# Magnetic, Spectroscopic, and Structural Properties of Bis[bromo-, chloro-, and nitrato-(*N*-n-butyl-5-chloro-α-phenyl-2-hydroxybenzylidene)aminato-μ-*O*-copper(II)]

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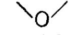
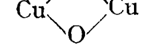
The title compounds were prepared by the action of copper nitrate or halide on bis[*N*-n-butyl(5-chloro-α-phenyl-2-hydroxybenzylidene)aminato] copper(II) which in turn was obtained from the reaction of copper(II) acetate with the n-butylamine adduct of 5-chloro-2-hydroxybenzophenone. The magnetic susceptibilities of the chloride, bromide, and nitrate adducts were determined as a function of temperature, and are interpreted in terms of binuclear molecules with the copper atoms in a four-co-ordinated, approximately planar, ligand environment, and bridged by the phenolic oxygens of the organic ligand. The electronic and i.r. spectra and a full three-dimensional *X*-ray crystal and molecular structure determination on the bromo complex support these conclusions. The precise environment about the  bridge in the bromo complex, and particularly the copper atoms, is in good agreement with that expected from the strength of antiferromagnetic interaction. All the complexes are believed to be four-co-ordinated, though the chlorine adduct is a dihydrate and the possibility of water co-ordination cannot be ruled out completely. A number of the i.r. peaks could be assigned unambiguously. E.s.r. spectra at 300 and 77 K of the binuclear complexes revealed only peaks due to the small trace of the monomeric parent complex remaining in these compounds.

It has been shown that binuclear copper(II) complexes derived from salicylaldimines or related ligands, exhibit antiferromagnetic interactions which depend more on the immediate environment of the  bridge than upon any other factors (such as ring substituents).[1-4] The environment about the copper atoms is particularly important, and as distortion from planarity increases toward tetrahedral, the strength of anti-

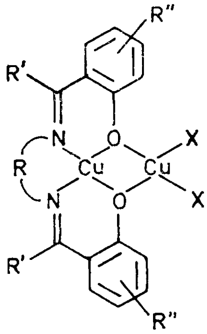
[1] E. Sinn and C. M. Harris, *Co-ordination Chem. Rev.*, 1969, **4**, 391.

[2] E. Sinn and W. T. Robinson, *J.C.S. Chem. Comm.*, 1972, 359.

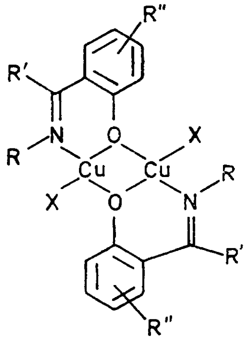
[3] C. A. Bear, J. M. Waters, and T. N. Waters, *Chem. Comm.*, 1971, 703.

[4] R. M. Countryman, W. T. Robinson, and E. Sinn, *Inorg. Chem.*, to be published.

ferromagnetic interactions decreases dramatically. This is true whether the ' tetrahedral ' distortion is applied to one of the two copper atoms of the binuclear molecule as in compounds of type (I), or to both copper atoms of the molecule as in the compounds (II).

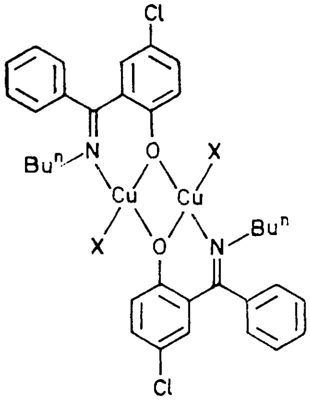


(I)



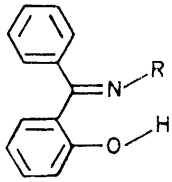
(II)

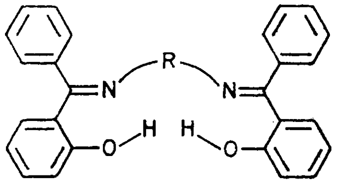
As part of a general investigation of the effect of structural changes upon the magnetic exchange interactions in such binuclear complexes, we have synthesized bis[bromo{*N*-n-butyl(5-chloro-α-phenyl-2-hydroxybenzylidene)aminato-μ-*O*}copper(II)] and the analogous complexes (IV) and (V). The structural changes have so far been effected by varying the groups R and R'.[1-5]



(III; X = Br)
(IV; X = Cl)
(V; X = ONO$_2$)

The addition of a phenyl ring in position 7 is an obvious steric factor which can assist in modifying the bridging structure. In addition, the insertion of this phenyl ring and the chloro group in position 5 should give some clues about the possibility of direct effects of the substituents on the magnetism aside from any structural changes they induce. The phenyl group in position 7 produces modifications of the properties of Schiff base complexes. One spectacular feature is the dramatic increase in the solubility in organic solvents of complexes derived from benzophenone ligands such as (VI) over those of related complexes, and ligands of type (VI) are considered to be an important general type.[6-9]





(VI)

EXPERIMENTAL

*Bis*[N-*n-butyl*(5-*chloro-α-phenyl*-2-*hydroxybenzylidene*)-*aminato*]*copper*, Cu(cbpb)$_2$.—To the n-butylamine adduct of 5-chloro-2-hydroxybenzophenone (2 g) dissolved in hot methanol (50 ml) was added copper acetate (1 g) dissolved in hot methanol (100 ml). Piperidine (3 ml) was added, and after boiling this solution for several minutes, bronze crystals of the complex precipitated from solution. These were filtered and washed with hot methanol and light petroleum (b.p. 40—60°) (Found: C, 64·35; H, 5·4; N, 4·05. Calc. for $C_{34}H_{34}Cl_2CuN_2O_2$: C, 64·10; H, 5·38; N, 4·40%).

*Bis*[*bromo*{N-*n-butyl*(5-*chloro-α-phenyl*-2-*hydroxybenzylidene*)*aminato*-μ-O}*copper*(II)].—Copper(II) bromide (1·2 g), dissolved in absolute ethanol (50 ml), was added to Cu(cbpb)$_2$ (2 g) in 2,2-dimethoxypropane (50 ml) and the mixture shaken for 1 h. The black crystals were then filtered off (Found: C, 47·6; H, 4·15; N, 3·25. Calc. for $C_{34}H_{34}Br_2Cl_2Cu_2N_2O_2$: C, 47·46; H, 3·98; N, 3·26%).

*Bis*[*nitrato*{N-*n-butyl*(5-*chloro-α-phenyl*-2-*hydroxybenzylidene*)*aminato*-μ-O}*copper*(II)].—Copper nitrate hexahydrate (1 g) was shaken with Cu(cbpb)$_2$ (2 g) in 2,2-dimethoxypropane (50 ml) for 1 h. The product was evaporated to dryness, washed with light petroleum, ground to a powder, and washed again with absolute ethanol (to remove any unreacted copper nitrate) (Found: C, 49·6; H, 4·25; N, 6·65. Calc. for $C_{34}H_{34}Cl_2Cu_2N_4O_8$: C, 49·52; H, 4·16; N, 6·79%).

*Bis*[*chloro*{N-*n-butyl*(5-*chloro-α-phenyl*-2-*hydroxybenzylidene*)*aminato*-μ-O}*copper*(II)]*dihydrate*.—Copper(II) chloride (1·5 g) dissolved in absolute ethanol (50 ml) was added to Cu(cbpb)$_2$ (2 g) in 2,2-dimethoxypropane (50 ml) and the mixture shaken until the bright red powder precipitated. This powder was then filtered off (Found: C, 50·65; H, 4·45; N, 3·5. Calc. for $C_{34}H_{38}Cl_4Cu_2N_2O_4$: C, 50·57; H, 4·74; N, 3·47%).

Microanalyses were carried out by Dr. E. Challen at the University of New South Wales. Magnetic susceptibility measurements were made on a Foner vibrating magnetometer.[10] Electronic spectra were measured on a Zeiss PMQ II spectrophotometer with a RA3 reflectance attachment calibrated with magnesium oxide. I.r. spectra were recorded in the range 1800—400 cm$^{-1}$ on a Hitachi EPI 63 spectrometer and in the range 400—200 cm$^{-1}$ on a Jasco DS 4039. E.s.r. spectra were recorded on a Varian V 4500-42-X spectrometer with a variable temperature attachment operating *ca.* 9·3 G Hz.

*Crystal Data for Complex* (III).—$M = 823·8$, Monoclinic, $P2_1/c$. $a = 10·895$ (7), $b = 8·978$ (5), $c = 19·90$ (2) Å, $\beta = 113·46$ (7)°, $U = 1786$ Å$^3$, $Z = 2$, $D_c = 1·54$; $D_0 =$

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[5] R. B. Coles, C. M. Harris, and E. Sinn, *Inorg. Chem.*, 1969, **8**, 2607.

[6] G. M. Mockler, G. W. Chaffey, E. Sinn, and H. Wong, *Inorg. Chem.*, 1972, **11**, 1308.

[7] D. P. Graddon and G. M. Mockler, *Austral. J. Chem.*, 1967, **20**, 21.

[8] D. P. Graddon and G. M. Mockler, *Austral. J. Chem.*, 1968, **21**, 907.

[9] D. P. Graddon and G. M. Mockler, *Austral. J. Chem.*, 1968, **21**, 1487.

[10] S. Foner, *Rev. Sci. Instr.*, 1959, **30**, 548.

1·55 (3) g cm$^{-3}$ by flotation, $F(000) = 792$. Mo-$K_\alpha$ Radiation using the procedure outlined in ref. 11, $\lambda = 0{\cdot}710$ Å, $\mu$(Mo-$K_\alpha$) = 38·0 cm$^{-1}$.

*Intensity Measurements.*—The crystal used was an irregular rectangular block of dimensions *ca.* 0·20 × 0·30 × 0·25 mm mounted with the *a* axis parallel to the $\phi$ axis of a Picker four circle diffractometer controlled by an XDS Sigma 2 computer. We are grateful to Dr. R. F. Bryan for access to this system and some of the computer programs used. Although the preliminary precession photography appeared normal, measurement of the peak profile on the diffractometer showed the peaks to be doubled, due either to the crystal being split along the plane perpendicular to the *c* axis, or to the growth of twinned crystals parallel to this plane. Investigation of several other crystals failed to produce any improvement. Symmetrical 3·5° $\theta$—$2\theta$ scans, 2° min$^{-1}$, were required to measure the complete peak. A quadrant containing the $hkl$ and $hk\bar{l}$ reflections was examined at 1668 independent reciprocal lattice points with $2\theta < 40°$, yielding 506 well resolved reflections with significant scattering intensity above the background. Two reference reflections showed no decline in intensity during the counting experiment. No absorption corrections were applied.

TABLE 1

Atomic positional and thermal parameters with estimated standard deviations in parentheses

| Atom | $x$ | $y$ | $z$ | $B$ |
|---|---|---|---|---|
| Cu | −0·0694(3) | 0·1484(3) | −0·0075(2) | [3·20(1)] * |
| Br | −0·0367(3) | 0·3523(5) | 0·0680(2) | [4·25(1)] * |
| Cl | 0·6400(8) | 0·2901(9) | 0·0682(5) | [3·73(4)] * |
| O | 0·109(2) | 0·063(2) | 0·031(1) | 3·6(5) |
| N | 0·241(2) | 0·796(2) | 0·090(1) | 2·3(6) |
| C(1) | 0·354(2) | 0·030(3) | 0·073(1) | 1·7(7) |
| C(2) | 0·235(2) | 0·119(3) | 0·042(1) | 1·3(6) |
| C(3) | 0·251(3) | 0·267(3) | 0·020(2) | 2·1(7) |
| C(4) | 0·371(4) | 0·317(4) | 0·025(1) | 3·4(8) |
| C(5) | 0·477(3) | 0·225(3) | 0·056(2) | 3·2(8) |
| C(6) | 0·477(3) | 0·079(3) | 0·084(1) | 1·0(6) |
| C(7) | 0·345(2) | 0·878(3) | 0·103(1) | 1·8(6) |
| C(8) | 0·479(3) | 0·816(3) | 0·162(1) | 2·6(7) |
| C(9) | 0·536(2) | 0·701(3) | 0·136(1) | 1·7(7) |
| C(10) | 0·667(3) | 0·655(5) | 0·190(2) | 4·3(8) |
| C(11) | 0·718(3) | 0·698(3) | 0·262(2) | 3·4(8) |
| C(12) | 0·650(3) | 0·813(3) | 0·285(1) | 3·6(8) |
| C(13) | 0·521(2) | 0·870(4) | 0·233(1) | 1·9(7) |
| C(14) | 0·235(3) | 0·655(4) | 0·129(1) | 3·1(7) |
| C(15) | 0·137(4) | 0·668(7) | 0·157(2) | 10·1(13) |
| C(16) | 0·141(6) | 0·777(7) | 0·198(3) | 15·1(22) |
| C(17) | 0·040(5) | 0·811(5) | 0·233(3) | 10·9(15) |

| Atom | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| Cu | 58(4) | 96(6) | 23(1) | −7(9) | −10(2) | 7(4) |
| Br | 101(4) | 118(5) | 30(1) | −13(8) | −2(2) | −10(4) |
| Cl | 62(10) | 107(18) | 36(4) | −45(11) | −5(5) | 8(7) |

The exponent has the form: $(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$.

* Isotropic $B$ values at $R$ 0·10 before introduction of anisotropic thermal parameters.

*Solution and Refinement of Structure.*—The positions of bromine, copper, and chlorine atoms were unambiguously located from an unmodified Patterson function computed on all data. The phases calculated from these atoms were used in subsequent three-dimensional electron density syntheses and all other atoms with the exception of the n-butyl group were readily located ($R$ 0·131, unit weights). A three-dimensional difference electron density synthesis at this stage showed a continuous area of positive electron density in the expected region of the n-butyl chain. Several model conformations were postulated with only the atom set in Table 1 refining satisfactorily ($R$ 0·101). At this stage, anisotropic thermal parameters were applied to the bromine, copper, and chlorine atoms and a weighting scheme adopted with $w = I/6000$ for reflections with intensity $I < 6000$ counts, $w = |F_o|/90$ for those with $|F_o| > 90$, and $w = 1{\cdot}0$ for the remainder ($R$ 0·073). Scattering curves for neutral atoms were used,[12] and those for bromine, copper, and chlorine were corrected to include the real and imaginary anomalous dispersion terms.[13] A final difference electron density synthesis showed no structurally significant features, the maximum peak height being 1e Å$^{-3}$.

## RESULTS AND DISCUSSION

*Structure of Complex* (III).—Table 1 contains the atomic parameters defining the crystal structure of the molecule and their estimated standard deviations, and Table 2 the bond distances and angles. The final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21027 (2 pp.).*

Figure 1 gives a stereoscopic view of the molecule, and Figure 2 the packing diagram. The molecules are discrete, neutral, dimeric units with a crystallographic centre of symmetry which requires the two copper and two oxygen atoms to lie in a plane. With the exception of the terminal n-butyl methylene and methyl groups, the molecule is constructed from several planar groups (Table 3).

The non-planarity of the copper environment, $(CuNOX)_2$, is conveniently measured by the dihedral angle, $\tau$, between the planes formed by the $Cu_2O_2$ and $Cu_2N_2X_2$. $\tau$ Ranges from 0 to 90° with distortion from a planar to a tetrahedral environment. The value of 35·6° found for this compound lies between the values found for chloro(*N*-ethylsalicylaldimino)copper(II), $(CuC_9H_{10}NOCl)_2$ and chloro(*N*-methylsalicylaldimino)-copper(II), $(CuC_8H_9NOCl)_2$[4] (Table 4). The possibility, common in copper stereochemistry, of co-ordination in the fifth copper position by a donor atom associated with an adjacent molecule is circumvented by the phenyl group in position 7. This, for example, restricts the closest approach of the chlorine atoms of the nearest molecule to 7·70 Å.

Each copper atom is coplanar with the associated 5-chloro-2-hydroxybenzylideneaminato bidentate ligand segment. The height of the bromine atom above this plane (1·95 Å) is clearly a steric effect. If the bromine atom were coplanar, the contact distance between Br and the $\alpha$-carbon would be 3·2 Å, compared with the sum of the Van der Waals contact radii, 3·95 Å. The experimentally measured distance is 3·58 Å.

As summarised in Table 4, similar geometric con-

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* For details of Supplementary Publications, see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20. (Items less than 10 pp. supplied as full-size copies).

[11] G. A. Melson, P. T. Greene, and R. F. Bryan, *Inorg. Chem.*, 1970, **9**, 1116.

[12] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[13] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

siderations apply to the chloro *N*-methyl and *N*-ethyl salicylaldimine copper(II) complexes.

The planarity imposed on the ligand by virtue of electron delocalisation and the tendency for the copper ion to assume an overall square planar geometry, rather than $CuO_2N$ being planar with the halogen atom highly distorted, results in a compromise whereby the phenol oxygens are twisted out of the plane, the degree of twist being dependent on the peripheral substituent interactions.

TABLE 2

Interatomic distances and angles with estimated standard deviations in parentheses

(a) Bonded distances/Å

| | | | |
|---|---|---|---|
| Cu–Br | 2·304(6) | C(7)–N | 1·29(3) |
| Cu–O | 1·95(2) | C(7)–C(8) | 1·57(4) |
| Cu–O′ | 1·96(2) | C(8)–C(9) | 1·41(5) |
| Cu–N | 2·01(2) | C(9)–C(10) | 1·46(4) |
| O–C(2) | 1·40(3) | C(10)–C(11) | 1·36(4) |
| C(1)–C(2) | 1·44(4) | C(11)–C(12) | 1·44(4) |
| C(2)–C(3) | 1·44(4) | C(12)–C(13) | 1·46(4) |
| C(3)–C(4) | 1·35(4) | C(13)–C(8) | 1·39(4) |
| C(4)–C(5) | 1·35(4) | N–C(14) | 1·50(5) |
| C(5)–C(6) | 1·42(4) | C(14)–C(15) | 1·39(5) |
| C(1)–C(6) | 1·35(4) | C(15)–C(16) | 1·26(8) |
| C(5)–Cl | 1·79(3) | C(16)–C(17) | 1·56(8) |
| C(1)–C(7) | 1·51(4) | | |

(b) Non-bonded distances/Å

| Atom 1 | | Atom 2 | Distance | Symmetry operation of atom 1 with respect to atom 2 symmetry |
|---|---|---|---|---|
| Cu | ··· | Cu | 3·019(7) | 2 |
| O | ··· | O | 2·48(3) | 2 |
| Cu | ··· | Cl | 7·70(8) | 3 |
| Cu | ··· | C(17) | 5·39(2) | 5 |
| Cu | ··· | Br | 4·898(6) | 6 |
| Br | ··· | Cl | 3·568(7) | 7 |
| Br | ··· | N | 4·92(2) | 1 |
| Br | ··· | C(14) | 3·85(2) | 1 |
| Br | ··· | C(15) | 3·48(2) | 1 |

Symmetry operation:

1 — $x, y, z$

2 — $\bar{x}, \bar{y}, \bar{z}$

3 — $x, \frac{1}{2} - y, \frac{1}{2} + z$

4 — $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$

5 — $x, 1 + y, z$

6 — $\bar{x}, 1 - y, \bar{z}$

(c) Bond angles (°)

| | | | |
|---|---|---|---|
| O–Cu–O′ | 78·8(8) | C(4)–C(5)–Cl | 118(2) |
| O–Cu–N | 152·1(8) | C(6)–C(5)–Cl | 113(2) |
| O–Cu–Br | 152·5(6) | C(1)–C(7)–C(8) | 115(3) |
| O′–Cu–N | 89·8(8) | N–C(7)–C(8) | 116(3) |
| O′–Cu–Br | 100·7(6) | C(7)–C(8)–C(9) | 114(2) |
| N–Cu–Br | 101·0(6) | C(7)–C(8)–C(13) | 118(2) |
| Cu–O–C(2) | 133(2) | C(9)–C(8)–C(13) | 128(3) |
| O–C(2)–C(1) | 122(2) | C(8)–C(9)–C(10) | 113(3) |
| C(2)–C(1)–C(7) | 119(2) | C(9)–C(10)–C(11) | 124(2) |
| C(1)–C(7)–N | 129(2) | C(10)–C(11)–C(12) | 119(3) |
| C(7)–N–Cu | 118(2) | C(11)–C(12)–C(13) | 121(2) |
| Cu–O–Cu′ | 101·2(9) | C(12)–C(13)–C(8) | 115(2) |
| C(1)–C(2)–C(3) | 117(2) | Cu–N–C(14) | 114(2) |
| C(2)–C(3)–C(4) | 121(2) | N–C(14)–C(15) | 109(4) |
| C(3)–C(4)–C(5) | 117(3) | C(14)–C(15)–C(16) | 119(5) |
| C(4)–C(5)–C(6) | 128(3) | C(15)–C(16)–C(17) | 126(5) |
| C(5)–C(6)–C(1) | 113(2) | C(7)–N–C(14) | 127(3) |
| C(6)–C(1)–C(2) | 124(3) | | |

Due to the inability of the bidentate ligand to adjust beyond narrow limits, increase in τ results in a lengthening of the oxygen bond to the second half of the dimer. As this Cu–O bond weakens, the interaction between the paramagnetic centers will decrease and the system will tend toward normal monomeric behaviour.

As expected, the phenyl group at position 7 is nearly orthogonal to the remainder of the ligand. Apart from ensuring intermolecular interactions in the crystal are minimised, it also plays a steric role in directing the conformation assumed by the *N*-alkyl chain, in particular the α-carbon. The importance of this function would increase as more bulky substituents were inserted on to the nitrogen atom.

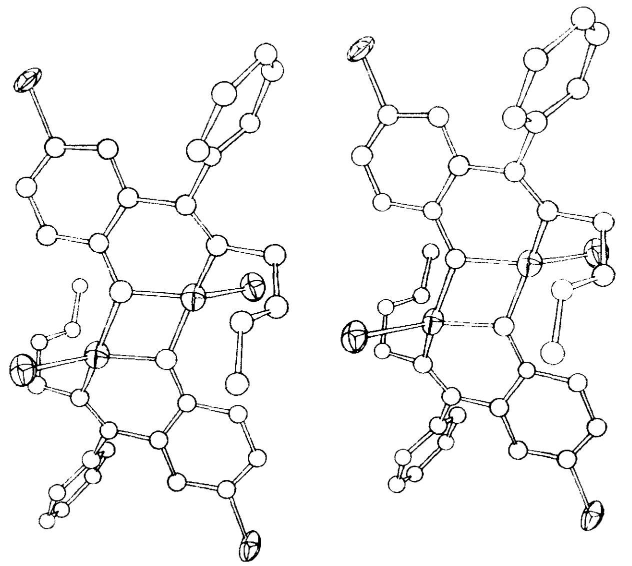

FIGURE 1 A stereoscopic view of complex (III) showing the labelling of atoms used in the text. 50% Probability envelopes of the copper, bromine, and chlorine atoms are included

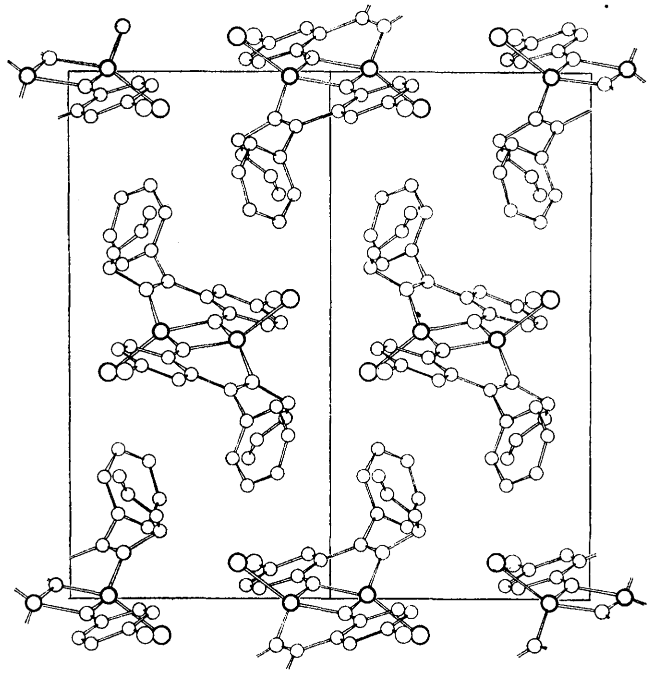

FIGURE 2 View of the unit cell of complex (III) projected on the *bc* plane

*Magnetic Properties.*—Magnetic susceptibilities (Table 5) indicate intramolecular interactions strongest in the

TABLE 3

Least squares planes in the form $AX + BY + CZ = D$, where $X = ax + cz\cos\beta$, $Y = by$, $Z = cz\sin\beta$. $x$, $y$, $z$ are fractional co-ordinates. All atoms are given unit weights

| Plane No. | Atoms | $A$ | $B$ | $C$ | $D$ | Minimum root |
|---|---|---|---|---|---|---|
| 1 | Cu Br O N O′ | −0·654 | −0·304 | 0·692 | 0·183 | 0·610 * |
| 2 | Cu Br O N Cu′ Br′ O′ N′ | −0·739 | −0·377 | 0·559 | 0·000 | 0·866 * |
| 3 | Cu O Cu′ | −0·446 | −0·143 | 0·883 | 0·000 | 0·000 |
| 4 | Cu C2 Cu′ | −0·299 | −0·059 | 0·952 | 0·000 | 0·000 |
| 5 | Cu Br N Cu′ Br′ N′ | −0·791 | −0·409 | 0·455 | 0·000 | 0·007 |
| 6 | C(1) C(2) C(3) C(4) C(5) C(6) | −0·230 | 0·361 | 0·904 | 0·569 | 0·003 |
| 7 | N O C(1) C(2) C(7) | −0·287 | 0·326 | 0·901 | 0·402 | 0·016 |
| 8 | O C(1) C(2) C(3) C(4) C(5) C(6) C(7) N Cl | −0·244 | 0·350 | 0·904 | 0·496 | 0·028 |
| 9 | C(8) C(9) C(10) C(11) C(12) C(13) | −0·643 | −0·721 | 0·258 | −0·538 | 0·007 |

* Non-planar.

Distances of atoms from planes/Å (atoms incorporated in exact planes have been omitted)

1 Cu (−0·226), Br (0·330), O (−0·580), N (0·262), O′ (0·213)
2 Cu (−0·063), Cu′ (0·063), Br (0·196), O (−0·593), N (0·198)
3 Br (1·063), Cl (−2·144), Cl (−0·471), N (0·866)
4 Br (1·276), Cl (−0·894), O (0·266), N(1·108)
5 Cu (−0·055), Br (0·014), N (−0·014), O (−0·719)
6 C(1) (−0·025), C(2) (−0·003), C(3) (0·027), C(4) (−0·022), C(5) (−0·005), C(6) (0·027), Cu (−0·052), Br (1·909), Cl (0·015), N (−0·176)
7 Cu (0·110), Br (2·01), Cl (−0·275), C(2) (−0·001), O (0·024), C(7) (0·093), N (−0·060), C(14) (0·267)
8 Cu (0·016), O (−0·014), C(1) (0·001), C(2) (0·027), C(3) (0·038), C(4) (−0·034), C(5) (−0·019), C(6) (0·030), C(7) (0·107), N (−0·109), Cl (−0·025), Br (1·954), C(14) (0·176)
9 C(8) (−0·041), C(9) (0·050), C(10) (−0·044), C(11) (0·025), C(12) (−0·010), C(13) (0·020)

Dihedral angles (°)

| Planes | Angle | Planes | Angle |
|---|---|---|---|
| 3,8 | 31·8 | 5,8 | 62·6 |
| 3,5 | 35·6 | 6,7 | 3·4 |
| 8,9 | 83·1 | | |

TABLE 4

Comparison of the structural and magnetic parameters of the complexes discussed in the text

| Compound | $\tau$ | Cu–Cu | Cu–N–C$_\alpha$ | X–C$_\alpha$ † | | X–C$_\beta$ | $\lvert J\rvert$/cm$^{-1}$ |
|---|---|---|---|---|---|---|---|
| | | | | Experimental | Calc. planar | | |
| $[CuC_8H_9NOCl]_2$ | 39·3 | 3·04 | 118 (1) | 3·26 (3·8) | 2·8 | | 146 |
| $[CuC_{17}H_{17}NOBr]_2$ | 35·6 | 3·02 | 114 (2) | 3·85 (3·95) | 3·2 | 3·48 (3·95) | 220 |
| $[CuC_9H_{10}NOCl]_2$ | 33·1 | 3·05 | 118 (1) | 3·37 (3·8) | 3·2 | 3·79 (3·95) | 240 |

† Van der Waals radii for non-bonded contact distances are given in parentheses.

TABLE 5

Magnetic susceptibilities and moments (c.g.s.u.); assumed $g = 2·15$

| | $Cu_2(cbpb)_2Br_2$ | | $Cu_2(cbpb)_2Cl_2,2H_2O$ | | $Cu_2(cbpb)_2(NO_3)_2$ | |
|---|---|---|---|---|---|---|
| $T$/K | $10^6\chi$ | $\mu$ | $10^6\chi$ | $\mu$ | $10^6\chi$ | $\mu$ |
| 4·6 | 4390 | 0·40 | | | | |
| 7·6 | 2761 | 0·40 | | | | |
| 17·4 | 1259 | 0·41 | | | | |
| 27·7 | 703 | 0·38 | | | | |
| 53·8 | 398 | 0·41 | | | | |
| 79·2 | 366 | 0·44 | 730 | 0·65 | 4581 | 1·69 |
| 83·9 | 250 | 0·36 | 720 | 0·67 | 4578 | 1·74 |
| 91·8 | 269 | 0·39 | 648 | 0·66 | 4487 | 1·80 |
| 101 | 265 | 0·41 | 640 | 0·68 | 4261 | 1·84 |
| 111 | 280 | 0·44 | 618 | 0·70 | 3973 | 1·86 |
| 122 | 310 | 0·49 | 571 | 0·71 | 3589 | 1·86 |
| 178 | 402 | 0·70 | 580 | 0·86 | 2539 | 1·88 |
| 196 | 429 | 0·76 | 617 | 0·93 | 2285 | 1·87 |
| 216 | 495 | 0·87 | 645 | 1·00 | 2104 | 1·88 |
| 238 | 539 | 0·95 | 638 | 1·05 | 1893 | 1·87 |
| 252 | 583 | 1·03 | 654 | 1·09 | 1750 | 1·85 |
| 277 | 568 | 1·06 | 644 | 1·14 | 1644 | 1·87 |
| 298 | 608 | 1·14 | 698 | 1·23 | 1482 | 1·84 |
| 314 | 630 | 1·20 | 691 | 1·26 | 1392 | 1·83 |
| | $J \doteqdot -220$ cm$^{-1}$<br>$p = 0·045$ | | $J \doteqdot -220$ cm$^{-1}$<br>$p = 0·13$ | | $J \doteqdot -15$ cm$^{-1}$ | |

bromo complex (III) and weakest in the nitrate adduct. From its structure, (III) is expected to have a singlet–triplet separation ($-2J$) between those for dichlorobis(*N*-methylsalicylaldimino)dicopper(II) and its *N*-ethyl analogue, and closer to the latter value. The $J$ value of *ca.* $-200$ cm$^{-1}$ conforms very well with this expectation. In fact, the magnetic susceptibility is so weak that the contribution of paramagnetic impurities was significant in (III). The measurements were extended to liquid helium temperatures for this complex, to improve the estimation of the impurity contribution, and the results were fitted to equation (1) for a dimer with proportion of paramagnetic impurity $p$:

$$\chi = \frac{L\beta^2 g^2}{3kT}\,[(1 + \tfrac{1}{3}e^{-2J/kT})^{-1}(1 - p) + 0·75p] + N\alpha \tag{1}$$

$N\alpha$ is the temperature independent paramagnetism, assumed to be $6 \times 10^{-5}$ c.g.s.u. and the other symbols have their usual meaning. The value of $p$ corresponds to 4% paramagnetic impurity if the impurity is assumed to conform to the Curie Law and have the molecular weight of the dimeric complex (of course a smaller percentage of a more strongly paramagnetic impurity would have the same effect; no impurities are evident on microscopic examination of the crystals). The uncertainties in this procedure and the absence of a maximum in the $\chi$ *vs.* $T$ data in the available temperature range produce some inherent uncertainties in the $J$ value, which can probably not be overcome with the available instrumentation. A $g$ value of 2·15 was assumed, to permit direct comparison with the complexes of type (II) (Table 4). A range of $g$ values would produce a satisfactory fit to the experimental data, by adjustment of $J$ and $p$. However, given the absence of a susceptibility maximum and the limits of experimental accuracy, nothing is gained by doing this. Attempts to measure $g$ directly by e.s.r. were not successful. The e.s.r. spectra at 300 and 77 K closely resembled the powder spectrum of the parent complex Cu(cbpb)$_2$, and the peak intensities grew markedly with decreasing temperature, as expected for a normal paramagnet, and not an exchange-coupled dimer.

The susceptibilities indicate that the chloro complex, (IV), contains considerably more paramagnetic impurity than (III), so that estimation of $J$ is far more uncertain. It can only be said that the $J$ values have approximately similar magnitudes, which constitutes some evidence for a similar structure in the two complexes. The nitrato complex, (V), shows remarkably little exchange interaction, and a somewhat different structure is not ruled out for this complex. There is good evidence [14,15] that copper salicylaldimine complexes and complexes based on the ligands (VI) form binuclear nitrato adducts of type (I) and (II), but so far no crystal structures of such compounds have been determined. Unfortunately we failed to obtain any samples of (IV) or (V) suitable for *X*-ray work.

*Electronic Spectra.*—The electronic spectra (Table 6) are in keeping with approximately planar four-co-ordinated copper(II) environments, for the chloride, bromide, and nitrate adducts. In the parent compound Cu(cbpb)$_2$, weak Cu–O bonds are possible between neighbouring molecules as in the case of bis(*N*-methylsalicylaldimino)copper(II).[16] The resulting square pyramidal arrangement would not be a large perturbation from a square planar configuration.

TABLE 6

Solid state electronic spectra of copper complexes [a]

| Complex | Maxima | |
|---|---|---|
| Cu(cbpb)$_2$ | 16 500sh | 13 500sh |
| Cu$_2$(chpb)$_2$Cl$_2$,2H$_2$O | 12 400 | 11 000sh |
| Cu$_2$(cbpb)$_2$Br$_2$ | 13 000br | 10 000sh |
| Cu$_2$(chpb)$_2$(NO$_3$)$_2$ | 15 000 | 11 500sh |

[a] $\bar{\nu}$ in cm$^{-1}$.

*Infrared Spectra.*—The change in i.r. spectra upon formation of such binuclear complexes as (III) from the monomeric Schiff base complex is of considerable interest. A shift in the band *ca.* 1540 cm$^{-1}$ was found to be a reliable criterion for binuclear complex formation *via* bridging phenolic oxygens in complexes of types (I) and (II).[1,5,14,15] The expected shift is indeed observed between the parent Cu(cbpb)$_2$ complex and its binuclear derivatives. Some assignments are summarised in Table 7, and others are discussed below.

TABLE 7

Spectra/cm$^{-1}$

Infrared and empirical assignments

| Cu(cbpb)$_2$ | Complex (III) | (V) | (IV) | Assignment |
|---|---|---|---|---|
| 1603 | 1600 | | | ν(C–C)phenyl [a] |
| 1595 | 1584 | 1590 | 1600 | ν(C=N) |
| 1525 | 1545 | 1530 | 1540 | ν(C=N) + ν(C–O) + ν(C–C) coupled [b] |
| 1491 | 1489 | 1495 | 1490 | phenyl (C–C) [a] |
| 1409 | 1396 | 1405 | 1395 | ν(C–N) [c] |
| 1344 | 1282 | 1285 | 1280 | ν(C–O) [d] |
| 1325 | 1326 | 1325 | 1325 | CH$_2$ wagging |
| 1252<br>1237 | 1237 | 1235 | 1235 | phenyl ring vibrations |
| 1200<br>700 | | | | β(CH) inplane vibr. and γ(CH) out of plane vibr. of mono- and tri-substituted benzene rings |
| 623 | 633 | 628 | 634 | δ(C–O (?) |
| | 539 | | 590 | |
| 539 s | 550 | 538 | 552 | ν(M–O) + ligand vibration |
| 525 sh | | 515 | 535 | |
| 521 s | | | 525 w | |
| 496 | | | | |

[a] L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' 2nd edn., Wiley, New York, 1968; K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' Wiley, New York, 1963. [b] A. Bigotti, V. Galasso, and G. DeAlti, *Spectrochim. Acta*, 1972, **28A**, 1581. [c] G. C. Perry and D. A. Thornton, *J. Inorg. Nuclear Chem.*, 1972, **34**, 3357; G. Dudek, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 241. [d] J. E. Kovacic, *Spectrochim. Acta*, 1967, **23A**, 183.

The nitrato and chloro complexes exhibited bands which were broader and less well resolved than those of (III) and the parent complex, so the latter two were most closely studied. The data are considered accurate to 1—2 cm$^{-1}$ while those on complexes (IV) and (V) generally have errors of $\pm 3$ cm$^{-1}$ or more. The shifts observed with (IV), particularly of the band *ca.* 1540 cm$^{-1}$ are unusually small, which again may be an indication of a significant structure difference, *e.g.* weaker bridging bonds, but resolution is not good enough to state this definitely. No bands were observed in (V) which could confidently be assigned to any of the NO$_2$ modes. However this is not too surprising, since in simpler analogous nitrato complexes, these modes were also difficult to observe.[14]

The chloro complex showed no bands in the region 750—1000 cm$^{-1}$, characteristic of co-ordinated water, other than the C–H vibrations which were also observed in (III) and in the parent complex. Large broad peaks characteristic of O–H stretching modes in lattice water were observed in the region 3200—3500 cm$^{-1}$, though the H–O–H bending mode was not observed at 1600—1630 cm$^{-1}$. Thus water co-ordination to the metal atom is not supported by the i.r. data, though it is not conclusively ruled out.

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[14] J. O. Miners, E. Sinn, R. B. Coles, and C. M. Harris, *J.C.S. Dalton*, 1972, 1149.

[15] G. M. Mockler and E. Sinn, unpublished work.

[16] D. Hall, S. V. Sheat, and T. N. Waters, *Chem. Comm.*, 1966, 436.

The absence of splitting in the band *ca.* 540 cm$^{-1}$ has been taken as indicative of a *trans* structure, as postulated here, rather than *cis*.[17] Other bands of interest are a probable Cu–O stretching mode at 365—375 cm$^{-1}$ and Cu–N *ca.* 330 and 300 cm$^{-1}$, though coupling modes and overlapping ligand skeletonal deformation bands increase intensities within the region and make assignments tentative. A band at 278 cm$^{-1}$ in the bromo complex is tentatively assigned to a terminal Cu–Br vibration.[18] It is anticipated that further crystallographic studies will be of great value in understanding the i.r. spectra of such complexes, just as it has already been invaluable in demonstrating the relation between magnetic interaction and structural features.

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[17] N. S. Biradar, V. H. Kulkarni, and N. N. Sirmokadam, *J. Inorg. Nucl. Chem.*, 1972, **34**, 3651.

[18] D. E. Billing, A. E. Underhill, D. M. Adams, and D. M. Morris, *J. Chem. Soc.* (*A*), 1966, 902; M. Goldstein, E. F. Mooney, A. Anderson, and A. Gebbie, *Spectrochim. Acta*, 1965, **21**, 105; C. W. Frank and L. B. Rogers, *Inorg. Chem.*, 1956, **5**, 615.