Crystal and Molecular Structures and Magnetic Properties of Tetrameric Copper(II) Complexes with 3-Hydroxy-5-hydroxymethyl-4-(4′-hydroxy-4′-phenyl-2′-azabut-1′-en-1′-yl)-2-methylpyridine (H_2L^3), $[Cu_4L^3{}_4]\cdot 9CH_3OH$ and 3-Hydroxy-5-hydroxymethyl-4-(4′-hydroxy-3′-methyl-4′-phenyl-2′azabut-1′-en-1′-yl)-2-methylpyridine (H_2L^1), $[Cu_4L^1{}_4]\cdot 8CH_3CH_2OH$: Two Complexes with Ferromagnetic Ground States †

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The crystal and molecular structures of the title compounds $[Cu_4L^3{}_4]\cdot 9CH_3OH$ (3) and $[Cu_4L^1{}_4]\cdot 8CH_3CH_2OH$ (4) have been determined from single-crystal *X*-ray diffraction data and refined to final *R* values of 0.062 (R' = 0.052) using 2 191 independent reflections for (3) and 0.062 (R' = 0.055) using 2 458 independent reflections for (4). Both tetrameric complexes crystallize in the tetragonal space group $P4_2/n$ with two molecules in an unit cell with dimensions a = 18.193(4) and c = 12.615(4) Å for (3) and a = 17.991(4) and c = 14.296(4) Å for (4). Both molecules exhibit the highest possible point symmetry $\bar{4}$. While compound (3) is comparable with its 4′-(3″,4″-dichlorophenyl) derivative $[Cu_4L^2{}_4]\cdot 9CH_3OH$ (2) which crystallizes in a monoclinic lattice having an infinite network of hydrogen bonds, (4) is isomorphous to $[Cu_4L^1{}_4]\cdot 8CH_3OH$ (1). Moreover these two forms of structures are distinguishable by the considerably larger Cu–O distance between two pseudo-monomeric units within the pseudo-dimeric unit in (1) and (4) compared with (2) and (3). The magnetism of the two complexes can be explained on the basis of the isotropic Heisenberg–Dirac–van Vleck model. Compound (4) is very similar in its magnetic behaviour [g = 2.16(2), J_{12} = 0 (fixed), J_{13} = 17.4(2.0) cm^{-1}, and θ = −1.8(1.0) K] to (1). In contrast to (2), compound (3) definitely has a ferromagnetic ground state [g = 2.085(20), J_{12} = −7.1(2.0), and J_{13} = 28.5(2.0) cm^{-1}]. The principal difficulties of fitting theoretical magnetic susceptibility equations to experimental ones in ferromagnetically coupled systems is discussed. The discrepancy of the magnetic exchange constants between (3) and (2) which has really C_1 symmetry is discussed in order to test by which model of higher symmetry the magnetism of this compound can be optimally described. It can be shown that a C_{2v} model leads to more plausible exchange constants for (2) with regard to the geometrical sizes of the highly distorted molecule.

Of the great number of known tetrameric oxygen-bridged copper(II) complexes of the cubane type most belong to the group of (dialkylaminoalcoholato)[(pseudo)halogeno]-copper(II) complexes.[1-3] Many have been structurally and magnetically investigated and the variety of this class of substances led to the possibility of correlating their magnetic behaviour with their structures.[3-5] However, the number of tetrameric copper(II) complexes derived from iminoalcohols is rather small. *X*-Ray studies and magnetic measurements are limited to three complexes: $[\{Cu(MeCOCHCMe{=}NCH_2CH_2O)\}_4]$ which exists in two principal different molecular structures, the α form [6] having a singlet ground state [7] while the spin coupling in the β form [8] is ferromagnetic in the ground state;[9] $[Cu_4L^1{}_4]\cdot 8CH_3OH$ (1) in which the Schiff-base ligand H_2L^1 is derived from pyridoxal and 2-amino-1-phenylpropan-1-ol; and $[Cu_4L^2{}_4]\cdot 9CH_3OH$ (2) where H_2L^2 is derived from pyridoxal and 2-amino-1-(3′,4′-dichlorophenyl)ethanol. We have recently described the complexes (1) [10] and (2) [11] as type II complexes.

In order to get a better understanding of the different forms of molecular structures of (1) and (2) as well as of the different hydrogen bonds in these from the chemical point of view of very similar substances and to obtain a larger number of complexes for magneto-structural correlations we have synthesized two new compounds: $[Cu_4L^3{}_4]\cdot 9CH_3OH$ (3) where H_2L^3 is the pyridoxal Schiff base with 2-amino-1-phenylethanol and $[Cu_4L^1{}_4]\cdot 8CH_3CH_2OH$ (4). The reason for preparing a second form of (1) was that different solvents employed for crystallization can lead to different molecular structures. This was observed in the case of $[\{Cu[OCH_2CH_2N(C_2H_5)_2](NCO)\}_4]$. Structures containing chloroform and also different amounts of tetrachloromethane are known and were recently determined.[5,12]

The syntheses and the crystal and molecular structures as well as the magnetic properties of compounds (3) and (4) are reported in this paper. Compound (3) is a good example with which we can point out the principal difficulties of fitting theoretical equations to the experimental susceptibility data of tetrameric copper(II) complexes having ferromagnetic ground states. With the help of the results for this compound we have the possibility to determine whether the magnetic behaviour of (2) should also be described by a model other than the simplest one of $\bar{4}$ symmetry.[11]

Results and Discussion

Description of the Structures.—In Tables 1 and 2 the positional parameters of each compound are presented. The structures comprise four asymmetric units leading to molecules of the Cu_4O_4 cubane type. One asymmetric unit without solvent is shown in Figure 1, and the tetrameric molecule of (3) is shown in Figure 2. The compounds crystallize in tetragonal lattices with the crystallographic $\bar{4}$ axes parallel to the molecular $\bar{4}$ ones. A comparison between compounds

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† *Supplementary data available* (No. SUP 56045, 9 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Positional parameters for $[Cu_4L^3_4]\cdot9CH_3OH$ (3) with estimated standard deviations in parentheses

Atom	X/a	Y/b	Z/c
Cu	0.072 7(1)	0.059 2(1)	0.578 6(1)
O(1)	0.062 (2)	−0.050 1(2)	0.573 0(4)
O(2)	0.094 2(3)	0.160 4(2)	0.585 8(4)
O(3)	0.112 1(5)	0.163 (5)	1.010 8(6)
O(1M) [a]	−0.001 0(16)	0.071 8(12)	0.970 3(27)
O(21M) [b]	−0.018 3(17)	−0.260 6(13)	0.024 7(18)
O(22M) [b]	−0.028 1(10)	−0.330 4(12)	1.020 3(17)
O(31M) [b]	0.201 8(9)	0.456 8(9)	0.711 2(17)
O(32M) [b]	0.168 8(15)	0.468 3(14)	0.705 (24)
N(1)	0.106 8(3)	0.041 1(3)	0.720 7(5)
N(2)	0.157 0(4)	0.316 8(4)	0.729 7(7)
C(1)	0.119 2(4)	0.195 5(4)	0.667 4(7)
C(2)	0.137 3(4)	0.166 1(4)	0.765 6(7)
C(3)	0.131 7(4)	0.087 4(4)	0.787 1(6)
C(4)	0.163 6(4)	0.213 1(5)	0.849 6(8)
C(5)	0.171 7(5)	0.286 4(5)	0.825 2(8)
C(6)	0.131 1(5)	0.273 5(5)	0.653 7(8)
C(7)	0.114 5(6)	0.307 5(4)	0.546 9(8)
C(8)	0.176 6(6)	0.184 6(6)	0.960 6(8)
C(9)	0.106 4(4)	−0.037 5(4)	0.746 7(6)
C(11)	0.116 3(4)	−0.078 3(4)	0.642 3(6)
C(121) [b]	0.095 0(7)	−0.162 2(6)	0.668 3(10)
C(131) [b]	0.058 7(7)	−0.186 4(6)	0.759 2(10)
C(141) [b]	0.048 3(7)	−0.261 4(6)	0.776 3(10)
C(151) [b]	0.074 2(7)	−0.312 3(6)	0.702 4(10)
C(161) [b]	0.110 5(7)	−0.288 1(6)	0.611 5(10)
C(171) [b]	0.120 9(7)	−0.213 0(6)	0.594 4(10)
C(122) [b]	0.129 9(6)	−0.157 7(6)	0.648 4(10)
C(132) [b]	0.192 4(6)	−0.185 7(6)	0.697 9(10)
C(142) [b]	0.201 3(6)	−0.261 5(6)	0.708 8(10)
C(152) [b]	0.147 6(6)	−0.309 2(6)	0.670 3(10)
C(162) [b]	0.085 0(6)	−0.281 2(6)	0.620 8(10)
C(172) [b]	0.076 2(6)	−0.205 4(6)	0.609 (10)
C(1M)	0.000 0	0.000 0	1.000 0
C(21M) [b]	−0.016 5(17)	0.255 8(19)	0.932 6(34)
C(22M) [b]	0.027 5(17)	0.422 6(19)	0.016 3(30)
C(31M) [b]	0.187 3(10)	0.488 9(10)	0.813 8(17)
C(32M) [b]	0.134 (19)	0.483 6(20)	0.782 4(40)

[a] s.o.f. = 0.25. [b] s.o.f. = 0.5.

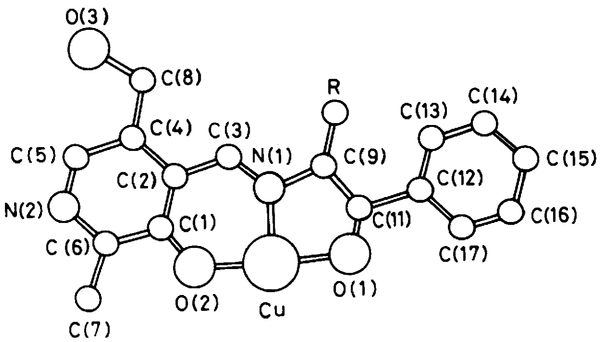


Figure 1. Schematic representation of the asymmetric unit with R = H for $[Cu_4L^3_4]\cdot9CH_3OH$ (3) and R = CH_3 for $[Cu_4L^1_4]\cdot8CH_3CH_2OH$ (4)

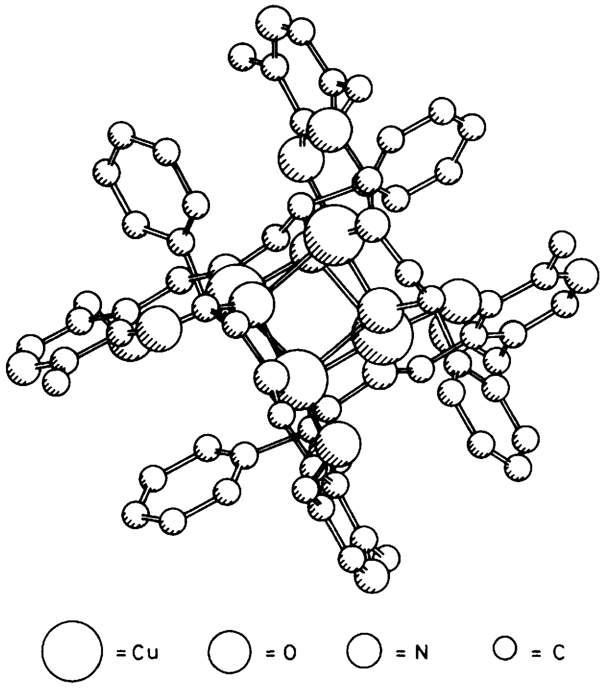


Figure 2. Perspective view of the tetrameric molecule of $[Cu_4L^3_4]\cdot9CH_3OH$ (3)

(1)[10] and (4) shows that the methanol molecules of (1) are substituted by ethanol molecules leading to a small change in the lattice constants [(1): a = 17.226(4), c = 14.667(3) Å], whereas (3) crystallizes with the same number of methanol molecules as its derivative (2) chlorinated at the phenyl ring. Recently we have described[11] the transformation of the monoclinic $I2/c$ lattice of (2) into a pseudo-tetragonal $P4_2/n$ lattice. This space group is preferred for such types of molecules. Whereas the substitution of the solvent molecules of crystallization does not change the crystallographic symmetry [(1) ⟶ (4)] as well as changes in the 'inner-sphere' region [(1) ⟶ (3)], the substitution of two hydrogen atoms in the 'outer-sphere' region by two chlorine atoms leads to a decrease in symmetry [(3) ⟶ (2)].

In Table 3 selected distances and angles of the two Cu_4O_4 cores are listed. A comparison shows that the distances and angles are nearly equivalent except those where the Cu–O(1^{II}) bonds are involved [Cu–O(1^{II}); (3), 2.475(4); (4), 2.749(4); (1), 2.734(4);[10] (2), 2.327(5)—2.690(6) Å [11]]. Both tetrameric molecules are type II complexes.[13] The distances and angles of compounds (1) and (4) are equivalent within the error limits. Since in the case of (2) the whole tetrameric cluster is the asymmetric unit, the crystal data of this compound cannot be compared directly with those of (3), except by use of the mean values which are equivalent. We interpret the difference in the Cu–O(1^{II}) distances from 2.47 Å in compounds (2) and (3) to 2.74 Å in (1) and (4) as a consequence of the steric influence of the methyl group C(10). This group has an elongating effect on the Cu–O(1^{II}) bonds within the four-membered Cu_2O_2 ring formed by the atoms Cu, O(1), Cu^{II}, and O(1^{II}) of two pseudo-monomers in a pseudo-dimer. Due to the presence of eight shorter Cu–O distances (*ca.* 2.0 Å) and four very long ones (*ca.* 2.75 Å) we can also describe the centre of the molecule as a puckered eight-membered Cu_4O_4 ring. It can be shown that the magnetic properties are also dependent on the influence of the methyl group C(10), since a Cu–O distance of 2.75 Å prevents exchange interaction. Whereas the Schiff-base ligand within compound (4) is nearly

Table 2. Positional parameters for $[Cu_4L^1_4]\cdot 8CH_3CH_2OH$ (4) with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Cu	0.077 8(1)	0.058 9(1)	0.573 7(1)	C(8)	0.197 3(4)	0.16 77(4)	0.914 4(4)
O(1)	0.074 1(2)	−0.050 5(2)	0.556 3(2)	C(9)	0.135 3(3)	−0.046 9(4)	0.704 9(4)
O(2)	0.087 6(2)	0.162 4(2)	0.596 9(3)	C(10	0.073 1(4)	−0.081 6(4)	0.763 6(4)
O(3)	0.141 1(3)	0.127 0(3)	0.962 8(3)	C(11)	0.139 3(3)	−0.078 2(3)	0.605 3(4)
O(4)	0.008 2(4)	0.196 4(4)	0.986 0(6)	C(12)	0.150 3(4)	−0.160 6(3)	0.603 7(4)
O(5)	0.179 9(4)	0.465 6(4)	0.727 3(5)	C(13)	0.218 2(4)	−0.187 5(4)	0.628 8(4)
N(1)	0.122 1(2)	0.033 7(3)	0.693 1(3)	C(14)	0.233 7(5)	−0.262 4(5)	0.632 3(5)
N(2)	0.149 3(3)	0.312 9(3)	0.739 2(4)	C(15)	0.179 5(6)	−0.310 5(4)	0.611 5(6)
C(1)	0.115 7(3)	0.194 4(3)	0.670 7(4)	C(16)	0.112 6(5)	−0.285 1(4)	0.585 2(6)
C(2)	0.142 3(3)	0.159 3(3)	0.750 3(4)	C(17)	0.096 5(4)	−0.209 8(4)	0.582 4(5)
C(3)	0.146 6(3)	0.079 7(3)	0.754 9(4)	C(181)	0.004 4(6)	0.279 0(8)	0.965 1(9)
C(4)	0.169 4(3)	0.201 9(3)	0.825 8(4)	C(182)	−0.035 8(8)	0.278 8(8)	0.883 4(8)
C(5)	0.171 7(3)	0.276 4(4)	0.816 9(4)	C(191)	0.128 5(10)	0.507 2(8)	0.775 7(10)
C(6)	0.121 7(3)	0.274 3(3)	0.668 3(4)	C(192)	0.120 4(14)	0.488 2(11)	0.866 2(8)
C(7)	0.099 3(4)	0.314 6(4)	0.580 2(5)				

Table 3. Selected distances (Å) and angles (°) with estimated standard deviations for the Cu_4O_4 cores of $[Cu_4L^3_4]\cdot 9CH_3OH$ (3) and of $[Cu_4L^1_4]\cdot 8CH_3CH_2OH$ (4)

	(3)	(4)		(3)	(4)
$Cu \cdots Cu^{I}$	3.124(1)	3.258(1)	Cu–O(1)	1.998(4)	1.986(4)
$Cu \cdots Cu^{II}$	3.412(2)	3.512(1)	$Cu–O(1^{I})$	1.958(4)	1.942(4)
Cu–O(2)	1.884(5)	1.899(4)	$Cu–O(1^{II})$	2.475(4)	2.749(4)
Cu–N(1)	1.924(6)	1.937(5)			
O(1)–Cu–O(2)	173.1(2)	175.6(3)	$O(1^{I})–Cu–O(1^{II})$	76.4(2)	70.7(2)
N(1)–Cu–O(2)	93.2(2)	92.2(2)	$O(1^{II})–Cu–O(2)$	105.9(2)	99.3(2)
O(1)–Cu–N(1)	83.8(2)	83.8(2)	$O(1^{II})–Cu–N(1)$	109.7(2)	118.4(2)
$O(1)–Cu–O(1^{I})$	88.9(2)	90.6(2)	$Cu–O(1)–Cu^{II}$	104.4(2)	94.4(2)
$O(1)–Cu–O(1^{II})$	81.0(2)	84.3(2)	$Cu–O(1)–Cu^{III}$	99.0(2)	112.0(2)
$O(1^{I})–Cu–O(2)$	93.2(2)	93.0(2)	$Cu^{II}–O(1)–Cu^{III}$	88.8(2)	86.1(2)
$O(1^{I})–Cu–N(1)$	169.5(2)	168.6(2)			

Superscripts represent the following positions: I $-y, x, 1 - z$; II $-x, -y, z$; III $y, -x, 1 - z$.

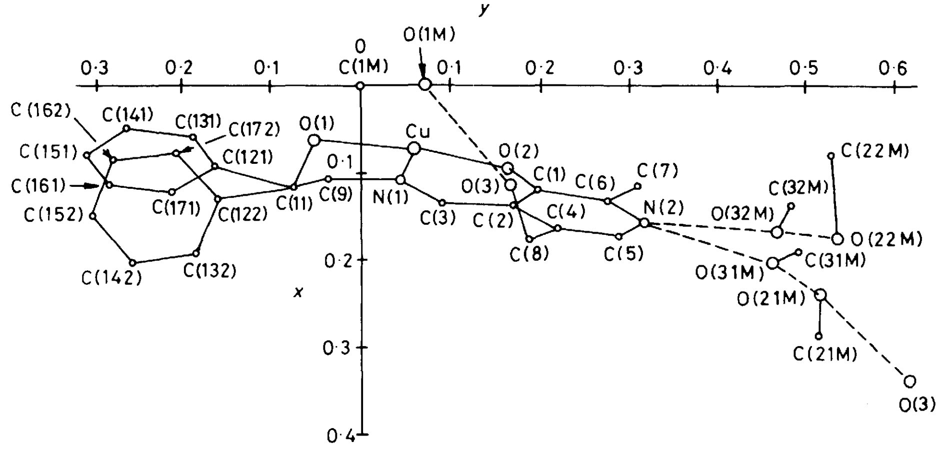


Figure 3. Asymmetric unit showing the statistical disorder of the phenyl ring and the methanol molecules of $[Cu_4L^3_4]\cdot 9CH_3OH$ (3). The hydrogen bridges are symbolized by dashed lines

identical with that within (1), the ligand within (3) shows a disorder with regard to two equivalent positions of the phenyl ring. In Figure 3 we present these two equivalent positions [C(121)—C(171) and C(122)—C(172), respectively]. The low thermal parameters of all 12 carbon atoms with a site occupation factor (s.o.f.) of 0.5 show that the disorder is static and not dynamic.

Analogous to the disorder of the phenyl groups, the methanol molecules are also disordered. The methanol molecule 1 [O(1M) and C(1M), Table 1] is positioned between the tetrameric units on the $\bar{4}$ axis with the C(1M) atom on the special position and the O(1M) on a general position with an s.o.f. of 0.25. The disorder of the methanol molecules 2 and 3 [namely atoms O(21M), C(21M), O(22M), C(22M), and O(31M), C(31M), O(32M), C(32M), respectively] is also shown in Figure 3. In Table 4 the distances within the solvent

Table 4. Distances within the solvent molecules and hydrogen-bridge distances for $[Cu_4L^3{}_4]\cdot9CH_3OH$ (3) and $[Cu_4L^1{}_4]\cdot8CH_3CH_2OH$ (4)

(3)		(3)	
O(1M)–C(1M)	1.36(4)	O(31M)–C(31M)	1.44(3)
O(1M) ··· O(3)	2.70(4)	O(31M) ··· O(21M)	2.69(4)
O(21M)–C(21M)	1.33(4)	O(31M) ··· O(22M)	2.80(4)
O(21M) ··· O(31M)	2.69(4)	O(31M) ··· N(2)	2.69(4)
O(21M) ··· O(32M)	2.78(4)	O(32M)–C(32M)	1.18(4)
O(21M) ··· O(3)	2.46(4)	O(32M) ··· O(21M)	2.78(4)
O(22M)–C(22M)	1.68(4)	O(32M) ··· O(22M)	2.58(4)
O(22M) ··· C(31M)	2.80(4)	O(32M) ··· N(2)	2.78(4)
O(22M) ··· O(32M)	2.58(4)		
[··· O(3)	3.40(4)]		
(4)		(4)	
O(4)–C(181)	1.52(2)	O(5)–C(191)	1.38(2)
O(4) ··· O(3)	2.72(2)	O(5) ··· N(2)	2.81(2)
O(4) ··· O(3)	2.73(2)	C(191)–C(192)	1.35(2)
C(181)–C(182)	1.37(2)		

The distance O(4) ··· O(3) exists twice due to the $\bar{4}$ symmetry.

molecules are presented together with the distances interpreted as hydrogen-bond bridges. It should be noted that it is due to the disorder that there are other shorter as well as longer distances, for instance O(22M) ··· O(3) 3.40(4) Å, which are not interpreted as hydrogen bonds. The hydrogen-bond bridges in compound (3) are identical with the two-dimensional infinite network in (2). Between each of two tetrameric units along *a* and *b* there is a two-fold hydrogen bridge of the type N(2) ··· O(3M) ··· O(2M) ··· O(3). The methanol molecule 1 additionally forms hydrogen-bond bridges of the type O(1M) ··· O(3).

The hydrogen-bond bridges within compound (4) are equivalent to those within (1). The O(4) atom of the first solvent molecule acts as a member of the 16-membered ring between two tetrameric units perpendicular to (001), while the O(5) atom belonging to the second solvent molecule forms bridges to N(2). The stabilization of the crystal structures of compounds (1) and (4) as well as of (2) and (3) with different numbers of solvent molecules, namely eight and nine, respectively, has to be interpreted in terms of the presence or absence of the methyl group C(10). In the first case [(1) and (4)] four methyl groups, C(10), occupy the region around 0,0,0 and four around $\frac{1}{2},\frac{1}{2},\frac{1}{2}$, whereas in the second case [(2) and (3)] one methanol molecule occupies 0,0,0 and one occupies $\frac{1}{2},\frac{1}{2},\frac{1}{2}$. This is also in good agreement with the fact that the cell volume of (1) (4 352 Å^3)[10] is bigger than that of (3) (4 175 Å^3), because the eight methyl groups in (1) (see Figure 1) are replaced by only eight hydrogen atoms together with two methanol molecules.

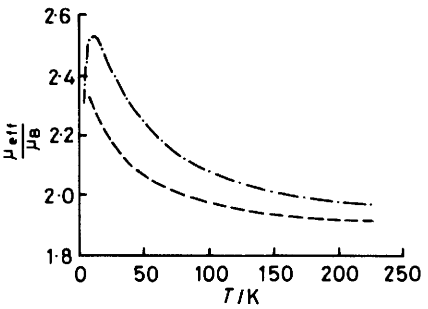


Figure 4. Temperature dependence of the magnetic moments of $[Cu_4L^3{}_4]\cdot9CH_3OH$ (3) (— · —) and $[Cu_4L^2{}_4]\cdot9CH_3OH$ (2) (– – –)

$$\chi_{tet.} = (1 - x) \left[\frac{N_A\beta^2g^2}{4k(T - \theta)} \cdot \frac{10e^{2u} + 2e^{-2u} + 4e^{-2v}}{5e^{2u} + 3e^{-2u} + 6e^{-2v} + e^{-4v}}\right] + x\chi_{para.} + N\alpha + \chi_{dia.} \qquad (i)$$

Magnetic Properties.—The magnetic susceptibilities of compound (3) in the temperature range from 10.6 to 216 K are shown in Table 5. While the susceptibility increases steadily with decreasing temperature the magnetic moment reaches a maximum at about 10 K and decreases at lower temperatures. This is shown in Figure 4. The magnetic moments are higher than those of monomeric copper(II) complex ions and show a predominant ferromagnetic spin coupling. If we compare the magnetic moments of (3) with those of its dichloro-derivative (2) also given in Figure 4 we see a considerable difference. In case of (2) the values at low temperature are distinctly smaller. This will be discussed later in more detail. For (3), fitting equation (i), where $u = J_{13}/kT$ and $v = J_{12}/kT$, to the experimental susceptibilities yields $g = 2.085(20)$, $J_{12} = -7.1(2 0)$. and $J_{13} = 28.5(2.0)$ cm^{-1}, $x = 0.036$, $\theta = 0$ K (fixed), and $N\alpha = 60 \times 10^{-6}$ c.g.s. units (fixed); x is the molar fraction of the paramagnetic impurity and θ is related to the conventional Weiss constant. For compound (4) the susceptibilities are listed in Table 6. The fitting procedure leads to the values of $g = 2.16(2)$, $J_{12} = 0$ (fixed), $J_{13} = 17.4(2.0)$ cm^{-1}, and $\theta = -1.8(1.0)$ K. These values are the same as for (1) within the error limits. This is to be expected due to the nearly identical structures, consequently we need not discuss the magnetic behaviour of (4).

The calculated exchange integrals of complex (3) show the simultaneous presence of ferromagnetic and antiferromagnetic spin coupling. It must be emphasized that the numerical values for g, J_{12}, and J_{13} are averages from the results of several fitting procedures having a comparable quality. The correlations within the least-squares calculations for compound (3) are a new example of the difficulties in fitting theoretical $\chi(T)$ equations to experimental values, but they do enable the error limits to be estimated. Within the error limits given above, the error in the results of the fitting procedures, Δ, is calculated according to the formula (ii) and is nearly constant (±3%). Outside this range some other minima were found, but these have to be rejected because of their lack of physical meaning.

$$\Delta = (\chi_{obs.} - \chi_{calc.})^2T^2 \qquad (ii)$$

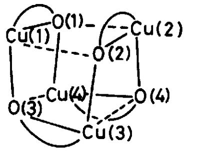
Also of interest is a comparison of the results of the magnetic measurements on compound (3) with those on the dichloro-derivative (2). We recently[11] described complex (2), which is actually strongly distorted from point symmetry $\bar{4}$, as a pseudo-$\bar{4}$ molecule. To describe exactly a Cu_4O_4 core with point symmetry C_1 we need six exchange constants. In the case of (2) we made the approximation shown in Figure 5. Table 7 shows the 12 different Cu–O distances of compound (2), Cu–O(real), together with the mean values Cu–O(av.) and values for (3). A comparison of the mean values of (2) with the distances in (3) which are nearly equal suggests that there should be very similar magnetic behaviour, in contrast to the considerable differences actually observed. While (3) definitely has a ferromagnetic ground state, we cannot determine whether the spin coupling within (2) is ferromagnetic or antiferromagnetic in the ground state ($J_{12} = -9.9$, $J_{13} = 20.5$ cm^{-1}).[11] Looking at the real Cu–O distances in (2) one can see that the Cu(1)–O(1) distances as well as the Cu(1)–O(3) distances vary in a small range and the deviations from the

Table 5. Experimental and calculated susceptibilities of $[Cu_4L^3_4]\cdot 9CH_3OH$ (3)

	$10^6\chi$/cm^3 mol^{-1}			$10^6\chi$/cm^3 mol^{-1}	
T/K	exptl.	calc.	*T*/K	exptl.	calc.
10.6	74 078	75 106	78.1	7 420	7 202
15.3	51 244	51 002	89.6	6 127	6 106
19.0	40 360	40 097	98.5	5 479	5 455
25.4	28 812	28 583	112.5	4 748	4 665
30.6	22 937	22 821	123.5	4 271	4 185
36.6	18 231	18 312	139.9	3 612	3 625
42.0	15 266	15 442	161.8	3 056	3 073
48.8	12 517	12 820	181.8	2 694	2 697
65.7	8 775	8 887	204.5	2 352	2 368
70.5	8 328	8 154	215.9	2 183	2 232

Table 6. Experimental and calculated susceptibilities of $[Cu_4L^1_4]\cdot 8CH_3CH_2OH$ (4)

	$10^6\chi$/cm^3 mol^{-1}			$10^6\chi$/cm^3 mol^{-1}	
T/K	exptl.	calc.	*T*/K	exptl.	calc.
3.8	159 659	154 656	77.0	7 255	7 289
4.3	144 656	141 788	79.6	7 090	7 009
6.7	99 751	101 335	87.1	6 359	6 306
10.6	66 531	68 747	93.3	5 926	5 821
15.5	46 237	47 801	103.7	5 208	5 153
19.8	36 484	36 881	114.2	4 680	4 617
25.9	27 156	27 170	126.0	4 188	4 132
33.1	20 454	20 273	139.2	3 743	3 697
40.2	15 840	15 999	150.0	3 450	3 404
46.5	13 252	13 389	165.3	3 082	3 060
55.2	10 767	10 864	184.4	2 732	2 718
61.2	9 608	9 589	207.8	2 401	2 391
68.1	8 452	8 435	219.4	2 265	2 257
71.2	8 019	7 998			



Cu(1)-O(1) = Cu(2)-O(2) = Cu(3)-O(3) = Cu(4)-O(4) = Cu(1)-O(1) (av.)

Cu(1)-O(2) = Cu(2)-O(1) = Cu(3)-O(4) = Cu(4)-O(3) = Cu(1)-O(2) (av.)

Cu(1)-O(3) = Cu(2)-O(4) = Cu(3)-O(2) = Cu(4)-O(1) = Cu(1)-O(3) (av.)

Figure 5. Scheme for calculating average distances in Cu_4O_4 cores with symmetry lower than $\bar{4}$ leading to pseudo-$\bar{4}$ symmetry

Table 7. Cu–O(1) distances (Å) of the Cu_4O_4 cores of $[Cu_4L^2_4]\cdot 9CH_3OH$ (2) and of $[Cu_4L^3_4]\cdot 9CH_3OH$ (3) together with the mean values for (2) calculated according to Figure 5

	(2)		(3)
Distance	Cu–O (real)	Cu–O (av.)	Cu–O (real)
Cu(1)–O(1)	1.952(5)	2.009	1.998(4)
Cu(2)–O(2)	2.057(5)		
Cu(3)–O(3)	1.998(5)		
Cu(4)–O(4)	2.029(5)		
Cu(1)–O(2)	2.572(6)	2.496	2.475(4)
Cu(2)–O(1)	2.393(5)		
Cu(3)–O(4)	2.690(6)		
Cu(4)–O(3)	2.327(5)		
Cu(1)–O(3)	1.980(5)	1.956	1.958(4)
Cu(2)–O(4)	1.958(5)		
Cu(3)–O(2)	1.970(5)		
Cu(4)–O(1)	1.917(5)		

mean values are not important. Consequently the main distortion of the molecule is due to the considerable differences between the Cu(1)–O(2) distances. Taking into account this distortion the molecule should be described more realistically in terms of C_{2v} symmetry which splits the exchange interaction within the pseudo-dimeric units into two different parts. Fitting of the experimental susceptibility data by the theoretical susceptibility equation derived from the Hamiltonian (iii) leads to the values $g = 2.06$, $J_{12} = -9.3(3.0)$, $J_{34} = -14.8(3.0)$, and $J_{13} = +24.9(3.0)$ cm^{-1}. These values are more plausible from two points of view. The higher negative exchange constants indicate a higher antiferromagnetic spin coupling within the pseudo-dimeric units which is to be expected since there is one considerably smaller Cu(1)–O(2) distance in both pseudo-dimeric units in (2) than in (3). The resulting exchange constant corresponding to the ferromagnetic coupling between the pseudo-dimeric unit, J_{13}, increases and is now closer to that of (3). This is in agreement with the very similar distances in compounds (2) and (3) between the two pseudo-dimeric units. Consequently (3) as a molecule with exact $\bar{4}$ symmetry enables us to determine the constraints upon the choice of a model for a molecule of low symmetry like (2).

$$\mathcal{H} = -2J_{12}S_1S_2 - 2J_{34}S_3S_4 - 2J_{13}(S_1S_3 + S_1S_4 + S_2S_3 + S_2S_4) \quad \text{(iii)}$$

Experimental

Preparation.—The preparation of compound (3) as well as of (4) was carried out in analogy to the procedure given for

(1) and (2).[10,11] As amine component of the Schiff base for (3), 2-amino-1-phenylethanol was used with methanol as solvent; (4) was obtained by using 2-amino-1-phenylpropanol with ethanol as solvent. The dark green crystals which cannot be recrystallized are obtained directly from the mother-liquors. Compound (3) crystallizes as flat crystals, while crystals of (4) are needle-like. Both compounds easily lose their solvent of crystallization and decay to amorphous powders.

Crystallography.—Crystal data. (3), $C_{64}H_{64}Cu_4N_8O_{12}\cdot 9CH_3OH$, $M = 1\,679.81$, tetragonal, space group $P4_2/n$ (no. 86),[14] $a = 18.193(4)$, $c = 12.615(4)$ Å, $U = 4\,175$ Å^3, D_m (flotation) $= 1.36(3)$, $Z = 2$, $D_c = 1.34$ g cm^{-3}, $F(000) = 1\,756$, graphite monochromatized Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) $= 10.21$ cm^{-1}.

(4), $C_{68}H_{72}Cu_4N_8O_{12}\cdot 8CH_3CH_2OH$, $M = 1\,816$, tetragonal, space group $P4_2/n$ (no. 86),[14] $a = 17.991(4)$, $c = 14.296(4)$ Å, $U = 4\,627$ Å^3, D_m (flotation) $= 1.31(3)$, $Z = 2$, $D_c = 1.30$ g cm^{-3}, $F(000) = 1\,912$, graphite monochromatized Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) $= 9.23$ cm^{-1}.

Cell constants for compounds (3) and (4) were obtained by least-squares fits of strong reflections [45 for (3) and 51 for (4)] using a computer-controlled Stoe Stadi 4 four-circle diffractometer. The systematic absences were $hk0$ for $h + k = 2n + 1$ and $00l$ for $l = 2n + 1$.

Data collection and reduction. Compound (3). To avoid decomposition of the crystal during the data collection by loss of the lattice-stabilizing methanol molecules, a crystal of dimensions *ca.* 0.4 × 0.4 × 0.6 mm was sealed in a Lindemann capillary containing a small amount of mother-liquor. A total of 4 616 hkl reflections were collected in the range $3 \leqslant 2\theta \leqslant 45°$ on the Stoe diffractometer (scan $\omega : \theta = 1 : 1$). After data processing only those 2 191 unique reflections having $F_o^2 \geqslant 2\sigma(F_o^2)$ were used in the subsequent calculations. The intensity data were corrected for Lorentz polarization and absorption effects.

Compound (4). The data collection was carried out on the same type of diffractometer in the range $3 \leqslant 2\theta \leqslant 45°$ with the same scan. 2 458 Unique reflections having $F_o^2 \geqslant 2\sigma(F_o^2)$ out of 3 267 measured hkl reflections were used for the calculations. The intensity data were corrected for Lorentz polarization and absorption effects.

Structure determination. Compound (3). The position of the Cu atom could be derived from a three-dimensional Patterson map. The remaining non-hydrogen atoms were located after several Fourier syntheses which showed also that the benzene ring occupies two positions. Because two positions are not allowed from a crystallographic point of view, additional photographic data were collected to confirm the systematic extinctions of the space group $P4_2/n$. In the subsequent calculation, two positions of the benzene ring were assumed with a s.o.f. of 0.5. Block-matrix least-squares refinement with isotropic thermal parameters converged to a R value of 0.18. At this stage the positions of the methanol molecules could be located from a ΔF synthesis. Refinement with anisotropic thermal parameters led to a R value of 0.102. A ΔF synthesis showed that, additionally to the two positions of the benzene ring, the methanol molecules also occupy two positions. The ninth methanol molecule was also found with the carbon atom on the position 0,0,0. Taking into account the disorder of the methanol molecules and geometrical positioning of the hydrogen atoms (C–H 1.08 Å), successive least-squares cycles led to the final R value of 0.062 ($R' = 0.052$). During the last cycles of refinement only the parameter shifts of the methanol molecules were greater than their associated standard deviations.

Compound (4). The position of the copper atom was derived from a three-dimensional Patterson map, and several Fourier maps revealed all other non-hydrogen atoms. Refinement with isotropic thermal parameters converged at R 0.147, and with anisotropic thermal parameters and geometrical positioning of the hydrogen (C–H 1.08 Å) gave a final R value of 0.062 ($R' = 0.055$). All shifts of the parameters in the last least-squares cycles were considerably smaller than the estimated standard deviations, a final ΔF map showing no peak higher than 0.46 e Å^{-3}.

Magnetic Measurements.—The magnetic susceptibilities of compounds (3) and (4) were recorded by the Faraday method at 6.3G^2 cm^{-1} (G $= 10^{-4}$T) in the temperature range 4.2—216 K. To prevent loss of the solvent molecules during measurements, solvent was added. Experimental susceptibility data were corrected for underlying diamagnetism and the temperature independent paramagnetism. Magnetic moments were calculated using the formula (iv). To convert into S.I. units χ should be multiplied by $4\pi \times 10^{-6}$ and μ is then given by $797.74\,(\chi T)^{\frac{1}{2}}$.

$$\mu = 2.828(\chi T)^{\frac{1}{2}} \qquad \text{(iv)}$$

Calculations.—The structure calculations were carried out with the program SHELX 76,[15] scattering factors for Cu were taken from Cromer and Mann,[16] and others are stored in the program. The calculations were performed on an IBM 370/168 computer at the Technische Hochschule Darmstadt as were the calculations of theoretical $\chi(T)$ curves.

Acknowledgements

We are grateful to Dr. Paulus for his help in the use of the automated diffractometer and to the Firma Stoe and Cie., Darmstadt, in whose application laboratory the data collection was carried out. This work was supported by the Deutsche Forschungsgemeinschaft, Bonn, and the Fonds der Chemischen Industrie, Frankfurt. F. N. thanks the Deutscher Akademischer Austauschdienst for financial support.

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Received 9th *January* 1984; *Paper* 4/036