3 contain the bond lengths and angles. Estimated standard deviations were derived from the inverse matrix in the course of least-squares refinement calculations.

Figures 1 and 2 show the molecules of (Ia) and (Ib), while Figures 3 and 4 show the molecular packing in the unit cells. Complex (Ia) contains dimeric molecules stacked quite close along the b axis such that intermolecular Cu · · · O and Cu · · · Cu distances of 3.1 and 3.6 Å are observed (Table 4), *vs.* 3.0 Å for the intramolecular Cu · · · Cu separation. These intermolecular separations are too long for bonding interactions and the complex cannot be considered polymeric. However, these distances are by far the shortest known for complexes of this type and are likely to account for its low solubility. The mass spectrum of (Ia) has no peaks corresponding to the dimeric molecule, the highest peak being that of half the molecule, presumably containing three-co-ordinate copper. This indicates that conditions sufficient to remove the dimeric molecule from the lattice are more than sufficient to break them up into monomers.

Complex (Ib) contains well separated dimeric molecules

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue.

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TABLE 1

Positional and thermal parameters, and estimated standard deviations

(*a*) For (Ia)

Atom	x/a	y/b	z/c	B	Atom	x/a	y/b	z/c	B
Cu	0.087 2(5)	−0.286(1)	0.516 4(3)	*	C(8)	0.274(3)	−0.299(9)	0.402(2)	3.5(10)
O(1)	0.048(2)	−0.548(6)	0.448(1)	*	C(9)	0.168(3)	−0.392(8)	0.351(2)	3.9(11)
O(2)	0.095(2)	−0.028(5)	0.593(1)	2.7(6)	C(10)	0.098(3)	−0.609(7)	0.372(2)	2.6(9)
O(3)	0.520(2)	0.741(7)	0.624(1)	6.5(8)	H(3)	0.104(3)	0.274(8)	0.709(2)	†
O(4)	0.428(2)	0.833(6)	0.723(2)	5.9(8)	H(4)	0.251(3)	0.585(7)	0.741(2)	†
N(1)	0.236(2)	−0.154(6)	0.470(1)	2.8(7)	H(6)	0.437(3)	0.398(6)	0.553(2)	†
N(2)	0.440(3)	0.680(8)	0.669(2)	5.8(10)	H(7)	0.366(3)	0.094(7)	0.467(2)	†
C(1)	0.289(3)	0.143(7)	0.566(2)	2.9(9)	H(81)	0.329(3)	−0.453(8)	0.423(2)	†
C(2)	0.178(3)	0.116(7)	0.611(2)	1.5(8)	H(82)	0.330(3)	−0.199(8)	0.373(2)	†
C(3)	0.175(3)	0.291(9)	0.676(2)	3.9(10)	H(91)	0.186(3)	−0.427(8)	0.296(2)	†
C(4)	0.258(3)	0.467(8)	0.694(2)	2.7(9)	H(92)	0.099(3)	−0.264(8)	0.346(2)	†
C(5)	0.356(3)	0.488(8)	0.649(2)	2.5(9)	H(101)	0.157(3)	−0.771(7)	0.380(2)	†
C(6)	0.365(3)	0.365(7)	0.588(2)	2.4(9)	H(102)	0.029(3)	−0.681(7)	0.331(2)	†
C(7)	0.299(3)	0.016(8)	0.502(2)	2.5(9)					

* Anisotropic thermal parameters in the form: $\exp[B_{11}{*}h{*}h + B_{22}{*}k{*}k + B_{33}{*}l{*}l + B_{12}{*}h{*}k + B_{13}{*}h{*}l + B_{23}{*}k{*}l]$ with parameters

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu($\times 10^4$)	50(3)	54(3)	23(1)	8(3)	28(4)	2(2)
O(1)($\times 10^3$)	6(3)	5(2)	26(9)	0(1)	2(3)	12(7)

† Isotropic thermal parameters B = 5.0 Å^2.

(*b*) For (Ib)

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	0.015 04(5)	0.086 0(1)	0.862 91(5)	0.002 85(3)	90(1)	267(3)	2(1)	184(4)	−8(1)
Cu(2)	0.119 71(5)	0.123 6(1)	0.770 36(4)	0.002 84(3)	91(1)	225(2)	−2(1)	146(4)	−9(1)
O(1)	0.065 9(3)	0.231 0(5)	0.825 9(2)	0.003 9(2)	76(7)	31(1)	5(6)	30(3)	−1(6)
O(2)	−0.026 5(3)	−0.084 0(5)	0.885 9(2)	0.003 3(2)	78(7)	30(1)	−12(6)	22(3)	−20(5)
O(1′)	0.072 9(3)	−0.020 7(6)	0.810 7(3)	0.005 0(2)	104(8)	43(2)	−13(7)	57(3)	−23(6)
O(2′)	0.164 7(3)	0.291 4(5)	0.750 4(2)	0.004 6(2)	100(7)	31(1)	−32(7)	37(3)	−31(6)
N(1)	−0.034 7(3)	0.211 6(6)	0.918 4(3)	0.002 0(2)	70(8)	25(2)	12(7)	4(3)	−6(6)
N(1′)	0.164 0(3)	0.002 0(6)	0.710 8(3)	0.002 4(2)	87(8)	26(2)	−2(7)	9(3)	−6(7)
C(1)	−0.080 9(4)	0.010 5(8)	0.974 6(3)	0.002 3(2)	72(9)	22(2)	11(9)	0(4)	−5(8)
C(2)	−0.053 2(4)	−0.100 6(8)	0.932 6(3)	0.001 9(2)	115(11)	25(2)	−10(9)	0(4)	9(9)
C(3)	−0.087 0(4)	−0.242 2(8)	0.942 5(4)	0.002 8(3)	102(11)	28(2)	2(9)	9(4)	−21(9)
C(4)	−0.124 4(4)	−0.275 0(9)	0.991 5(4)	0.002 9(3)	103(12)	35(3)	−19(10)	4(5)	18(9)
C(5)	−0.139 4(4)	−0.169 0(9)	1 032 9(4)	0.002 8(2)	138(12)	25(2)	−14(10)	18(4)	2(9)
C(6)	−0.117 4(4)	−0.029 2(9)	1 024 9(4)	0.002 5(2)	117(11)	25(2)	3(10)	5(4)	−7(9)
C(7)	−0.063 1(3)	0.162 7(8)	0.966 8(3)	0.001 8(2)	111(11)	21(2)	14(9)	9(3)	−3(8)
C(8)	−0.028 4(4)	0.369 4(8)	0.910 6(4)	0.003 0(3)	84(10)	35(2)	14(9)	19(4)	4(9)
C(9)	−0.009 4(4)	0.416 4(8)	0.847 2(4)	0.004 0(3)	77(10)	33(2)	28(10)	14(5)	6(9)
C(10)	0.059 2(4)	0.381 4(8)	0.831 5(3)	0.003 8(3)	85(10)	26(2)	2(10)	17(4)	−13(9)
C(11)	−0.082 8(4)	0.267 6(8)	1.017 0(4)	0.003 2(3)	99(11)	28(2)	6(10)	13(4)	−33(9)
C(1′)	0.202 6(4)	0.208 4(8)	0.652 0(3)	0.001 9(2)	101(10)	26(2)	−8(9)	6(4)	−12(8)
C(2′)	0.187 2(4)	0.317 4(9)	0.696 1(4)	0.002 2(2)	104(11)	34(2)	3(9)	19(4)	−5(9)
C(3′)	0.197 9(4)	0.462 4(8)	0.679 7(4)	0.003 5(3)	71(10)	38(3)	1(10)	17(5)	−5(9)
C(4′)	0.219 8(4)	0.498 2(8)	0.622 7(4)	0.003 3(3)	86(11)	38(3)	−2(10)	18(4)	40(9)
C(5′)	0.231 3(4)	0.394 8(9)	0.580 4(4)	0.003 7(3)	134(12)	26(2)	−15(11)	16(4)	10(9)
C(6′)	0.223 1(4)	0.252 4(8)	0.594 4(3)	0.002 8(2)	129(12)	19(2)	−10(10)	16(4)	−10(9)
C(7′)	0.199 8(4)	0.051 3(8)	0.666 2(3)	0.002 2(2)	132(12)	21(2)	−18(9)	−1(4)	−7(9)
C(8′)	0.161 8(4)	−0.159 1(8)	0.719 8(4)	0.003 6(3)	79(11)	31(2)	25(9)	20(4)	−15(8)
C(9A′)	0.138 2(10)	−0.196 0(18)	0.792 1(11)	0.005 2(8)	57(20)	84(9)	−6(23)	29(14)	65(24)
C(9B′)	0.092 1(7)	−0.209 5(13)	0.743 4(6)	0.003 0(5)	42(16)	17(3)	−26(16)	11(7)	−15(14)
C(11′)	0.241 0(4)	−0.059 1(8)	0.627 9(4)	0.003 5(3)	104(11)	25(2)	18(9)	26(4)	−24(8)

	x/a	y/b	z/c	B		x/a	y/b	z/c	B
C(10A′)	0.069 9(7)	−0.172(2)	0.794 8(6)	3.4(3)	H(101)	0.068 3(5)	0.428 5(10)	0.790 7(4)	†
C(10B′)	0.089 9(9)	−0.175(1)	0.815 9(6)	2.9(3)	H(102)	0.089 8(5)	0.419 3(10)	0.864 1(4)	†
H(3)	−0.076 7(5)	−0.319 8(10)	0.911 3(4)	†	H(3′)	0.189 5(5)	0.540 3(10)	0.709 7(5)	†
H(4)	−0.140 2(5)	−0.375 7(10)	0.996 8(5)	†	H(4′)	0.226 3(5)	0.602 5(10)	0.611 8(5)	†
H(5)	−0.165 9(5)	−0.193 4(11)	1.069 4(4)	†	H(5′)	0.246 6(5)	0.422 1(11)	0.538 5(5)	†
H(6)	−0.128 3(5)	0.045 6(10)	1.055 6(4)	–	H(6′)	0.232 3(4)	0.173 2(10)	0.561 7(4)	†
H(81)	−0.070 4(5)	0.416 0(10)	0.919 7(5)	†	H(81′)	0.198 6(5)	−0.192 3(9)	0.748 5(4)	†
H(82)	0.006 0(5)	0.404 7(10)	0.941 6(5)	†	H(82′)	0.169 0(5)	−0.209 2(9)	0.677 6(4)	†
H(91)	−0.039 4(5)	0.367 0(10)	0.816 5(5)	†	H(83′)	0.130 5(5)	−0.205 6(9)	0.688 4(4)	†
H(92)	−0.015 5(5)	0.523 1(10)	0.844 3(5)	½	H(84′)	0.206 7(5)	−0.202 9(9)	0.711 4(4)	†

* The form of the anisotropic thermal parameter is defined in footnote to Table 1(*a*). † B = 5.0 Å^2.

TABLE 2

Bond distances (Å)

(*a*) For (Ia)

Cu–O(1)	1.91(3)	N(2)–C(5)	1.42(4)
Cu–O(1′)	1.88(2)	C(1)–C(2)	1.53(3)
Cu–O(2)	1.93(2)	C(1)–C(6)	1.50(4)
Cu–N(1)	2.04(2)	C(1)–C(7)	1.33(4)
O(1)–C(10)	1.52(3)	C(2)–C(3)	1.48(4)
O(2)–C(2)	1.22(3)	C(3)–C(4)	1.34(4)
O(3)–N(2)	1.29(3)	C(4)–C(5)	1.41(3)
O(4)–N(2)	1.27(4)	C(5)–C(6)	1.27(3)
N(1)–C(7)	1.24(4)	C(8)–C(9)	1.48(4)
N(1)–C(8)	1.52(4)	C(9)–C(10)	1.48(4)

(*b*) For (Ib)

Cu–O(1)	1.904(7)	O(2)–C(2)	1.299(12)
Cu–O(2)	1.871(7)	O(1′)–C(10A′)	1.441(7)
Cu–O(1′)	1.951(7)	O(1′)–C(10B′)	1.472(7)
Cu–N(1)	1.989(8)	O(2′)–C(2′)	1.305(12)
Cu(2)–O(1)	1.946(7)	N(1)–C(7)	1.305(11)
Cu(2)–O(1′)	1.886(7)	N(1)–C(8)	1.477(13)
Cu(2)–O(2′)	1.872(7)	N(1′)–C(7′)	1.322(12)
Cu(2)–N(1′)	1.968(8)	C(1′)–C(7′)	1.488(14)
N(1′)–C(8′)	1.504(13)	C(2′)–C(3′)	1.408(14)
C(1)–C(2)	1.430(13)	C(3′)–C(4′)	1.372(14)
C(1)–C(6)	1.401(13)	C(4′)–C(5′)	1.352(14)
C(1)–C(7)	1.468(13)	C(5′)–C(6′)	1.365(14)
C(2)–C(3)	1.419(14)	C(7′)–C(11′)	1.547(14)
C(3)–C(4)	1.374(14)	C(8′)–C(9A′)	1.694(11)
C(4)–C(5)	1.374(14)	C(8′)–C(9B′)	1.620(12)
C(5)–C(6)	1.385(14)	C(9A′)–C(10A′)	1.435(0)
C(7)–C(11)	1.524(13)	C(9A′)–C(9B′)	1.396(0)
C(8)–C(9)	1.507(14)	C(9A′)–C(10B′)	1.161(0)
C(9)–C(10)	1.510(15)	C(9B′)–C(10A′)	1.271(0)
C(1′)–C(2′)	1.434(14)	C(9B′)–C(10B′)	1.606(0)
C(1′)–C(6′)	1.394(13)	C(10A′)–C(10B′)	0.605(0)
O(1)–C(10)	1.405(11)		

TABLE 3

Bond angles (°)

(*a*) For (Ia)

O(1)–Cu–O(1′)	73.9(10)	O(2)–C(2)–C(1)	123(3)
O(1)–Cu–O(2)	168.8(8)	O(2)–C(2)–C(3)	122(2)
O(1′)–Cu–O(2)	95.4(9)	C(1)–C(2)–C(3)	115(3)
Cu–O(1)–Cu′	106.1(10)	C(2)–C(3)–C(4)	125(3)
Cu–O(1)–C(10)	130(2)	C(3)–C(4)–C(5)	118(3)
Cu–O(1′)–C(10)	124(2)	N(2)–C(5)–C(4)	116(3)
Cu–O(2)–C(2)	129(2)	N(2)–C(5)–C(6)	119(3)
C(7)–N(1)–C(8)	123(3)	C(4)–C(5)–C(6)	125(3)
O(3)–N(2)–O(4)	114(4)	C(1)–C(6)–C(5)	124(2)
O(3)–N(2)–C(5)	121(4)	N(1)–C(7)–C(1)	132(3)
O(4)–N(2)–C(5)	123(3)	N(1)–C(8)–C(9)	112(2)
C(2)–C(1)–C(6)	113(3)	C(8)–C(9)–C(10)	121(3)
C(2)–C(1)–C(7)	122(3)	O(1)–C(10)–C(9)	107(3)
C(6)–C(1)–C(7)	123(3)		

(*b*) For (Ib)

O(1)–Cu–O(2)	166.8(3)	C(1)–C(6)–C(5)	122.3(10)
O(1)–Cu–O(1′)	75.4(3)	O(2)–Cu–O(1′)	91.7(3)
O(1)–Cu–N(1)	98.8(3)	O(2)–Cu–N(1)	94.3(3)
O(1)–Cu(2)–O(1′)	75.9(3)	O(1′)–Cu–N(1)	172.8(4)
O(1)–Cu(2)–O(2′)	91.3(3)	O(1′)–Cu–O(2′)	164.9(3)
O(1)–Cu(2)–N(1′)	172.7(3)	O(1′)–Cu(2)–N(1′)	99.3(3)
Cu–O(1)–Cu(2)	104.0(3)	O(2′)–Cu(2)–N(1′)	94.2(3)
Cu–O(1)–C(10)	127.1(7)	N(1)–C(7)–C(11)	119.7(9)
Cu(2)–O(1)–C(10)	128.4(6)	C(1)–C(7)–C(11)	117.0(9)
Cu–O(2)–C(2)	126.7(7)	N(1)–C(8)–C(9)	114.7(9)
Cu–O(1′)–Cu(2)	104.5(3)	C(8)–C(9)–C(10)	115.4(10)
Cu–O(1′)–C(10A′)	127.5(5)	O(1)–C(10)–C(9)	109.2(9)
Cu–O(1′)–C(10B′)	126.6(4)	C(2′)–C(1′)–C(6′)	118.3(10)
Cu(2)–C(0′)–C(10A′)	126.5(4)	C(2′)–C(1′)–C(7′)	122.5(10)
Cu(2)–O(1′)–C(10B′)	126.6(4)	C(6′)–C(1′)–C(7′)	119.1(10)
Cu(2)–O(2′)–C(2′)	124.2(7)	O(2′)–C(2′)–C(1′)	124.6(10)
Cu–N(1)–C(7)	123.1(7)	O(2′)–C(2′)–C(3′)	118.0(11)
Cu–N(1)–C(8)	117.3(7)	C(1′)–C(2′)–C(3′)	117.4(10)
C(7)–N(1)–C(8)	118.7(9)	C(2′)–C(3′)–C(4′)	121.2(11)
Cu(2)–N(1′)–C(7′)	124.9(8)	C(3′)–C(4′)–C(5′)	120.8(10)
Cu(2)–N(1′)–C(8′)	117.7(7)	C(4′)–C(5′)–C(6′)	120.4(10)
C(7′)–N(1′)–C(8′)	117.2(9)	C(1′)–C(6′)–C(5′)	121.8(10)
C(2)–C(1)–C(6)	117.8(10)	N(1′)–C(7′)–C(1′)	121.1(10)
C(2)–C(1)–C(7)	123.1(11)	N(1′)–C(7′)–C(11′)	121.2(10)
C(6)–C(1)–C(7)	119.1(9)	C(1′)–C(7′)–C(11′)	117.7(10)
O(2)–C(2)–C(1)	125.7(10)	N(1′)–C(8′)–C(9A′)	109.3(7)
O(2)–C(2)–C(3)	116.4(10)	N(1′)–C(8′)–C(9B′)	111.0(7)
C(1)–C(2)–C(3)	118.0(10)	C(8′)–C(9A′)–C(10A′)	109.3(4)
C(2)–C(3)–C(4)	122.0(10)	C(8′)–C(9B′)–C(10B′)	108.3(4)
C(3)–C(4)–C(5)	119.8(11)	O(1′)–C(10A′)–C(9A′)	97.4(3)
C(4)–C(5)–C(6)	119.9(10)	O(1′)–C(10B′)–C(9B′)	97.8(3)
N(1)–C(7)–C(1)	123.3(9)		

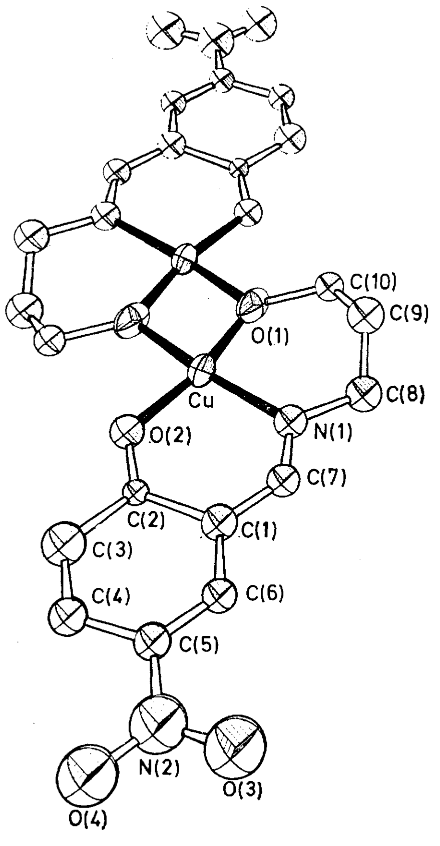


FIGURE 1 Molecule (Ia)

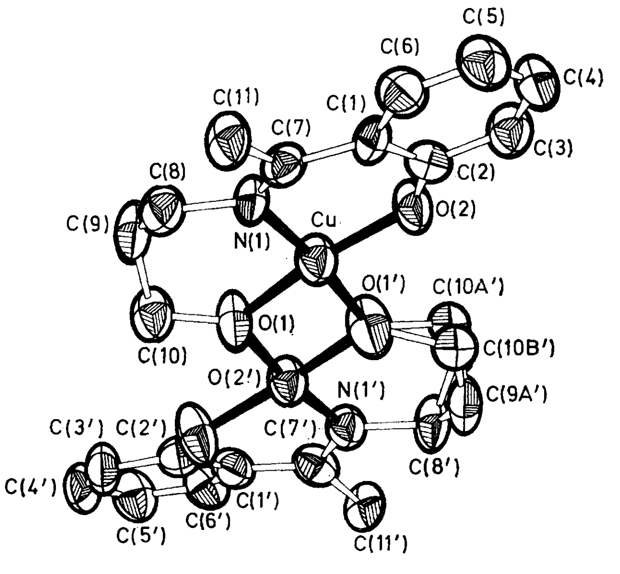


FIGURE 2 Molecule (Ib)

and is similar to other molecules of type (I), except that the two halves of the molecule are not crystallographically related. The mass spectrum resembles those of (I; c—e) in that it contains the molecular ion for the dimeric unit as well as the monomer.

The i.r. spectra of both complexes contain bands at 1 540 $\mathrm{cm^{-1}}$ *cf.* 1 560 $\mathrm{cm^{-1}}$ for related dimeric complexes containing phenolic oxygen bridges,[3] good supporting evidence for the assignment of this band to the phenolic C–O stretch in such Schiff-base complexes.

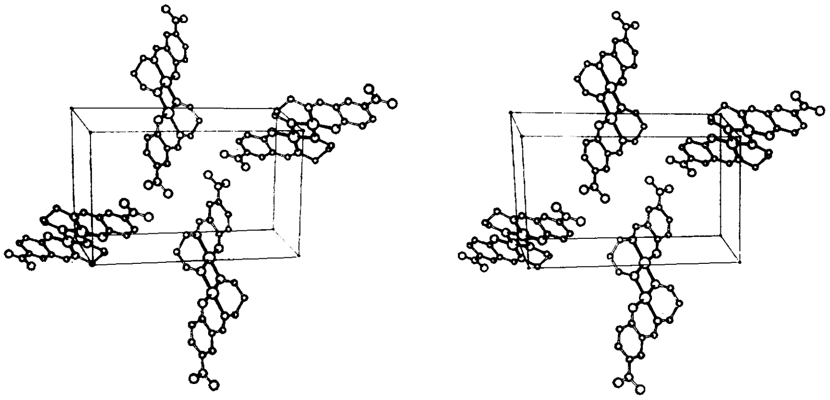


FIGURE 3 Molecular packing in (Ia)

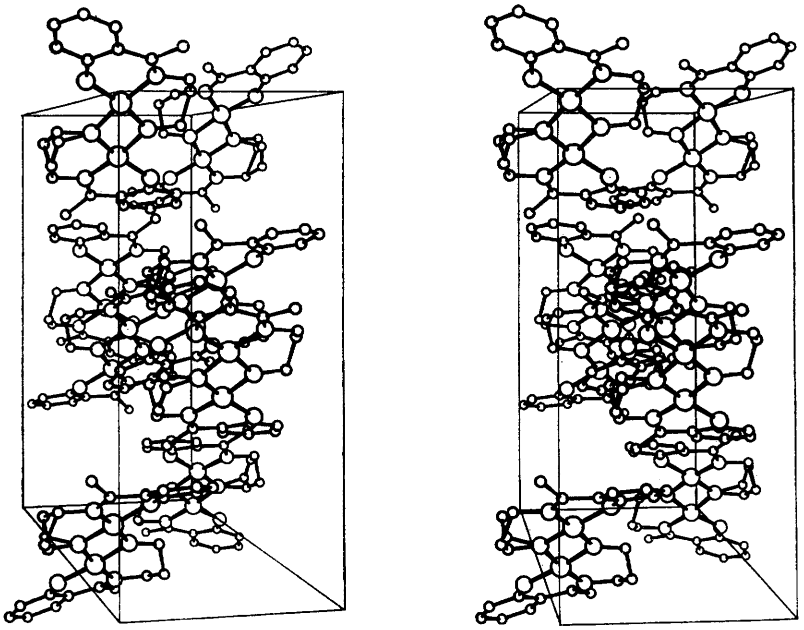


FIGURE 4 Molecular packing in (Ib)

TABLE 4

Closest intermolecular distances (Å)

(*a*) In (Ia)		
	Cu · · · Cu	3.65
	Cu · · · O(2)	3.10
(*b*) In (Ib)		
	Cu · · · C(9)	3.12
	Cu · · · C(5)	3.43
	Cu · · · Cu(2)	3.94
	O(1) · · · C(5)	3.40
	O(2) · · · C(9B′)	3.27

The magnetic moments of the complexes show little temperature dependence: 0.30 (Ia) and 0.26 (Ib) at 273 K; 0.31 and 0.33 B.M. at 305 K. Thus the complexes are almost diamagnetic, owing to very strong antiferromagnetic coupling between the adjacent copper atoms, and a singlet–triplet separation, $|2J|$, of the order of 1 000 $\mathrm{cm^{-1}}$ is implied. Because of the very low observed paramagnetism, the $|J|$ values cannot be estimated accurately, though a lower limit can be given.

A convenient albeit somewhat crude way to parametrise the degree of distortion from planarity of complexes of types (I) and (II) is the angle, τ, between the plane of the $\mathrm{Cu_2O_2}$ bridge and that of the remaining ligands. Values of 0 and 90°, respectively, for τ, are then necessary but not sufficient conditions for planar and tetrahedral copper(II) environments. Table 5 gives approximate least-squares planes which show that the general structural features of (Ia) and (Ib) closely resemble those of other type (I) complexes. Table 6 gives τ and $|J|$ values for the present complexes as well as others of types (I) and (II). These results demonstrate that the correlation between the copper geometry and strength of antiferromagnetic interaction, originally suggested for a few complexes of type (II), is quite well supported, and that the correlation is definitely not confined to complexes of type (II). The data support the hypothesis that the strength of antiferromagnetic interaction is determined by the efficiency of the Cu–O–Cu superexchange overlap: on this basis the $-2J$ values for complexes of type (I) should be large, as observed. The difference between the interplanar angles is dramatic (Table 4). Complex (Ia) is far closer to being totally coplanar, a property which distinguishes it from all the known complexes of type (I).

TABLE 5

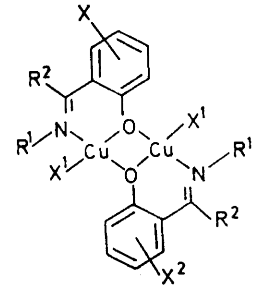
Coefficients of least-squares planes in the form $AX + BY + CZ = D$. Distances $(\text{Å} \times 10^4)$ of relevant atoms from the planes are given in square brackets

Atoms in plane	10^4A	10^4B	10^4C	10^4D
(a) In (Ia)				
(I): C(1)—(6)				
	−4 827	6 286	−6 098	−64 374
[C(1) −614, C(2) 392, C(3) 12, C(4) −208, C(5) −69, C(6) 489]				
(II): Cu, Cu(2), O(1), O(1′)				
	−5 687	5 866	−5 767	−6 0364
[Cu 0, Cu(2) 0, O(1) 0, O(1′) 0]				
(III): Cu, Cu(2), O(2), O(2′), N(1), N(1′)				
	−5 270	5 694	−6 309	−65 010
[Cu 35, Cu(2) −35, O(2) −9, O(2′) 9, N(1) −9, N(1′) 9]				
(IV): Cu, O(2), N(1)				
	−5 252	5 719	−6 301	−64 949
(V): N(2), O(3), O(4)				
	−6 119	5 525	−5 660	−66 278
(VI): O(2), O(2′), N(1), N(1′)				
	−5 268	5 697	−6 308	−65 013
[O(2) 0, O(2′) 0, N(1) 0, N(1′) 0]				
(b) In (Ib)				
(I): C(1)—(6)				
	−8 057	2 067	−5 550	96 049
[C(1) 205, C(2) −142, C(3) −3, C(4) 92, C(5) −27, C(6) −124]				
(I′): C(1′)—(6′)				
	−9 306	507	−3 625	83 215
[C(1′) −203, C(2′) 194, C(3′) −35, C(4′) −126, C(5′) 118, C(6′) 53]				
(II): Cu, Cu(2), O(1), O(1′)				
	−6 677	594	−7 421	13 4865
[Cu 267, Cu(2) 269, O(1) −267, O(1′) −269]				
(III): Cu, Cu(2), O(2), O(2′), N(1), N(1′)				
	−6 694	1 799	−7 208	129 603
[Cu −55, Cu(2) −99, O(2) −563, O(2′) −553, N(1), 626, N(1′) 644]				
(IV): Cu, O(2), N(1)				
	−6 641	1 403	−7 344	1.32 933
(VI′): Cu(2), O(2′), N(1′)				
	−6 770	2 187	−7 028	1.263 92
(VI): O(2), O(2′), N(1), N(1′)				
	−6 696	1 798	−7 206	1.295 42
[O(2) −596, O(2′) −597, N(1), 954, N(1′) 599]				

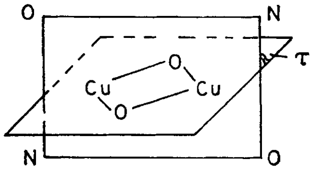
Planes:	(I)–(I′)	(I)′–(II)	(I′)–(II)	(I)–(IV)	(I′)–(IV)–(I)	(V)
I(a)	0	5.8	(5.8)	4.2	(4.2)	9.0
I(b)	16.0	12.4	26.7	13.7	27.0	

	(I)–(VI)	(I′)–(VI)	(II)–(III)	(II)–(IV)	(II)–(VI)
	4.0	(4.0)	4.0	4.0	4.0
	12.4	27.6	7.0	4.7	7.0

Planes:	(III)–(VI)	(IV)–(VI)	(IV′)–(VI)
1(a)	0.0	0.2	
1(b)	0.0	2.4	2.5



	R^1	R^2	X^1	X^2
(II) a;	Et	H	Cl	H
b;	Bu	Ph	Br	5-Cl
c;	Et	H	Br	H
d;	Me	H	Cl	H



No systematic relation is observed between the magnetic interactions and the Cu–O–Cu′ angle, in complexes of types (I) and (II). This does not mean that this angle is unimportant, but merely that it does not vary enough to play an important part, *i.e.* this variable has fortuitously been held approximately fixed over the range of complexes in Table 6, enabling the effect of the metal

TABLE 6

Some magnetic and structural features

Complex	$-J$/cm^{-1}	τ/°	Cu–O–Cu
(Ia) *	>500	4.0	106
(Ib) *	>400	7.0	104.2
(Ic) †		13.7	103.7
(Id) †		9.6	103.5
(Ie) †		10.4	104.0
(IIa) ‡	240	33.1	103.3
(IIb) ¶	220	35.5	101.2
(IIc) ‡	205	35.7	104.6
(IId) ‡	146	39.3	102.2

* Present work. † Ref. 3. ‡ Ref. 4. ¶ Ref. 5.

environment to be examined closely. Equally interesting is the absence of significant inductive effects upon varying substituents directly on the metal atoms (O, Cl, Br) as well as at other sites. Clearly the environments of the metal atoms and the bridging oxygens have the greatest effect on J and substituents are relatively unimportant except for any structural modifications they produce in the Cu_2O_2 bridge.

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