Crystal and Molecular Structure and Magnetic Properties of a Tetrameric Copper Complex formed by the Terdentate Ligand *N*-2-Pyridylsalicylaldimine

By **J. Drummond** and **J. S. Wood**,*† Chemistry Department, University of Southampton, Southampton

The crystal and molecular structure of the tetranuclear complex tetrakis[(aquo)-(*N*-2-pyridylsalicylaldiminato)-copper(II)] tetranitrate has been determined from counter-collected single-crystal X-ray diffraction data and refined to R 0·072 for 1570 independent reflections. Two complex cations, having crystallographically imposed $D_2(222)$ point symmetry, occupy a tetragonal unit cell, space group $P4_22_12$, of dimensions: $a = 14·83$ and $c = 13·58$ Å. The four copper atoms in the tetranuclear cluster are situated in an almost square arrangement, the two independent copper–copper distances being 3·077(2) and 3·171(2) Å. The tridentate Schiff-base ligand is co-ordinated to three different copper atoms, the phenolic oxygen bridging two of the atoms, while the pyridine nitrogen atom is co-ordinated to the third. The water molecule occupies the axial position of a distorted square pyramidal co-ordination sphere about the copper atom, while the nitrate ion is not co-ordinated and appears to be statistically disordered between two sites in the crystal.

The magnetic susceptibility measured over the range 90—300 K indicates an antiferromagnetic coupling between the pairs of oxygen bridged copper atoms, with an interaction constant J/k of ca. -60 K. There appears to be little, if any, interaction between the two binuclear units making up the tetrameric complex ion.

A MAJORITY of the complexes of copper with terdentate Schiff-base ligands exhibit magnetic moments appreciably reduced from the values normally observed for magnetically dilute copper(II) complexes.[1-3] While it has often been possible to account quantitatively for the magnetic behaviour of several of these species in terms of one or other polynuclear (most often binuclear) models,[4-6] the interpretations are not without ambiguity, even when the molecular geometry of the complex is known from X-ray study.[7]

A group of copper complexes formed by several terdentate Schiff-base ligands derived from salicylaldehyde and substituted salicylaldehydes has recently
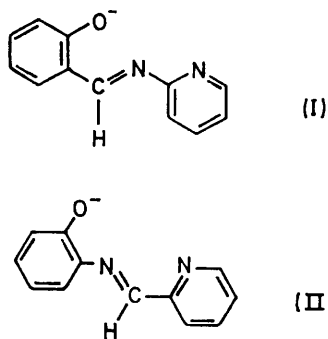
been described by Hatfield and Bunger.[8] For one of these formed by 2-pyridylsalicylaldimine, (I), a trimeric structure was suggested on the basis of its magnetic properties. By contrast, the copper complex formed by the structural isomer of this ligand (II) has a magnetic moment consistent with a monomeric structure. Several other copper complexes containing similar potentially

terdentate Schiff-base ligands derived from 2-amino-pyridine have also been reported,[9] but these have a ligand–metal ratio of 2 : 1 and their magnetic properties are consistent with a monomeric formulation. In these compounds the Schiff bases therefore only appear to be functioning as bidentate ligands.

In order to obtain more information on the co-ordination mode of this class of Schiff-base ligands and to derive a model for the interpretation of magnetic properties, an X-ray structure analysis of the 1 : 1 complex formed by ligand (I), was undertaken and its magnetic susceptibility was measured over a temperature range. While this study was in progress, it was suggested that a trimeric structure would be unlikely on stereochemical grounds,[10] and our analysis confirms this.

EXPERIMENTAL

Preparation.—The general method of preparation of the complexes as described in ref. 8 was used for the isolation of the 2-aminopyridine derivative. However, it proved difficult to obtain products which as indicated by the analytical data were of uniform composition. The dark green-brown equant crystals which were obtained from ethanolic solutions of the reactants were recrystallized and washed with isopropanol [Found: C, 41·8; H, 3·36; N, 11·04. Calc. for $Cu(C_{12}H_9N_2O)NO_3(H_2O)$ (established by structure analysis): C, 42·25; H, 3·25; N, 12·32%]. The analytical data are appreciably different from those reported in ref. 8 in which the complex was formulated as containing 2·5 molecules of water per copper atom. None of our samples gave analyses supporting this formulation.

Magnetic Measurements.—The magnetic susceptibility of a powdered sample was recorded over a temperature range,

† *Present address:* Chemistry Department, University of Massachusetts, Amherst, Massachusetts 01002, U.S.A.

[1] K. Ison and E. Kokot, *Austral. J. Chem.,* 1970, **23,** 661.
[2] M. Kishita, Y. Muto, and M. Kubo, *Austral. J. Chem.,* 1957, **10,** 386.
[3] W. E. Hatfield and F. L. Bunger, *Inorg. Chem.,* 1966, **5,** 1161.
[4] W. E. Hatfield and G. W. Inman, *Inorg. Chem.,* 1969, **8,** 1376.
[5] E. Sinn, *Inorg. Chem.,* 1970, **9,** 2376.

[6] W. E. Hatfield and G. W. Inman, *Inorg. Chem.,* 1970, **9,** 2379.
[7] G. A. Barclay and B. F. Hoskins, *J. Chem. Soc.,* 1965, 1979.
[8] W. E. Hatfield and F. L. Bunger, *Inorg. Chem.,* 1969, **8,** 1194.
[9] S. Yamada and K. Yumanouchi, *Bull. Chem. Soc. Japan,* **42,** 2562.
[10] R. Beckett, R. Colton, B. F. Hoskins, R. L. Martin, and D. G. Vince, *Austral. J. Chem.,* 1969, **22,** 2527.

on a Newport Instruments variable-temperature balance system. Solid HgCo(CNS)$_4$ was used as calibrant. Apart from the two high-temperature measurements, the sample exhibited Curie–Weiss behaviour with θ —56°. The results are given in Table 1.

TABLE 1

Magnetic data (per copper atom) [a] for the complex ion

T/K	χ_M' [b]	μ/BM	T/K	χ_M' [b]	μ/BM
291·0	992	1·52	173·0	1304	1·34
273·0	1005	1·48	153·0	1452	1·33
253·0	1018	1·44	133·0	1609	1·31
233·0	1071	1·41	113·0	1823	1·28
213·0	1140	1·39	93·0	2003	1·23
193·0	1209	1·37			

[a] Observed values: see Figure 3 and text for corrected values based on amount of copper in sample. [b] All entries $\times 10^6$ c.g.s. units. Diamagnetic correction included: $\chi_d = -120 \times 10^{-6}$ c.g.s. units, estimated from Pascal's constants.

Crystal Data.—(C$_{12}$H$_{11}$CuN$_3$O$_5$)$_4$, $M = 1363\cdot0$, Tetragonal, $a = 14\cdot83(2)$, $c = 13\cdot58(2)$ Å, $U = 2965\cdot8$ Å^3, $D_m = 1\cdot58$ (by flotation), $Z = 2$, $D_c = 1\cdot52$, $F(000) = 1384$. Precession photographs and diffractometer data. Laue symmetry $4/mmm$. The systematic absences, $h00$ ($0k0$) for $h(k) \neq 2n$ and $00l$ for $l \neq 2n$ uniquely defined the space group $P4_22_12$ (No. 94). Mo-K_α radiation, $\lambda = 0\cdot7107$ Å, μ(Mo-K_α) = 15·3 cm^{-1}.

A crystal of dimensions $0\cdot5 \times 0\cdot5 \times 0\cdot5$ mm having rhombic dodecahedral morphology was selected for intensity measurement and was mounted with the a (or b) axis coincident with the ϕ axis of a General Electric manual diffractometer equipped with a single-crystal orienter. Angle settings for the diffractometer were computed using the program DIFSET [11] and the integrated intensities of 1570 independent reflections within the sphere $0 \leqslant 2\theta \leqslant 50°$ were measured at an instrument take-off angle of 1° by use of the θ—2θ scan technique and a scan rate of 2° min^{-1}. Zirconium-filtered Mo-K_α radiation was used, together with a scintillation counter equipped with pulse-height selector. A symmetrical scan range was used and the net intensities were calculated as $I = P - (B_1 + B_2)$ where P is the measured peak counts and B_1 and B_2 are the stationary background counts at each limit of the scan range, each taken for one half of the scan time. On the basis of this formula, 559 reflections had a net intensity of zero, and they were included in the structure determination with an intensity value one quarter of the appropriate background count. Instrumental and crystal stability were monitored by measuring the intensities at frequent intervals, of a total of seven standard reflections, located at different positions in reciprocal space. A uniform decrease in intensity amounting to a total of *ca.* 7% was noted and this affected all the standard reflections equally. The intensities were therefore scaled appropriately to obtain a set on the same relative scale. The intensity data were assigned standard deviations according to the formula: [12] $\sigma(I) = [P + B_1 + B_2 + (0\cdot04I)^2]^{1/2}$, and they were reduced to F^2 values by the application of Lorentz and polarization factors. In view of the near-spherical shape of the crystal and the low absorption coefficient, no absorption corrections were made. The maximum range of transmission factors for a sphere with $\mu R = 0\cdot4$ is $0\cdot55$—$0\cdot57$ and this together with the

observed invariance of the intensities of the reflections at $\chi = 90°$, to rotation in ϕ, justifies the neglect of such corrections.

Structure Determination.—The copper atoms were located from a three-dimensional Patterson map and their positions immediately suggested that the unit cell contained two tetrameric molecules. Two successive three-dimensional electron-density calculations then served to locate all the light atoms in the Schiff-base ligand and the oxygen of a co-ordinated water molecule; R at this stage was 0·24. Examination of the region around the copper atom indicated that all atoms in the co-ordination sphere had been located and that contrary to earlier suggestions,[8] the nitrate ion is not co-ordinated. However, there was no indication of the position of this ion in a difference electron-density map calculated at this point. Least-squares refinement was therefore commenced and after one cycle, with unit weights [the function minimized being $\Sigma w(|F_o| - |F_c|)^2$], R was 0·134 and the weighted value R' was 0·193 $\{R' = [\Sigma\omega(|F|_o - |F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}\}$.

A second difference Fourier map revealed two sets of peaks in different regions, having heights only *ca.* one-third to one-half that expected for nitrogen or oxygen atoms. Refinement of various models was therefore attempted, but the only one which was found to behave reasonably and to lead to satisfactory convergence assumed each of the two sets of peaks to correspond to half nitrate ions. Several cycles of full-matrix least-squares refinement were carried out with this model, assigning weights, to the individual reflections calculated according to $\omega^{1/2} = 2(Lp)F_o/\sigma(I)$, where L and p are the Lorentz and polarization factors.

Initially all positional and thermal parameters were treated as variables with the copper atom being assigned anisotropic thermal parameters. Three cycles of refinement lowered R and R' from 0·098 and 0·152 to 0·075 and 0·114 respectively and convergence was achieved for all the cation parameters, no shift to σ ratio being $>0\cdot3$. However, the nitrate atom co-ordinates tended to oscillate over a wide range and the dimensions and geometries of both ions were chemically unreasonable. Further refinement was therefore undertaken, keeping the nitrogen and oxygen atom positional parameters fixed at the values obtained from the difference map, but allowing their thermal parameters to vary. This procedure did not produce any changes of significance in the cation parameters and so refinement was terminated after two cycles. The nitrate ion thermal parameters converged to relatively high values and they suggest, as do the peaks on the difference map, that the fractional occupancy of one site [nitrate (1)] might be larger than the other. While it would have been preferable to have treated the nitrate ions as rigid groups and to have refined the occupancy factors of the two sites, the version of the least-squares program which was used here did not offer this option. The final values of R and R' were 0·072 and 0·113 respectively, calculated for all data, and the standard deviation of an observation of unit weight was 1·3. A final difference map indicated no peaks $>0\cdot3$ eÅ^{-3} apart from two in the vicinity of the copper and bridging oxygen atoms of *ca.* 0·5 eÅ^{-3}.

The final positional and thermal parameters for all atoms are listed in Table 2 while the observed and calculated structure factors are listed in Supplementary Publication

[11] DIFSET: A program for calculating diffractometer angle settings written for the ICL 1905 computer, M. Webster, University of Southampton, 1969.

[12] P. Corfield, R. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 197.

No. SUP 20254 (12 pp., 1 microfiche).* The majority of calculations were carried out using the X-ray '63 program system as adapted for use on the ATLAS computer at Harwell.[13] The neutral atom scattering factors used in the analysis were taken from ref. 14.

TABLE 2

Atomic positional and thermal parameters with estimated standard deviations in parentheses

Atom	x	y	z	$B/\text{Å}^2$
Cu(1)	0·1480(1)	0·0046(1)	0·0240(1)	*
O(1)	0·0789(4)	0·1026(4)	0·0857(4)	2·56(12)
C(1)	0·0812(7)	0·1236(7)	0·1812(7)	2·89(19)
C(2)	0·0998(8)	0·0542(8)	0·2522(7)	3·29(20)
C(3)	0·0952(8)	0·0773(8)	0·3522(7)	3·84(22)
C(4)	0·0766(8)	0·1644(8)	0·3842(8)	3·84(24)
C(5)	0·0643(8)	0·2353(8)	0·3121(7)	3·67(21)
C(6)	0·0704(8)	0·2108(8)	0·2142(7)	3·39(19)
C(7)	0·1144(8)	−0·0391(8)	0·2305(7)	3·17(20)
N(1)	0·1261(6)	−0·0726(5)	0·1399(6)	2·89(15)
C(8)	0·1362(7)	−0·1719(7)	0·1321(8)	3·32(20)
N(2)	0·0917(5)	−0·2100(5)	0·0588(5)	2·82(15)
C(9)	0·1901(8)	−0·2167(8)	0·2005(7)	3·90(22)
C(10)	0·1987(10)	−0·3133(10)	0·1822(10)	5·36(28)
C(11)	0·1537(10)	−0·3513(10)	0·1045(10)	5·35(30)
C(12)	0·1035(8)	−0·2976(8)	0·0413(8)	3·66(22)
O(2)	0·2719(7)	0·0756(7)	0·0742(7)	5·76(20)
N(3)	0·1025	0·4710	0·2575	8·5(12)
O(3)	0·0718	0·4960	0·3360	8·9(14)
O(4)	0·1745	0·4645	0·2407	10·8(20)
O(5)	0·0485	0·4515	0·1955	11·7(23)
N(4)	0·2870	0·3410	0·0330	9·1(13)
O(6)	0·2815	0·2612	0·0184	11·8(18)
O(7)	0·2280	0·3915	0·0650	13·4(22)
O(8)	0·3620	0·3640	0·0163	12·1(20)

* Anisotropic thermal parameters (Å^2) for the copper atom: $B_{11} = 2\cdot65(6)$, $B_{22} = 2\cdot63(7)$, $B_{33} = 1\cdot91(6)$, $B_{12} = 0\cdot11(4)$, $B_{13} = -0\cdot06(4)$, $B_{23} = 0\cdot15(6)$ where the form of the thermal ellipsoid is $\exp - (\Sigma_i\Sigma_j h_i h_j r_i^* r_j^* B_{ij}/4)$ and r_i^* is the ith reciprocal axis.

RESULTS AND DISCUSSION

Structure of the Complex.—The final structural information is presented in Tables 3 and 4 and in Figures 1 and 2. The unit cell contains two tetrameric complex ions each having crystallographically imposed $D_2(222)$ point symmetry. The four copper atoms lie in an almost square configuration with adjacent atoms 0·326(2) Å above and below the plane of the square respectively. Each individual copper atom is five-co-ordinate and has an approximate square pyramidal geometry with the water molecule occupying the axial position. The four atoms defining the basal plane of the square pyramid deviate considerably from coplanarity however, while the copper atom is located 0·25 Å above the weighted least-squares plane and is displaced towards the axial water molecule. The copper–nitrogen and copper–oxygen bond distances are comparable with the lengths of similar bonds in other Schiff-base complexes of copper [3,15] and the longer Cu–O axial distance is typical for the ' 4 + 1 ' co-ordination geometry of this element.[15a]

* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20.

[13] J. M. Stewart and D. High, ' X-Ray '63 System of Crystallographic Programs,' University of Washington and University of Maryland.

O

TABLE 3

Bond distances (Å) and angles (°) with estimated standard deviations in parentheses

(i) Co-ordination geometry

Cu(1) $\cdots$ Cu(2)	3·077(2)	O(2)–Cu(1)–N(2)	97·4(3)
Cu(1) $\cdots$ Cu(3)	3·171(2)	O(1)–Cu(1)–N(1)	90·2(3)
Cu(1) $\cdots$ Cu(4)	4·259(2)	O(1)–Cu(1)–N(2)	173·5(3)
Cu(1)–O(1)	1·965(6)	O(1′)–Cu(1)–N(2)	97·5(3)
Cu(1)–N(1)	1·975(8)	O(2)–Cu(1)–N(1)	99·6(3)
Cu(1)–O(1′)	1·971(6)	N(1)–Cu(1)–N(2)	96·2(3)
Cu(1)–N(2)	2·036(8)	Cu(1)–O(1)–Cu(2)	102·9(3)
Cu(1)–O(2)	2·225(10)		
		C(1)–O(1)–Cu(1)	125·0(6)
Cu(2) $\cdots$ Cu(1) $\cdots$ Cu(3)	85·9(6)	C(7)–N(1)–Cu(1)	122·6(7)
		C(8)–N(2)–Cu(3)	125·0(7)
O(1)–Cu(1)–O(1′)	74·4(3)	C(1)–O(1)–Cu(2)	131·9(6)
O(1)–Cu(1)–O(2)	87·1(3)	C(8)–N(1)–Cu(1)	120·1(6)
O(1′)–Cu(1)–N(1)	150·5(3)	C(8)–N(1)–Cu(1)	120·1(6)
O(1′)–Cu(1)–O(2)	104·4(3)	C(12)–N(2)–Cu(3)	115·7(7)

(ii) Ligand geometry

C(1)–O(1)	1·335(11)	C(3)–C(4)–C(5)	119·3(10)
C(1)–C(2)	1·437(15)	C(5)–C(6)–C(1)	124·5(10)
C(2)–C(3)	1·401(14)	C(7)–C(2)–C(1)	125·7(9)
C(3)–C(4)	1·391(17)	C(2)–C(7)–N(1)	124·6(9)
C(1)–C(6)	1·378(15)	N(1)–C(8)–N(2)	115·2(9)
C(6)–C(5)	1·382(14)	N(2)–C(8)–C(9)	125·8(10)
C(5)–C(4)	1·448(16)	C(8)–N(2)–C(12)	119·0(9)
C(2)–C(7)	1·431(16)	C(9)–C(10)–C(11)	123·3(13)
N(1)–C(7)	1·338(13)	O(1)–C(1)–C(6)	122·1(9)
C(8)–C(9)	1·392(16)	C(2)–C(3)–C(4)	122·6(10)
C(10)–C(11)	1·368(19)	C(4)–C(5)–C(6)	116·8(10)
C(8)–N(2)	1·322(13)	C(6)–C(1)–C(2)	118·5(9)
N(1)–C(8)	1·484(14)	C(7)–C(2)–C(3)	116·3(10)
C(9)–C(10)	1·461(19)	C(7)–N(1)–C(8)	116·6(8)
C(11)–C(12)	1·389(18)	N(1)–C(8)–C(9)	118·9(9)
C(12)–N(2)	1·331(13)	N(2)–C(12)–C(11)	120·7(10)
		C(8)–C(9)–C(10)	114·8(10)
O(1)–C(1)–C(2)	119·3(9)	C(10)–C(11)–C(12)	117·0(13)
C(1)–C(2)–C(3)	117·7(10)		

(iii) Nitrate ions

Nitrate (1)		Nitrate (2)	
N(3)–O(3)	1·21	N(4)–O(6)	1·20
N(3)–O(4)	1·10	N(4)–O(7)	1·23
N(3)–O(5)	1·20	N(4)–O(8)	1·19
O(3)–N(3)–O(4)	121·8	O(6)–N(4)–O(7)	126·4
O(3)–N(3)–O(5)	116·2	O(6)–N(4)–O(8)	111·4
O(4)–N(3)–O(5)	118·5	O(7)–N(4)–O(8)	126·3

TABLE 4

Equations of least-squares planes * and, in square brackets, distances (Å $\times$ 10^{-3}) of atoms from the planes

	l	m	n	d
Plane (1):				
C(1)—(6)	−0·9825	−0·1861	0·0104	−1·542

[C(1) 43, C(2) −26, C(3) −8, C(4) 27, C(5) 0, C(6) 36]

	l	m	n	d
Plane (2):				
C(8)—(12), N(2)	−0·7916	−0·1803	0·5839	−0·068

[C(8) −25, C(9) 5, C(10) 18, C(11) 3, C(12) −24, N(2) 19]

	l	m	n	d
Plane (3):				
O(1), O(1′), N(1), and N(2′)	0·8751	0·4408	0·1996	1·763

[O(1) 164, O(1′) −148, N(1) −223, N(2′) 204]

* In the form: $lX + mY + nZ = d$ where X, Y, and Z are Cartesian co-ordinates in Å. The weights are calculated as $w_i = 1/(a\,\sigma_{x_i} + b\,\sigma_{y_i} + c\,\sigma_{z_i})^{2/3}$ for the ith atom.

[14] ' International Tables for X-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1952, Table 3.31A.

[15] (a) D. Hall, G. R. Clark, and T. N. Waters, *J. Chem. Soc. (A)*, 1969, 823; (b) D. Hall, S. V. Sheat-Rumball, and T. N. Waters, *J. Chem. Soc., (A)* 1968, 2721.

The mode of co-ordination of the Schiff-base ligand is of interest and is to a large extent controlled by its steric requirements. The formation of a four-membered chelate ring by the co-ordination of both nitrogen atoms to the same metal would produce unsatisfactory C–N–M
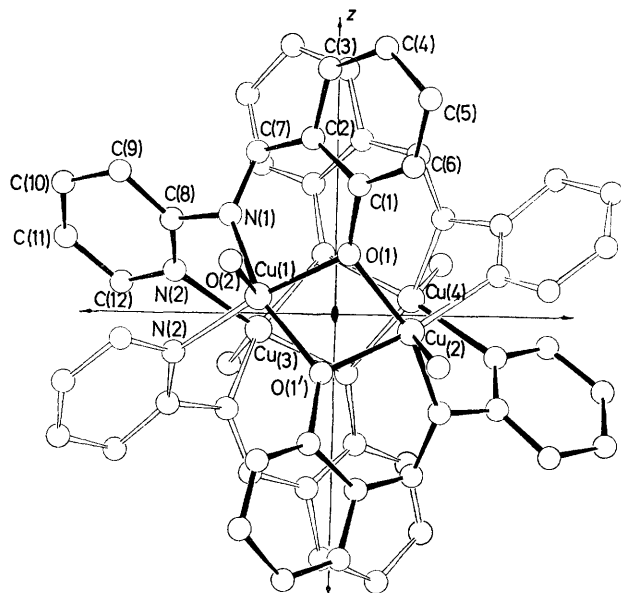

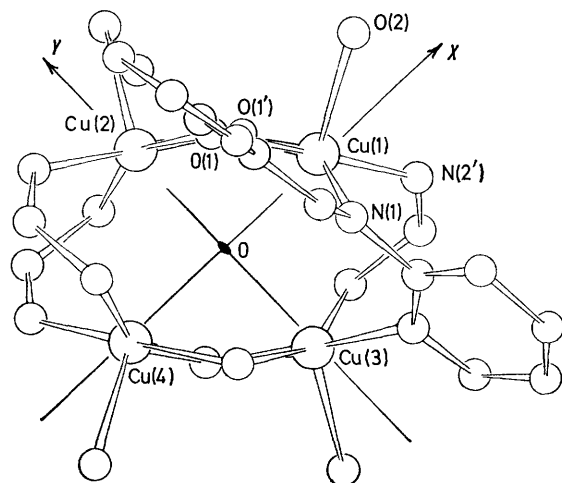FIGURE 1 The tetrameric complex ion projected on (110). The locations of the twofold axes are indicated

FIGURE 2 Projection of the tetrameric copper cluster on (001) and showing the linking of the four co-ordination polyhedra. For clarity only the ligand comprising the asymetric unit is illustrated

angles, and the simultaneous co-ordination of all three donor atoms to the same central atom (with acceptable M–O and M–N bond distances) would lead to considerable deviation of the angles within the four- and six-membered chelate rings, from their normal values. A ternuclear complex with the structure suggested by Hatfield and Bunger [8] is therefore very unlikely and Martin and co-workers also reached this conclusion from an examination

of molecular models.[10] Moreover it is difficult to devise an alternative ternuclear structure in which each ligand is co-ordinated to two metal atoms and such a structure would not have the three metal atoms in identical environments.

In contrast the Schiff-base ligand (II) is able to form two five-membered chelate rings quite readily and can then probably function as a terdentate ligand so that the formation of a monomeric complex with normal magnetic properties is not unexpected.

Figures 1 and 2 show that the ligand consists approximately of two planar units, defined by the pyridine and the benzene rings which have a dihedral angle of 54°. The least-squares planes parameters for the two rings are listed in Table 4. The N(1)–C(8) distance which is indicative of a single bond, suggests that there is little if any conjugation between the –C=N– bond and the pyridine ring, so that the group of atoms N(1), C(8), N(2) would not be expected to provide a very efficient pathway for spin–spin exchange between Cu(1) and Cu(3). The magnetic data in fact indicate that there is probably no such exchange, so it may also be concluded that the distance of 3·17 Å precludes any direct interaction. All remaining bond distances and angles within the ligand are comparable with those observed for other salicylaldimines [16] and in pyridine itself.

Despite their complexity the tetrameric complex ions can be viewed very approximately as large spherical groups which pack together in a roughly cubic, body-centered array. The nitrate ions seem to have very little influence on the crystalline arrangement, merely occupying interstices between the complex cations.

Magnetic Properties of the Tetramer.—The magnetic susceptibility of the tetrameric complex and its temperature dependence, obtained in the present study differs appreciably from that reported previously,[8] in which measurements were made at only two temperatures. In addition to the measurements reported here, an independent study of the magnetism of the compound has also been made by Martin and co-workers,[17] and for the reasons now outlined, we believe their results to be those for the pure complex. On the basis of the analytical data obtained for the sample used in the present susceptibility measurements, it appears that this was almost certainly contaminated by a small amount of free ligand or a compound giving an equivalent analysis. The amount of copper present was only 72·3% of that calculated for the structurally established formulation (18·6%) and so on the assumption that the contaminant was solely diamagnetic material, the observed apparent molar susceptibilities were appropriately scaled to the values corresponding to 100% copper. Although the results of this operation must be viewed with some caution, it is of some relevance that they correspond quite closely, apart from the measurements at the highest temperature, to those of Martin and

[16] R. L. Braun and E. C. Lingafelter, *J. Amer. Chem. Soc.*, 1966, **88**, 2951.

[17] R. L. Martin, personal communication.

co-workers. The various sets of data are illustrated in Figure 3.

No attempt has been made to obtain the best fit of the observed plot of the molar susceptibility with temperature, to any theoretical expression for four magnetically interacting ions, in view of the uncertainties in
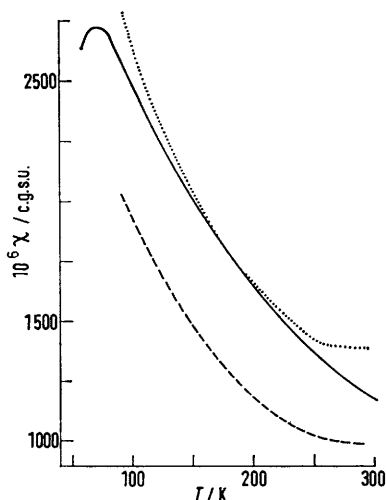

FIGURE 3 Experimental and calculated plots of χ_M' vs. T; full line is calculated for $g = 2.07$ and $J_{12}/k = -60$ K, broken and dotted lines show observed and corrected values

the measured susceptibilities (*vide supra*). It appears however, that the magnetic properties can be fairly closely approximated over the temperature range studied, by the Bleaney–Bowers equation (1) for two interacting spins,[18] where J_{12} is the integral in the

$$\chi_{Cu} = \frac{Ng^2\beta^2}{kT} (3 + e^{-2J_{12}/kT})^{-1} + N\alpha \qquad (1)$$

exchange term of the Hamiltonian, $-2J_{12}S_1 \cdot S_2$, and all the other symbols have their usual meaning. The tetramer can thus be treated as essentially two independent binuclear units, the interactions between which are either very weak or nonexistent.

[18] B. Bleaney and K. D. Bowers, *Proc. Roy. Soc.*, 1952, (*A*), **214**, 451.

The full curve in Figure 3 was accordingly calculated from equation (1) with $g = 2.07$ and $J/k = -60$ K, but ignoring the temperature-independent contribution $N\alpha$. A reasonable fit to the observed data is obtained with these parameters and the copper atoms are coupled antiferromagnetically, with an exchange integral typical for this type of oxygen double-bridging system. This model is compatible with the structure of the complex ion described earlier, for the geometries of the bridging groups of atoms between Cu(1) and Cu(3), and Cu(2) and Cu(4) probably preclude any superexchange interaction and the metal–metal distances themselves appear too long for any but very weak direct exchange.

Various qualitative models for the superexchange between the atoms in the Cu⟨O⟩Cu and related systems have been described,[3,19,20] and while these depend on the nature of the remainder of the ligand, they essentially reduce to two pathways, a σ-type and a π-type pathway.[20] On the basis of orbital overlap, the former is thought to be the more effective as an exchange pathway, but its effectiveness is more critical on the bond angles in the bridge system, while the π-type pathway is relatively insensitive to bond angles. Exchange integral magnitudes are therefore not readily correlated with solely metal–ligand or metal–metal bond distances. In the present instance the copper–oxygen distances are equivalent, so that the bridge is symmetrical, while the two Cu–O–C angles are 125 and 132°. We suggest that the σ-type of orbital overlap may be important here and so provide the major pathway for electron exchange between the two copper atoms.

[19] R. L. Martin in ' New Pathways in Inorganic Chemistry,' ed. E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Cambridge University Press, 1968, p. 175.
[20] Y. Muto, M. Kato, H. B. Jonassen, and L. C. Cusachs, *Bull. Chem. Soc. Japan*, 1969, **42**, 417.