Crystal and Molecular Structure and Magnetic Properties of a Tetrameric Copper(II) Complex with 3-Hydroxy-5-hydroxymethyl-4-(4′-hydroxy-3′-methyl-4′-phenyl-2′-azabut-1′-en-1′-yl)-2-methylpyridine (H_2L): $[Cu_4L_4]\cdot 8MeOH$, a Complex with a Ferromagnetic Ground State ‡

Jean-Pierre Laurent and Jean-Jacques Bonnet
Laboratoire de Chimie de Coordination du CNRS associé à l'Université Paul Sabatier, 205, route de Narbonne, 31400 Toulouse, France
Francoise Nepveu *,†
Laboratoire de Biospectroscopie, CTB SC 13 INSERM, 38, rue des Trente-Six-Ponts, 31400 Toulouse, France
Harald Astheimer, Leonhard Walz, and Wolfgang Haase
Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstrasse 20, D-6100 Darmstadt, West Germany

The crystal and molecular structure of the title compound has been determined from single-crystal *X*-ray diffraction data and refined to a final *R* value of 0.053 using 2 514 independent reflections. The compound belongs to the space group $P4_2/n$ of the tetragonal system with two tetrameric molecules in a unit cell of dimensions a = 17.226(4) and c = 14.667(3) Å. The tetrameric unit with a Cu_4O_4 core is of S_4 symmetry. Copper–copper distances are 3.481(1) (two), 3.259(1) Å (four) and Cu–O distances are 1.945(4) (four), 2.734(4) (four), and 1.977(4) Å (four). The co-ordination about the copper atom is distorted square pyramidal with copper bonded to phenolic oxygen O(2), imine nitrogen N(1), and three alkoxo-oxygen atoms O(1). The complex crystallizes with 16 methanol molecules per unit cell. It easily loses in air the methanol molecules of crystallization giving an amorphous powder. The magnetism of the crystallized complex can be explained on the basis of the isotropic Heisenberg–Dirac–van Vleck model. Taking into account intercluster interactions, the fitting procedure yielded the values g = 2.12, J_{13} = 17.1 cm^{-1}, θ = −1.1 K. These parameters indicate a predominance of ferromagnetic interactions with a quintet ground state (S' = 2). The magnetic behaviour of the amorphous powder is quite different and shows weak antiferromagnetic interactions.

Structural and magnetic investigations of a great number of tetrameric oxygen-bridged copper(II) complexes of the cubane type with *NN*-dialkylated amino-alcohols $[\{CuX(OCH_2CH_2NR_2)\}_4]$ (X = Cl, Br, NCS, NCO, $C_2H_2O_2Cl$, $C_2O_2Cl_3$; R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, *etc.*) have been reported.[1-4] For tetrameric copper complexes in which the amino-alcohol molecule is involved in a Schiff base,[5-7] *X*-ray structural studies are limited to one complex derived from acetylacetone and 2-aminoethanol $[\{Cu(MeCOCH_2CMe{=}NCH_2CH_2OH)\}_4]$ for which two principally different tetrameric molecular structures, α and β, are known in the crystalline state.[8,9] The α form has a singlet ground state whereas the β form has a quintet ground state.[10]

The present work is devoted to a new example of tetrameric copper(II) complex involving a Schiff base (L) derived from 3-hydroxy-5-hydroxymethyl-2-methyl-4-pyridinecarboxaldehyde (pyridoxal) and 2-amino-1-phenylpropan-1-ol. This complex has been isolated during our investigation[11-12] of non-enzymatic model systems for the oxidative deamination of biogenic amines.[13] Two forms have been obtained: a crystallized one $[Cu_4L_4]\cdot 8MeOH$ [H_2L = 3-hydroxy-5-hydroxymethyl-4-(4′-hydroxy-3′-methyl-4′-phenyl-2′-azabut-1′-en-1′-yl)-2-methylpyridine] and an amorphous one $[\{CuL\}_n]$ produced by loss of the solvent molecules. The synthesis and crystal and molecular structure for the crystallized compound and the magnetic properties for both compounds are reported in this paper.

Results and Discussion

Description of the Structure.—The final structural data are presented in Tables 1 and 2 and in Figures 1 and 2. The CuL 1 : 1 complex crystallizes with two tetrameric Cu_4L_4 molecules together with 16 methanol molecules per unit cell. In a given tetrameric molecule which has S_4 symmetry, each of the four Schiff bases acts as a tridentate ligand (Figure 1). This behaviour leads to the formation of two rings, one six-membered and one five-membered, which include the same copper atom. The six-membered ring is coplanar with the pyridine ring, together with the five-membered ring, but the carbon atom C(11) is 0.812 Å out of the mean plane (see Table 3).

The Cu_4O_4 core of the cubane type (Figure 2) represents a distortion from an idealized cube with four shorter [3.259(1) Å] and two longer [3.481(1) Å] Cu–Cu separations. This distortion is also obvious when the Cu–O distances within the Cu_4O_4 core are considered, *i.e.* eight shorter bonds of 1.945(4) and 1.977(4) Å (four each) and four longer ones of 2.734(4) Å. The two pairs of long Cu–O bonds, namely Cu–$O(1)^{ii}$, Cu^{ii}–O(1) and Cu^{i}–$O(1)^{iii}$, Cu^{iii}–$O(1)^{i}$, are mutually perpendicular. The tetrameric cubane type molecules are usually classified into groups,[1] according to their structural properties. Two extreme types exist (see ref. 1) which may be distinguished by the arrangement of the Cu–Cu and Cu–O bond distance. The present compound belongs to type II.

---

† *Present address:* Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstrasse 20, D-6100 Darmstadt, West Germany.

‡ *Supplementary data available* (No. SUP 23412, 19 pp.): observed and calculated structure factors, thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Non-S.I. units employed: 1 B.M. = 9.27×10^{-24} A m^2.

Table 1. Positional parameters for all non-hydrogen atoms with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu	0.079 03(5)	0.062 94(5)	0.572 81(5)	C(7)	0.091 4(5)	0.330 5(4)	0.586 0(6)
O(1)	0.078 4(2)	−0.050 7(2)	0.554 2(2)	C(8)	0.196 2(4)	0.173 2(4)	0.909 7(5)
O(2)	0.084 7(3)	0.170 1(3)	0.596 6(3)	C(9)	0.140 8(4)	−0.047 5(4)	0.699 0(4)
O(3)	0.136 7(3)	0.132 6(3)	0.954 8(3)	C(10)	0.077 9(5)	−0.086 5(5)	0.754 8(5)
O(4)	−0.004 3(5)	0.205 9(6)	0.974 0(7)	C(11)	0.147 0(4)	−0.078 8(4)	0.600 9(4)
O(5)	0.165 0(6)	0.489 0(5)	0.750 9(8)	C(12)	0.160 1(5)	−0.164 1(4)	0.598 7(4)
N(1)	0.126 1(3)	0.036 5(3)	0.688 9(3)	C(13)	0.230 9(5)	−0.189 9(5)	0.625 8(5)
N(2)	0.142 5(4)	0.328 0(4)	0.740 2(4)	C(14)	0.249 2(6)	−0.266 0(7)	0.629 5(6)
C(1)	0.112 6(4)	0.203 2(4)	0.669 6(5)	C(15)	0.196 5(6)	−0.321 0(7)	0.603 6(7)
C(2)	0.141 2(4)	0.165 3(4)	0.747 6(4)	C(16)	0.124 6(7)	−0.293 1(6)	0.571 9(8)
C(3)	0.148 4(4)	0.083 9(4)	0.750 2(4)	C(17)	0.106 5(5)	−0.216 2(4)	0.571 7(6)
C(4)	0.167 2(4)	0.210 2(4)	0.822 2(4)	C(18)	−0.019 8(7)	0.280 8(9)	0.927 9(10)
C(5)	0.166 3(4)	0.289 8(5)	0.851 1(5)	C(19)	0.106 9(8)	0.522 2(10)	0.795(2)
C(6)	0.116 7(4)	0.286 4(4)	0.670 7(5)				

Table 2. Selected distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Distances

Cu···Cu^{i}	3.259(1)	C(6)–C(1)	1.435(9)
Cu···Cu^{ii}	3.481(1)	C(2)–C(3)	1.408(9)
Cu–O(2)	1.880(4)	C(3)–N(1)	1.273(7)
Cu–N(1)	1.941(5)	N(1)–C(9)	1.477(8)
Cu–O(1)	1.977(4)	C(9)–C(10)	1.516(10)
Cu–O(1)^{i}	1.945(4)	C(9)–C(11)	1.540(9)
Cu–O(1)^{ii}	2.734(4)	C(11)–O(1)	1.448(7)
Cu···O(1)^{iii}	3.794(4)	C(11)–C(12)	1.488(9)
O(2)–C(1)	1.306(7)	C(12)–C(13)	1.358(10)
C(1)–C(2)	1.406(8)	C(13)–C(14)	1.349(12)
C(2)–C(4)	1.413(8)	C(14)–C(15)	1.365(14)
C(4)–C(8)	1.517(9)	C(15)–C(16)	1.409(14)
C(8)–O(3)	1.406(8)	C(16)–C(17)	1.360(12)
C(4)–C(5)	1.375(10)	C(17)–C(12)	1.347(10)
C(5)–N(2)	1.346(9)	C(18)–O(4)	1.48(1)
N(2)–C(6)	1.322(8)	C(19)–O(5)	1.32(1)
C(6)–C(7)	1.520(10)		

(*b*) Angles

O(1)–Cu–O(2)	176.1(2)	Cu^{iii}–O(1)–C(11)	118.7(3)
N(1)–Cu–O(2)	92.6(6)	Cu–O(2)–C(1)	126.9(4)
O(1)–Cu–N(1)	83.7(2)	Cu–N(1)–C(3)	126.5(5)
O(1)–Cu–O(1)^{i}	90.1(2)	Cu–N(1)–C(9)	113.0(4)
O(1)–Cu–O(1)^{ii}	84.5(2)	N(1)–C(3)–C(2)	126.4(6)
O(1)^{i}–Cu–O(2)	93.2(2)	C(3)–C(2)–C(1)	121.0(6)
O(1)^{i}–Cu–N(1)	168.0(2)	N(2)–C(6)–C(7)	117.1(7)
O(1)^{i}–Cu–O(1)^{ii}	70.5(2)	O(2)–C(1)–C(2)	126.4(6)
O(1)^{ii}–Cu–O(2)	98.4(2)	C(2)–C(1)–C(3)	115.9(6)
O(1)^{ii}–Cu–N(1)	118.9(2)	O(3)–C(8)–C(4)	111.6(6)
Cu–O(1)–Cu^{ii}	93.9(3)	N(1)–C(9)–C(10)	111.5(6)
Cu–O(1)–Cu^{iii}	112.4(3)	N(1)–C(9)–C(11)	105.2(6)
Cu^{ii}–O(1)–Cu^{iii}	86.6(3)	O(1)–C(11)–C(9)	105.6(5)
Cu–O(1)–C(11)	105.1(3)	O(1)–C(11)–C(12)	116.4(6)
Cu^{ii}–O(1)–C(11)	137.4(3)		

Superscripts represent the following positions: i $-y$, x, $1 - z$; ii $-x$, $-y$, z; iii y, $-x$, $1 - z$

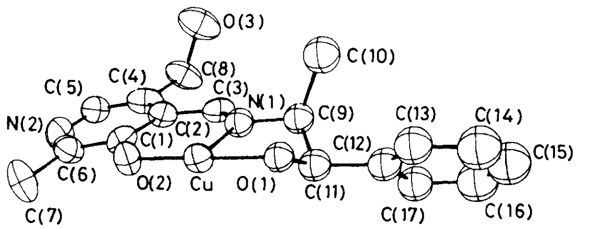

Figure 1. Perspective view of the asymmetric unit CuL. The thermal ellipsoids are drawn at the 50% probability level

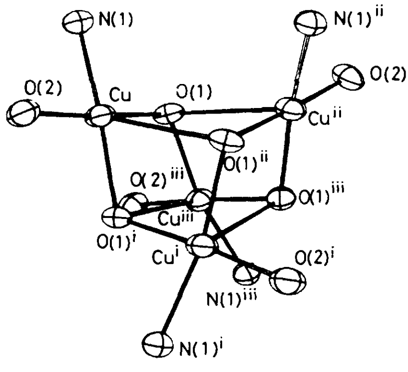

Figure 2. Perspective view of the tetrameric unit Cu_4L_4 in which only atoms of the ligand L bonded to copper are represented. Thermal ellipsoids are drawn at the 50% probability level

Each copper atom is five-co-ordinated through the phenolic oxygen O(2), the imine nitrogen N(1), and the two alkoxo-oxygens O(1) and O(1)^{i} in the basal plane, and the out-of-plane alkoxo-oxygen O(1)^{ii} at the top of the pyramid. The angles involving the out-of-plane oxygen atom and Cu [O(1)^{ii}–Cu–X; X = O(2), N(1), O(1), O(1)^{i}] are in the range 70.5—118.9°. Other angle values around the copper atom are given in Table 2.

There is no other atom in an eventual sixth position. Distances of atoms from the best plane which included atoms O(2), N(1), O(1), and O(1)^{i} (see Table 3) clearly indicate that these atoms do not lie in a good plane. The copper atom is out of this plane in the direction of the alkoxo-oxygen O(1)^{ii} atom at the top of the square pyramid, but only *ca.* 0.1 Å. Usually, in a regular square-pyramidal geometry this atom is shifted about 0.3 Å from the basal mean plane. The distortion of this geometry is induced by the basal atoms and essentially by the alkoxo-oxygen atom O(1)^{i}. Hence the co-ordination geometry around the copper atom may be best described as a highly distorted square pyramid.

Comparison of distances and angles within the Cu_4O_4 core with those observed in cubane type II complexes shows relatively good agreement.[9,14–16] In Table 4, a comparison of selected distances and angles within the Cu_4O_4 core is made between the present compound and tetrakis{bromo[(2-diethylamino)ethanolato]copper(II)}-tetrakis(tetrachloromethane)[14] which also possesses S_4 symmetry. A main difference arises from the axial Cu–O(1)^{ii} bond of 2.734(4) Å which is significantly longer than the values found in the

Table 3. Least-squares planes with deviations (Å) of atoms from planes in square brackets

Plane A

$$15.622x + 0.510y - 6.164z + 2.260 = 0$$

[Cu −0.004(1), C(2) −0.058(6), O(2) −0.007(5), C(3) −0.004(7), C(1) −0.004(7), N(1) 0.002(5), C(6) 0.095(7), C(9) 0.127(7), N(2) 0.091(6), O(1) 0.043(4), C(5) 0.018(7), C(11) [a] 0.812(7), C(4) −0.088(7)]

Plane B

$$15.558x + 0.872y - 6.252z + 2.296 = 0$$

[Cu −0.001(1), C(3) −0.014(7), O(2) 0.032(5), N(1) −0.018(5), C(1) 0.039(7), C(9) 0.075(7), C(2) −0.037(6), O(1) 0.006(4)]

Plane C [b]

$$16.105x + 0.448y - 5.177z + 1.562 = 0$$

[O(1) −0.063, N(1) 0.048, $O(1)^{I}$ 0.110, Cu [a] −0.097, O(2) −0.080, $O(1)^{II}$ [a] −2.543]

Dihedral angle between planes A—B = 1.3°

[a] Atom not included in the calculation of the plane. [b] Equation calculated by a local program, since ORFFE does not handle atoms related by equivalent positions.

Table 4. Selected distances (Å) and angles (°) within the Cu_4O_4 core in $[Cu_4L_4]\cdot 8MeOH$ and in $[\{CuBr(OCH_2CH_2NEt_2)\}_4]\cdot 4CCl_4$

	$[Cu_4L_4]\cdot$ 8MeOH	$[\{CuBr(OCH_2CH_2NEt_2)\}]\cdot$ $4CCl_4$ *
$Cu-Cu^{I}$	3.259(1)	3.176(2)
$Cu-Cu^{III}$	3.259(1)	3.176(2)
$Cu-Cu^{II}$	3.481(1)	3.523(2)
$Cu-O(1)$	1.977(4)	1.924(5)
$Cu-O(1)^{I}$	1.945(4)	1.982(5)
$Cu-O(1)^{II}$	2.734(4)	2.524(5)
$O(1)-Cu-O(1)^{I}$	90.1(2)	86.7(3)
$O(1)-Cu-O(1)^{II}$	84.5(2)	75.8(3)
$O(1^{I})-Cu-O(1)^{II}$	70.5(2)	71.9(3)
$Cu-O-Cu^{II}$	93.89(3)	104.1(3)

* See ref. 14.

previous complex, 2.524(5) (ref. 14) and 2.408(8) Å (ref. 9). This lengthening may be attributed to steric hindrance effects. Furthermore, the $Cu-O-Cu^{II}$ bridging angle in the ' pseudo-dimeric ' unit $Cu-O(1)-Cu^{II}-O(1)^{II}$ and the angle $O(1)-Cu-O(1)^{II}$ are markedly different from those in $[\{CuBr(OCH_2CH_2NEt_2)\}_4]\cdot 4CCl_4$ [14] (see Table 4).

Eight methanol molecules per tetrameric unit stabilize the crystal structure. The O(5)–N(2) distance of 2.80(1) Å between the oxygen O(5) of the first molecule of methanol and the pyridine N(2) nitrogen atom of the pyridoxal molecule strongly suggests a O–H ··· N hydrogen bond. Two other rather short distances, between O(4) of the second methanol molecule and O(3) of the hydroxymethyl group, also support the presence of O–H ··· O bonds: one involving O(3) of one pyridoxal molecule [O(3)–O(4) 2.75(1) Å], the other involving O(3) of a second pyridoxal molecule [O(3)*–O(4) 2.72(1) Å; O(3)* being in the $-y$, x, $-z + 2$ equivalent position]. These O–H ··· O bonds develop hydrogen-bond bridges including methanol molecules and hydroxymethyl groups between two tetrameric molecules leading to a sixteen-membered ring perpendicular to the S_4 axis. This ring is formed by four oxygen atoms O(3), two coming from one tetrameric molecule and two from another above the first along the $\bar{4}$ axis, four oxygen atoms from methanol molecules, and eight hydrogen atoms from methanol molecules and hydroxymethyl groups. Consequently, each tetrameric molecule is bonded to two others by these sixteen-membered rings developing infinite chains.

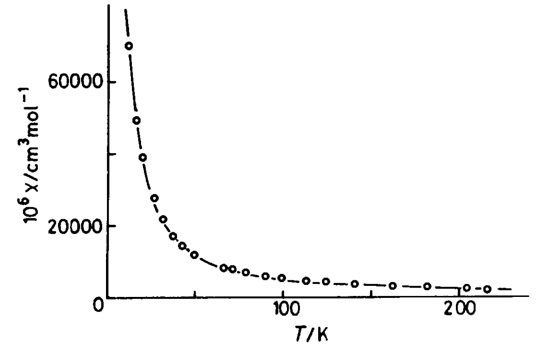

Figure 3. Temperature dependence of the magnetic susceptibility of $[Cu_4L_4]\cdot 8MeOH$. Experimental points (○) are plotted with values calculated from equations (3) and (4) (——), see text

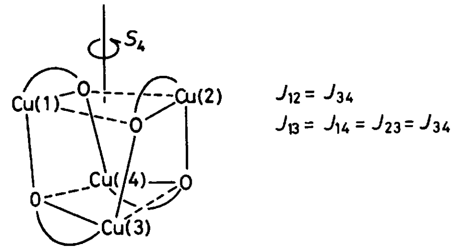

Figure 4. Principal structure of the Cu_4O_4 core and relations between the exchange integrals

Magnetic Properties.—The magnetic susceptibility of the crystallized complex under investigation in the temperature range 4.2—216 K is shown in Figure 3. The susceptibility increases steadily with decreasing temperature and does not reach a maximum in the investigated temperature range. The magnetic moment increases with decreasing temperature, reaching a constant value of 2.46 B.M. at *ca.* 10.6—19 K. Below 10.6 K the magnetic moment decreases again (Table 5). The graph $1/\chi = f(T)$ is linear in the range 70—216 K and has an intercept at 18 K. This is in accordance with an overall ferromagnetic exchange interaction. The susceptibility and magnetic moment values of the amorphous form are reported in Table 6. It is obvious that the crystallized and amorphous compounds vary significantly in magnetic properties.

Theory and Calculations.—In the case of the crystallized compound which is structurally well determined, a theoretical analysis of the data is possible. Spin-coupled metal complexes may be described by the isotropic Heisenberg–Dirac–van Vleck (HDvV) model [17–19] in which the effective Hamiltonian describing the various energy levels with different total spin S' has the form (1), where J_{ij} is the exchange integral between

$$\mathscr{H} = -2\sum_{i<j} J_{ij}S_iS_j \qquad (1)$$

the magnetic centres i and j. If four copper ions are arranged in a Cu_4O_4 core (Figure 4) with point symmetry S_4, this Hamiltonian becomes equation (2).

$$\mathscr{H} = -2\,J_{12}(S_1S_2 + S_3S_4) - 2\,J_{13}(S_1S_3 + S_1S_4 + S_2S_3 + S_2S_4) \qquad (2)$$

Table 5. Observed and calculated susceptibilities and magnetic moments (B.M.) for [Cu_4L_4]·8MeOH

T/K	$10^6\chi_{obs.}$/ cm^3 mol^{-1}	$10^6\chi_{calc.}$/ cm^3 mol^{-1}	$\mu_{eff.}/\mu_B$
4.2	151 630	155 453	2.257
6.4	111 767	109 944	2.391
10.6	69 909	69 940	2.434
15.3	49 551	48 498	2.462
19.0	39 138	38 324	2.438
25.4	27 717	27 365	2.372
30.6	21 973	21 839	2.318
36.6	17 351	17 513	2.253
42.0	14 602	14 766	2.214
48.8	11 920	12 262	2.155
65.7	8 352	8 522	2.093
70.5	7 978	7 828	2.120
78.1	6 943	6 926	2.079
89.6	5 890	5 889	2.051
98.5	5 303	5 274	2.042
112.5	4 630	4 526	2.036
123.5	4 104	4 071	2.009
139.9	3 515	3 540	1.980
161.8	2 961	3 014	1.954
181.8	2 647	2 655	1.959
204.5	2 308	2 339	1.943
215.9	2 127	2 208	1.916

Applying this Hamiltonian to the wavefunction of our spin systems leads to the corresponding energy values. This can be done by the standard procedure.[20] The susceptibility $\chi_{tet.}$ (tet. = tetramer) resulting from the van Vleck equation is given by equation (3), where $u = J_{13}/kT$, $v = J_{12}/kT$,

$$\chi_{tet.} = \frac{N\beta^2 g^2}{4kT'} \frac{10\exp(2u) + 2\exp(-2u) + 4\exp(-2v)}{5\exp(2u) + 3\exp(-2u) + 6\exp(-2v) + \exp(-4v)} \quad (3)$$

and $T' = T - \theta$ (θ is related to the conventional Weiss constant).

The calculated susceptibility, $\chi_{calc.}$, consists of $\chi_{tet.}$, $\chi_{para.}$ (which comes from eventual paramagnetic impurities), $\chi_{(N\alpha)}$ (the temperature-independent paramagnetism), and $\chi_{dia.}$; equation (4). The susceptibility $\chi_{para.}$ is, following the Curie–

$$\chi_{calc.} = (1 - x)\chi_{tet.} + x\chi_{para.} + \chi_{(N\alpha)} + \chi_{dia.} \quad (4)$$

$$\chi_{para.} = \frac{N_A\, \beta^2\, g^2}{4kT} \quad (5)$$

Weiss law, given by equation (5), where x is the mol fraction of the paramagnetic impurities. Interactions which significantly influence the magnetic properties at low temperature were taken into account by using T' in equation (3). Zero-field splitting or intercluster interactions are correlated to the value of θ for which, however, sources are not exact. The exchange integral J_{13}, the g factor, and θ are evaluated by fitting equations (3) (with $T' = T - \theta$) and (4) to the experimental values. The function minimized was $(\chi_{expt.} - \chi_{calc.})^2$-$(T')^2$.[21] The exchange integral J_{12} and the value of the temperature-independent paramagnetism $N\alpha$ were taken as constant ($J_{12} = 0$ cm^{-1}, $x = 0.03$, $N = 60 \times 10^{-6}$ c.g.s.u.). The J_{12} value was fixed to zero since the long Cu–O(1)^{III} distance [2.734(4) Å] cancels an antiferromagnetic exchange interaction, as recently reported.[21]

From the fitting procedure [22] the following values were obtained: $J_{13} = 17.1 \pm 5.0$ cm^{-1}, $g = 2.12 \pm 0.03$, $\theta = -1.1$ K. The good agreement between the experimental and calculated values is shown in Figure 3. Figure 5 shows the energy diagram of the spin states resulting from the interpretation of the exchange parameters with the isotropic HDvV model. The most interesting feature is the quintet ground state ($S' = 2$) for [Cu_4L_4]·8MeOH.

Table 6. Observed susceptibilities and magnetic moments (B.M.) for the amorphous form [{CuL}$_n$]

T/K	$10^6\chi_{obs.}$/ cm^3 mol^{-1}	$\mu_{eff.}/\mu_B$
4.2	63 347	1.458
6.4	47 823	1.564
10.6	30 762	1.614
15.3	22 779	1.669
19.0	18 830	1.691
25.4	14 535	1.718
30.6	12 212	1.728
36.6	10 233	1.730
42.0	8 777	1.717
58.8	7 501	1.711
65.7	5 620	1.718
70.5	5 329	1.733
78.1	4 932	1.755
89.6	4 311	1.757

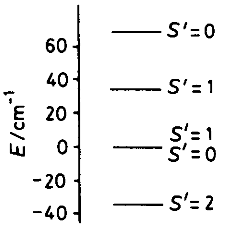

Figure 5. Schematic energy splitting diagram for [Cu_4L_4]·8MeOH

Ferromagnetic and antiferromagnetic interactions within the same molecule are a principal feature of tetrameric oxygen-bridged copper(II) complexes of the cubane type. In the case of [Cu_4L_4]·8MeOH, the overall magnetic behaviour resulting from ferromagnetic interaction between the ' pseudo-dimeric ' units is a consequence of the structural details within the Cu_4O_4 core. The overall ferromagnetic behaviour corresponds to a $S' = 2$ ground state. Cubane type copper(II) complexes with a ferromagnetic ground state have a similar structure and are classified as type II complexes.

It has been previously suggested that the antiferromagnetic exchange interaction within the pseudo-dimeric unit would depend on the values of the Cu–O–Cu bridging angle and the magnitude of the non-chelate-bonded Cu–O distance.[14,21,23] For instance, in [{CuBr($OCH_2CH_2NEt_2$)}$_4$]·4CCl_4, a type II complex with S_4 symmetry, the actual value of this integral ($J_{12} = -4.5 \pm 3$ cm^{-1}) is considered as resulting from two opposing effects: whereas a rather large Cu–O–Cu angle [104.1(3)°] [14] would give rise to a large antiferromagnetic interaction, the interaction in the present case is reduced by the length of the Cu–O bond [2.524(5) Å]. In [Cu_4L_4]·8MeOH, the very high value of the Cu–O(1)^{III} distance [2.734(4) Å] compared with the above complex causes the cancelling of the antiferromagnetic interaction.

From the consideration of the molecular structure and magnetic properties of several tetrameric copper(II) complexes involving *NN*-dialkylamino-alcohols as ligands, Merz[21] obtained a relation between the copper–alkoxo-oxygen distance perpendicular to the pseudo-dimeric unit and the value of the ferromagnetic exchange integral, $J_{\text{ferro.}}$, equation (6). For the present compound, the calculated value is

$$\ln (2J_{\text{ferro.}}/\text{cm}^{-1}) = -7.5\,(r/\text{Å}) + 19.26 \qquad (6)$$

53.5 cm^{-1} (fitted value, 17.1 cm^{-1}). For β-[{Cu(MeCOCH$_2$-CMe=NCH$_2$CH$_2$OH)}$_4$]·2C$_6$H$_6$, the calculation on the basis of the mean value of the four Cu–O bonds leads to a value of 49.1 cm^{-1} which conflicts with the fitted value[21] ($J_{13} = 23.4 \pm 5$ cm^{-1}). From these comparisons it appears that equation (6) obtained by Merz for the tetrameric alkoxo-bridged copper(II) complexes cannot be applied to the present two tetrameric Schiff-base copper(II) complexes.

Thus, regarding the antiferromagnetic as well as the ferromagnetic interactions, it is noteworthy that a quantitative comparison cannot be made between the complexes derived from Schiff bases and the other type II complexes. To date, the lack of structural data for other related Schiff-base complexes of the cubane type prevents a more detailed analysis of their magnetic behaviour in terms of structural properties.

However, it is noteworthy that the cubane type complex [Cu$_4$L$_4$]·8MeOH is the first example of a type II complex with S_4 symmetry including a Schiff base as ligand. In spite of the steric hindrance of the Schiff base this high symmetry may be favoured by the coplanarity of the pyridine and chelate rings. The slightly different values of the exchange integrals for [Cu$_4$L$_4$]·8MeOH (S_4 symmetry) and (C_1 symmetry), both derived from Schiff bases, emphasize the influence of structural details within the Cu$_4$O$_4$ core on the relative magnitude of the ferromagnetic and antiferromagnetic exchange integrals. The negative value of the Weiss constant θ (−0.38 K) indicates a weak antiferromagnetic interaction between the ferromagnetic coupled tetrameric molecules. An interpretation of θ values is not possible from measurements of isotropic susceptibilities.

The magnetic behaviour of the amorphous form derived from the crystallized one by loss of solvent molecules is very different. From 0—30 K the values of the magnetic moment are lower than expected for a monomeric copper(II) complex whereas these values become comparable at 30 K. This shows a very weak antiferromagnetic coupling. This magnetic behaviour could be accounted for by coupled dimers or by a one-dimensional model with an exchange integral of about −1 to −5 cm^{-1}.

Experimental

Preparation.—Pyridoxal base prepared from pyridoxal hydrochloride (0.51 g, 2.5 mmol) and sodium acetate (0.6 g, 5.0 mmol) in methanol was reacted with 2-amino-1-phenyl-propan-1-ol hydrochloride (0.47 g, 2.5 mmol). Copper acetate monohydrate (0.50 g, 25 mmol) was added and the resulting mixture was stirred for about 30 min. The volume was reduced and propan-2-ol was added to precipitate salts. The filtrate was reduced to a small volume and methanol was added. Dark green crystals were deposited on standing overnight, m.p. 209—219 °C. Yield, 0.62 g (65%). In air this crystallized complex easily loses the methanol molecules. Debye-Scherrer diagrams point to the absence of crystalline structure in the resulting powder.

Crystallography.—*Crystal data.* C$_{68}$H$_{72}$Cu$_4$N$_8$O$_{12}$·8CH$_3$OH, M = 1 703.8, tetragonal, $P4_2/n$, a = 17.226(4), c = 14.667(3) Å, U = 4 352 Å^3, D_m (flotation) = 1.33 g cm^{-3} Z = 2, D_c = 1.30 g cm^{-3}, F(000) = 1 656, Mo-K_α radiation, λ = 0.7107 Å, μ = 7.98 cm^{-1}.

Preliminary photographic data revealed that crystals belong to the $4/m$ Laue group of the tetragonal system and show systematic extinctions ($hk0$, $h + k = 2n + 1$; $00l$, $l = 2n + 1$) consistent with the space group C_4^4h–$P4_2/n$ (no. 86). Cell constants and corresponding standard deviations were obtained from a least-squares refinement of 25 reflections automatically centered on a Enraf-Nonius CAD4 diffractometer.

Data collection and reduction. To avoid decomposition of crystals by loss of methanol molecules of crystallization, a selected crystal of dimensions *ca.* 0.5 × 0.75 × 0.3 mm was sealed in a Lindemann capillary containing methanol. A total of 4 494 ($h, k, l > 0$) intensities were recorded at 20 °C (θ—2θ scan) in the range $3 < 2\theta < 52°$. After data processing only those 2 514 unique reflections having $F_o^2 > 3\sigma(F_o^2)$ were used in subsequent calculations.

Structure determination. The direct method approach, based on 500 normalized structure factors, yielded the correct positions of seven atoms, namely Cu, O(1), O(2), N(1), C(1), C(2), and C(3). The positions of the remaining non-hydrogen atoms, including those of the solvent molecules, O(4), O(5), C(18), C(19), were obtained through the usual combination of full-matrix least-squares refinements and difference-Fourier synthesis. Positions of hydrogen atoms were idealized (C–H 0.95 Å). Their contributions to F_c were calculated and then used in subsequent cycles of refinement. For each hydrogen atom, an isotropic thermal parameter was assigned with a value 1.0 Å^2 greater than of the C atom to which it is attached. The final least-squares calculations included anisotropic thermal parameters for all but the hydrogen atoms. The final values of the agreement factors were R 0.053 and R' 0.067. During the last cycle of refinement, no parameter shift was greater than its associated standard deviation. Final atomic co-ordinates are listed in Table 1.

Magnetic Measurements.—The magnetic susceptibilities of the samples were recorded by the Faraday method at *ca.* 1.0 T in the temperature range 4.2—216 K.[24] Methanol was added to prevent loss of solvent molecules during the measurements on the crystalline sample. Experimental susceptibility data were corrected for the underlying diamagnetism and the temperature-independent paramagnetism. Magnetic moments were calculated using the formula $\mu = 2.828\,(\chi T)^{\frac{1}{2}}$.*

Calculations for X-ray structural determination were performed by using the CII IRIS 80 computer of the Centre Universitaire de Calcul de Toulouse using previously reported procedures,[9] and for the theoretical $\chi(T)$ curve by using the IBM 370/168 of the Technische Hochschule Darmstadt.

References

1 R. Mergehenn and W. Haase, *Acta Crystallogr., Sect. B*, 1977, **33**, 1877 and refs. therein.
2 R. Mergehenn, Dissertation, Technische Hochschule Darmstadt, 1979.
3 M. Ahlgren, R. Hamalainen, U. Turpeinen, and K. Smolander, *Acta Crystallogr., Sect. B*, 1979, **35**, 2870; U. Turpeinen, M. Ahlgren, and R. Hamalainen, *Acta Chem. Scand., Ser. A*, 1979, **33**, 593.
4 B. Jezowska-Trzebiatowska, Z. Olejnik, and T. Lis, *J. Chem. Soc., Dalton Trans.*, 1981, 251.
5 S. J. Loeb and C. J. Willis, *Inorg. Chem.*, 1981, **20**, 2791.
6 C. R. Pauley and L. J. Theriot, *Inorg. Chem.*, 1974, **13**, 2033; A. Syamal and L. J. Theriot, *J. Coord. Chem.*, 1973, **2**, 241.

---

* To convert into S.I. units χ should be multiplied by 4π × 10^{-6}; this gives μ 797.74$(\chi T)^{\frac{1}{2}}$.

7 W. J. Jones, S. Gupta, L. J. Theriot, F. T. Helm, and W. A. Baker, jun., *Inorg. Chem.*, 1978, **17**, 87.
8 J. A. Bertrand and J. A. Kelley, *Inorg. Chim. Acta*, 1970, **4**, 203.
9 R. Mergehenn, L. Merz, W. Haase, and R. Allmann, *Acta Crystallogr., Sect. B*, 1976, **32**, 505.
10 L. Merz and W. Haase, *Z. Naturforsch., Teil A*, 1976, **31**, 177.
11 F. Nepveu, J. P. Laurent, and M. Massol, *C.R. Acad. Sci. Ser. C*, 1980, **290**, 117.
12 F. Nepveu, J. J. Bonnet, J. P. Laurent, and M. Massol, *J. Coord. Chem.*, 1981, **11**, 185.
13 G. A. Hamilton, 'Pyridoxal Catalysis, Enzyme and Model Systems,' eds. E. E. Snell, A. E. Braunstein, S. E. Severin, and Yu M. Torchinsky, Interscience, New York, 1968, p. 375.
14 R. Mergehenn, L. Merz, and W. Haase, *J. Chem. Soc., Dalton Trans.*, 1980, 1703.
15 R. Mergehenn, W. Haase, and R. Allmann, *Acta Crystallogr., Sect. B*, 1975, **31**, 1847.
16 K. Niemiken, *Acta Chem. Scand., Ser. A*, 1978, **32**, 493; 1979, **33**, 375.
17 A. P. Ginsberg, *Inorg. Chim. Acta Rev.*, 1975, **5**, 45.
18 R. L. Martin, 'New Pathways in Inorganic Chemistry,' eds. E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Cambridge University Press, Cambridge, 1968, ch. 9.
19 E. Sinn, *Coord. Chem. Rev.*, 1970, **5**, 313.
20 R. W. Jotham and S. F. A. Kettle, *Inorg. Chim. Acta*, 1970, **4**, 145.
21 L. Merz, Dissertation, Technische Hochschule Darmstadt, 1980.
22 D. M. Olsson, *J. Qual. Technol.*, 1974, **6**, 53.
23 L. Merz and W. Haase, *J. Chem. Soc., Dalton Trans.*, 1980, 875.
24 L. Walz, Diplomwork, Technische Hochschule Darmstadt, 1981.

Received 22nd March 1982; *Paper* 2/495