Crystal and Molecular Structure and Magnetic Properties of a Tetrameric Copper(II) Complex with 3-Hydroxy-4-[4'-(3'',4''dichlorophenyl)-4'-hydroxy-2'-azabut-1'-en-1'-yl]-5-hydroxymethyl-2methylpyridine (H_2L^2) , $[(CuL^2)_4]$ ·9CH₃OH †

Leonhard Walz, Helmut Paulus, and Wolfgang Haase * Institut fur Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstrasse 20, D-6100 Darmstadt, West Germany Harald Langhof Firma Stoe & Cie, Hilpertstrasse 10, D-6100 Darmstadt, West Germany Francoise Nepveu Laboratoire de Biospectroscopie, CTB SC 13 INSERM, 38, rue des Trente-Six-Ponts, 31400 Toulouse, France

The crystal and the molecular structure of the title compound has been determined using three-dimensional X-ray diffractometer data involving 7 045 independent reflections. The compound crystallizes in the monoclinic space group 12/c with eight formula units $[(CuL^2)_4]$ ·9CH₃OH in a unit cell with dimensions a = 27.062(5), b = 25.062(5), c = 26.390(5)Å, and $\beta = 92.39(1)^{\circ}$. The structure has been calculated by direct methods and refined by least-squares methods to a final R value of 0.054. In the cubane structure (C_1 symmetry) each copper atom is bonded to one deprotonated phenolic oxygen, one imine nitrogen, and three deprotonated alkoxo-oxygen atoms giving a distorted square-pyramidal co-ordination. The six copper-copper distances are in the range 3.021(1)-3.492(2) A (mean 3.254 \pm 0.184 A). Within the Cu₄O₄ core there are eight shorter copper-oxygen distances [1.917(5)—2.057(5) Å, mean 1.983 Å] and four longer ones [2.327(5)—2.690(6) Å, mean 2.496 ± 0.166 Å]. There are 72 methanol molecules per unit cell which are easily lost in air, giving an amorphous powder. The magnetic properties of the complex can be explained using the isotropic Heisenberg–Dirac–van Vleck model. The exchange parameters for the complex with approximate S_4 symmetry obtained $(J_{12} = -9.9 \pm 3.0 \text{ cm}^{-1}, J_{13} = 20.5 \pm 3.0 \text{ cm}^{-1}$, and $g = 2.08 \pm 0.02$) are in good agreement with those of similar substances and show the presence of both ferromagnetic and antiferromagnetic interactions. The amorphous modification shows a predominant ferromagnetic interaction.

Structural and magnetic investigations have been reported for a great number of dimeric and tetrameric oxygen-bridged copper(II) complexes of the cubane type with N,N-dialkylated aminoalcohols [{ $CuX(OCH_2CH_2NR_2)$ }_n]^{1,2} (n = 2, X = Cl, Br, or NCS, $R = C_2H_5$ or n-C₄H₉; n = 4, X = Cl, Br, NCS, NCO, Cl_3CCO_2 , F_3CCO_2 , etc., $R = CH_3$, C_2H_5 , n- C_3H_7 , n-C₄H₉). On the other hand tetrameric copper(II) complexes with Schiff bases as ligands are rarely described. X-Ray studies and magnetic measurements are limited to two tetrameric complexes: $[{Cu(MeCOCHCMe=NCH_2CH_2O)}_4]$, a complex with a Schiff-base ligand derived from acetylacetone and 2-aminoethanol, which exists in two principally different molecular structures, α^3 and β^4 ; (The α form is a type I complex according to the Mergehenn nomenclature 5 and has a singlet ground state, while the β form is a type II complex with a quintet ground state.⁶) [(CuL¹)₄]·8CH₃OH (1) in which the Schiff-base ligand L¹ is derived from 3-hydroxy-5-hydroxymethyl-2-methylpyridine-4-carbaldehyde (pyridoxal) and 2amino-1-phenylpropan-1-ol. This complex and also the title compound have been isolated during our investigations concerning the interactions between copper(II), pyridoxal, and biogenic amines in model systems.⁷⁻⁹ We have recently described complex (1) structurally and magnetically as a type II complex with a ferromagnetic ground state.¹⁰

The present work reports a new example of a tetrameric copper(II) complex with a Schiff base derived from pyridoxal and 2-amino-1-(3',4'-dichlorophenyl)ethanol. Two different

forms have been synthesized: a crystalline one $[(CuL^2)_a]$ 9CH₃OH (2) and an amorphous one $[(CuL^2)_m]$ (3); the latter can be obtained by loss of the solvent molecules from the former. The synthesis and crystal and molecular structure of complex (2) and the magnetic properties of both (2) and (3) are reported. The different hydrogen bonds observed in complexes (1) and (2) are compared.

Results and Discussion

Description of the Structure.—The final structural information is presented in Tables 1—7 and Figures 1 and 2. The unit cell contains eight tetrameric $[(CuL^2)_4]$ molecules with a cubane-like Cu₄O₄ core and 72 methanol molecules. The symmetry of the tetrameric molecule is C_1 ; consequently all distances and angles within the molecule are crystallographically different.

Each Schiff base acts as a tridentate ligand to one copper atom leading to a five-membered ring and a six-membered ring. Figure 1 shows the detailed geometry of one of these chelate units. The bond distances and angles within the four different Schiff-base chelate groups are identical within the error limits of the measurements. Significant differences are only observed for distances and angles involving copper atoms. Therefore only mean values are reported in Table 2. These values are similar to those observed for $[(CuL^1)_4]$ -8CH₃OH (1). The equations of the least-squares planes involving the six-membered chelate ring and the atom deviations therefrom are given in Table 3. Whereas the sixmembered chelate ring is nearly planar, the five-membered ring is corrugated, the greatest deviation being observed for the C(2) atom. The dichlorophenyl rings are twisted differently

⁺ Supplementary data available (No. SUP 23505, 47 pp.): thermal parameters, structure factors for the crystalline complex; magnetic data for the amorphous form. See Notices to Authors No. 7, J. Chem. Soc., Dalton Trans., 1981, Index issue.

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Atom	x	У	z	Atom	x	У	Z
Cu(1)	0.239 06(5)	0.656 29(5)	0.058 02(5)	C(15)	0.303 5(4)	0.776 3(4)	0 221 9(4)
Cu(2)	0.249 15(5)	0.657 72(5)	-0.07422(5)	C(25)	0.189 5(4)	0.796 0(4)	-0.2266(4)
Cu(3)	0.184 31(5)	0.579 69(5)	-0.01303(5)	C(35)	0.025 2(3)	0.470 4(4)	0.056 1(4)
Cu(4)	0.311 36(5)	0.577 04(5)	0.001 36(5)	C(45)	0.469 2(3)	0.453 0(4)	-0.0466(4)
Cl(11)	0.066 0(1)	0.606 7(1)	-0.1532(1)	C(16)	0.312 4(4)	0.689 7(4)	0.195 7(4)
Cl(21)	0.515 4(1)	0.757 0(1)	0.004 3(2)	C(26)	0.188 8(3)	0.704 6(4)	-0.216 8(4)
Cl(31)	0.388 2(1)	0.552 2(2)	-0.183 6(1)	C(36)	0.056 9(3)	0.555 1(4)	0.067 4(4)
Cl(41)	0.139 2(1)	0.595 6(1)	0.224 9(1)	C(46)	0.447 1(3)	0.541 2(4)	-0.058 9(3)
Cl(12)	0.051 5(1)	0.721 4(1)	-0.204 4(1)	C(17)	0.334 3(4)	0.635 5(4)	0.206 4(4)
Cl(22)	0.516 0(1)	0.709 7(2)	0.115 1(2)	C(27)	0.176 5(4)	0.650 6(4)	-0.237 1(4)
Cl(32)	0.339 0(1)	0.509 8(1)	-0.287 0(1)	C(37)	0.054 6(4)	0.609 1(4)	0.091 4(4)
Cl(42)	0.085 0(1)	0.484 2(1)	0.211 3(1)	C(47)	0.459 6(3)	0.596 0(4)	-0.077 3(4)
O(11)	0.196 0(2)	0.656 7(2)	-0.003 5(2)	C(18)	0.253 5(4)	0.845 9(4)	0.176 0(4)
O(21)	0.300 2(2)	0.650 9(2)	-0.014 3(2)	C(28)	0.221 0(4)	0.861 6(4)	-0.162 2(4)
O(31)	0.234 4(2)	0.581 7(2)	-0.066 8(2)	C(38)	0.060 2(4)	0.398 8(4)	0.002 6(4)
O(41)	0.251 5(2)	0.579 7(2)	0.045 3(2)	C(48)	0.421 6(4)	0.385 5(4)	0.000 1(4)
O(12)	0.275 1(2)	0.657 0(2)	0.120 9(2)	C(19)	0.181 5(3)	0.744 8(3)	0.023 8(3)
O(22)	0.218 9(2)	0.664 5(2)	-0.140 4(2)	C(29)	0.312 0(3)	0.740 2(3)	-0.035 8(3)
O(32)	0.1293(2)	0.581(2)	0.029 0(2)	C(39)	0.199 6(3)	0.496 6(3)	-0.082 0(3)
0(42)	0.3/1.6(2)	0.573 8(2)	-0.0327(2)	C(49)	0.276 2(3)	0.490 0(3)	0.056 8(4)
O(13)	0.2699(3)	0.8/2.3(3)	0.132 4(3)	C(111)	0.157 3(3)	0.695 0(3)	0.001 5(3)
O(23)	0.1910(3)	0.8/4 8(3)	-0.121 3(3)	C(211)	0.338 2(3)	0.687 3(3)	-0.027 7(3)
O(33)	0.1029(2)	0.308 5(3)	0.0171(3)	C(311)	0.213 I(3)	0.549 4(3)	-0.107 1(3)
O(43)	0.3771(3)	0.301 3(2)	-0.0172(3)	C(411)	0.258 6(3)	0.5393(3)	0.084 2(3)
O(1M)	0.0990(3)	0.333 7(4)	0.1100(3)	C(112)	0.1293(3)	0.7036(4)	-0.0486(3)
O(2M)	0.069.9(3)	0.6919(3) 0.2776(4)	-0.1303(3)	C(212)	0.3810(3)	0.6920(3)	$0.010 \ 3(4)$
O(3M)	-0.2001(4)	0.577 0(4)	0.030 4(4)	C(312)	0.2404(3)	0.540 4(5)	-0.1504(3)
O(5M)	0.0500(3)	0.869 8(4)	0.1250(3)	C(112)	$0.212 \ 5(3)$	0.5272(4)	-0.074.4(4)
O(6M)	0.565.8(3)	0.5070(4)	-0.114.6(4)	C(213)	0.109 0(3)	0.039 + (4)	-0.0744(4)
O(7M)	0.368 8(4)	0.3645(4)	-0.120.9(4)	C(313)	0.296 7(4)	0.549 6(4)	-0.1470(4)
O(8M)	0.378 1(5)	0.722.3(4)	0.319 4(4)	C(413)	0.1959(3)	0 562 9(3)	0 149 0(3)
O(9M)	0.132 7(3)	0.752 5(3)	-0.3393(3)	C(114)	0.086 8(3)	0.664 6(4)	-0.1224(4)
N(11)	0.215 7(3)	0.728 9(3)	0.065 5(3)	C(214)	0.464 0(4)	0.724 9(4)	0.026.8(6)
N(21)	0.272 1(2)	0.730 7(3)	-0.074 0(3)	C(314)	0.325 6(3)	0.540 7(4)	-0.1893(4)
N(31)	0.168 2(3)	0.510 0(3)	-0.039 4(3)	C(414)	0.156 7(4)	0.550 2(4)	0.178 7(3)
N(41)	0.317 3(3)	0.505 3(3)	0.026 0(3)	C(115)	0.080 7(4)	0.714 1(5)	-0.144 6(4)
N(12)	0.322 8(3)	0.727 2(3)	0.230 2(3)	C(215)	0.463 9(4)	0.704 5(5)	0.075 0(5)
N(22)	0.178 3(3)	0.747 2(4)	-0.245 2(3)	C(315)	0.303 8(4)	0.520 8(4)	-0.233 6(4)
N(32)	0.022 8(3)	0.519 5(3)	0.077 2(3)	C(415)	0.132 6(4)	0.501 8(4)	0.173 1(4)
N(42)	0.479 1(3)	0.501 8(3)	-0.065 6(3)	C(116)	0.098 5(4)	0.758 2(4)	-0.119 4(4)
C(11)	0.282 0(3)	0.697 8(4)	0.151 9(3)	C(216)	0.422 4(4)	0.679 3(5)	0.092 9(4)
C(21)	0.212 3(3)	0.708 9(4)	-0.166 3(4)	C(316)	0.254 4(4)	0.511 3(4)	-0.237 6(4)
C(31)	0.097 5(3)	0.543 5(4)	0.034 9(3)	C(416)	0.148 5(4)	0.466 0 (4)	0.138 2(4)
C(41)	0.401 7(3)	0.533 6(4)	-0.034 1(3)	C(117)	0.123 0(3)	0.753 6(4)	-0.071 6(4)
C(12)	0.261 2(3)	0.749 2(3)	0.144 7(3)	C(217)	0.381 0(4)	0.673 6(4)	0.060 1(4)
C(22)	0.226 8(3)	0.760 1(4)	-0.150 4(3)	C(317)	0.226 1(4)	0.520 8(4)	-0.195 9(4)
C(32)	0.0979(3)	0.492 1(3)	0.011 3(3)	C(417)	0.187 9(4)	0.478 5(4)	0.109 0(4)
C(42)	0.394 2(3)	0.482 9(3)	-0.0129(3)	C(IM)	0.054 1(5)	0.346 2(6)	0.141 2(6)
C(13)	0.227 / (3)	0.760 7(3)	0.101 4(4)	C(2M)	0.0397(7)	0.882 6(5)	-0.196 0(6)
C(23)	0.239 3(3)	0.700 9(3)	-0.103 8(3)	C(3M)	0.2400(3)	0.300 9(3)	-0.00/ 6(5)
C(33)	0.1330(3) 0.2520(4)	0.400 1(4)	-0.0272(3)	C(4M)	- 0.040 2(9)	0.342 0(9)	0.180 4(0)
C(43) C(14)	0.332 0(4)	0.472 2(4)	0.01/0(3)	C(SM)	0.391 /(0)	0.010 2(0)	$0.114 \delta(7)$
C(14)	0.273 0(4)	0.707 2(4)		$C(0\mathbf{M})$	0.363 0(0)	0.437 9(0)	-0.1190(7)
C(24)	0.213 1(4)	0 454 9(3)	0 024 2(4)	C(8M)	0.307 0(0)	0.773 6(6)	- 0.1444 4(7) 0 340 7(6)
C(44)	0.428 9(3)	0.4415(3)	-0.0201(3)	C(9M)	0.096 4(7)	0.793 2(6)	-0.334 2(5)
~~~~	0.120 7(0)	0.111 0(0)	0.020 1(5)	~~~~~	0.070 7(7)	0.190 2(0)	0.004 4(0)

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

with respect to the other planes of the ligands within the four chelate groups.

Each copper atom is strictly five-co-ordinate. There are no other Cu-O or Cu-N approaches of less than 3.570 Å. The copper atoms are co-ordinated by one imine nitrogen atom N(1), one phenolic oxygen atom O(2), and three alkoxooxygen atoms O(1) from three different Schiff-base molecules (two are in the basal plane, the third at the apical position). The co-ordination geometry around copper can be described as a tetragonal pyramid or a trigonal bipyramid (Figure 2, Table 3). The different Cu-O(2) and Cu-N(1) distances in the tetrameric molecule are quite similar [in the ranges 1.882(6)—1.893(6) and 1.915(7)—1.938(7) Å]. The O(2)-Cu-N(1) bond angles deviate little from each other [92.5(4) to 93.5(4)°].

Very important differences are observed in the bond distances and angles involving the O(1) atoms in the alkoxobridges (Table 4). Consequently the Cu₄O₄ core is distorted in contrast to the corresponding one in complex (1) which exhibits  $S_4$  symmetry. These differences are particularly obvious when examining the distances between copper and

O(2)-C(1)	1.305(11)	C(6)-C(1)	1.430(24)	C(13)-C(14)	1.389(13)
C(1) - C(2)	1.413(13)	C(2) - C(3)	1.448(24)	C(14)-C(15)	1.375(7)
C(2) - C(4)	1.418(6)	C(3) - N(1)	1.269(6)	C(14) - Cl(1)	1.734(11)
C(4) - C(8)	1.519(8)	N(1)-C(9)	1.462(7)	C(15)-C(16)	1.368(12)
C(8) = O(3)	1.413(7)	C(9) - C(11)	1.520(8)	C(15)-Cl(2)	1.734(10)
C(4) - C(5)	1.354(5)	C(11) - O(1)	1.435(7)	C(16)-C(17)	1.387(10)
C(5) - N(2)	1.350(3)	C(11) - C(12)	1.507(14)	C(17) - C(12)	1.388(7)
N(2) - C(6)	1.325(5)	C(12) - C(13)	1.385(6)	C(M) - O(M)	1.413(18)
C(6)-C(7)	1.497(6)				
C(3)=N(1)=C(9)	121.0(5)	Cu=N(1)=C(9)	112.0(9)	C(2)-C(1)-C(6)	116.8(5)
Cu=O(1)=C(11)	106.0(3.1)	N(1) - C(3) - C(2)	125.7(5)	O(3)-C(8)-C(4)	113.5(6)
$Cu^{1} - O(1) - C(11)$	128.1(7.4)	C(3)-C(2)-C(1)	120.8(4)	N(1)-C(9)-C(11)	107.4(1.1)
$Cu^{ii} = O(1) = C(11)$	119.3(10.1)	N(2) - C(6) - C(7)	118.4(1.5)	O(1) - C(11) - C(9)	105.6(6)
Cu=O(2)=C(1)	126.9(3)	O(2) - C(1) - C(2)	126.0(4)	O(1) - C(11) - C(12)	113.7(1.5)
Cu-N(1)-C(3)	126.9(5)		()	- (-) - ()	(11)

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

Table 3. Equations of least-squares planes and atomic deviations (Å) therefrom

(a) Six-member	red chelate rings	5					
	(	Chelate: 1	0.7865 <i>X</i>	x + 0.2859 Y - 0.5	5474Z - 8.9932 =	0	
		2	$-0.8217\lambda$	(+0.1468 Y - 0.5)	5507Z + 4.6015 =	0	
		3	-0.6014	(+0.3748Y - 0.7)	7056Z - 2.9296 =	0	
		4	0.5029 <i>X</i>	X + 0.3125 Y + 0.8	8059Z - 8.5299 =	0	
Deviations							
n	N(n1)	C(n9)	C(n10)	C(n11)	O(n2)	Cu( <i>n</i> ) *	O(n1) *
1	0.009	-0.016	0.013	-0.004	-0.002	0.109	0.052
2	0.006	-0.028	0.045	-0.042	0.018	0.258	- 0.066
3 –	- 0.011	0.027	-0.031	0.021	0.006	0.094	0.146
4	0.003	0.006	-0.020	0.024	-0.013	-0.031	0.159
Dihedral an	gles (°)						
	n		chelate(n)/pyridine(n)	chelate(n)/pher	nyl( <i>n</i> ) pyridin	e(n)/phenyl(n)	
	1		1.26	23.97		22.73	
	2		7.67	52.83		57.94	
	3		4.70	48.08		50.61	
	4		3.78	43.01		40.62	
(b) Basic plane	es around the co	opper atoms	<b>i</b>				
		Chelate: 1	0.7940X -	+ 0.2872 Y - 0.533	58Z - 9.0938 = 0		
		2	0.7873X -	+ 0.2528 Y + 0.562	24Z + 2.5492 = 0		
		3	0.6480 <i>X</i> -	+ 0.3051 Y - 0.697	78Z - 1.7775 = 0		
		4	0.5422 <i>X</i>	+ 0.2930Y + 0.78	75Z - 8.6367 = 0	)	
Deviations							
n	N( <i>n</i> 1)		O(n2)	O(n1)	Cu( <i>n</i> ) *	n	O(n1)
1	0.008		0.007	0.008	0.092	4	0.007
2	-0.121		-0.112	-0.119	0.158	3	0.110
3	0.029		-0.028	-0.029	-0.191	1	0.028
4	-0.019		0.018	0.020	-0.083	2	0.019
Atoms not incl	luded in the calc	culation of t	the plane.				

the oxygen atom O(1) at the top of the pyramid, varying over the range 2.327(5)—2.690(6) Å, mean 2.496 Å. This mean value is considerably smaller than the corresponding one [2.734(4) Å] for complex (1), where the lengthening of the Cu-O(1) bond can be explained by the steric effect of the methyl group at the C(9) atom. The present values are better comparable to those of  $\beta$ -[{Cu(MeCOCHCMe=NCH₂-CH₂O)}₄]·2C₆H₆⁴ which exhibits the same C₁ symmetry. The four Cu-O-Cu angles within the pseudodimeric unit [Cu(1)-O(11)-Cu(2), Cu(1)-O(21)-Cu(2), Cu(3)-O(31)-Cu(4), and Cu(3)-O(41)-Cu(4)] vary from 93.4(1) to 106.5(1)° (mean 100.4°) and are, on average, 6.5° larger than in complex (1). This is due to the differences in the Cu-O(1) distances. For  $\beta$ -[{Cu(MeCOCHCMe=NCH₂CH₂O)}₄]·2C₆H₆ the mean value is 97.4°. Table 5 shows a comparison between the Cu-Cu distances in this compound and in (2). The six Cu-Cu distances can be divided into two groups: one with two longer and one with four shorter distances. The mean value of the four shorter Cu-Cu distances is shorter in complex (2) (3.147 Å) than in (1), while the two longer distances are nearly the same (Table 6). This is also due to the presence of the methyl group at the C(9) atom in complex (1).

According to the Mergehenn classification,⁵ complex (2) belongs to the type II complexes. Whereas [{Cu(MeCOCH-CMe=NCH₂CH₂O)}₄] is known to exist in the type I as well as type II forms, type I structures for (1) and (2) have not been

Cu(1)-O(12)	1.882(6)	Cu(2)-O(22)	1.896(6)	Cu(3)-O(32)	1.890(6)	Cu(4)-O(42)	1.893(6)
Cu(1)-N(11)	1.938(7)	Cu(2)-N(21)	1.932(6)	Cu(3)-N(31)	1.922(7)	Cu(4)-N(41)	1.915(7)
Cu(1)-O(11)	1.952(5)	Cu(2)-O(21)	2.057(5)	Cu(3)-O(31)	1.998(5)	Cu(4)O(41)	2.029(5)
Cu(1)0(41)	1.980(5)	Cu(2)-O(31)	1.958(5)	Cu(3)-O(11)	1.970(5)	Cu(4)0(21)	1.917(5)
Cu(1)-O(21)	2.572(6)	Cu(2)-O(11)	2.393(5)	Cu(3)-O(41)	2.327(5)	Cu(4)0(31)	2.690(6)
O(12)-Cu(1)-N(11)	93.5(4)	O(22)-Cu(2)-N(21)	92.5(4)	O(32)-Cu(3)-N(31)	93.3(4)	O(42)-Cu(4)-N(41)	93.3(4)
O(12)-Cu(1)-O(11)	174.0(4)	O(22)-Cu(2)-O(21)	163.4(4)	O(32)-Cu(3)-O(31)	170.4(3)	O(42)-Cu(4)-O(41)	173.7(4)
O(12)-Cu(1)-O(41)	94.1(3)	O(22)-Cu(2)-O(31)	95.5(4)	O(32)-Cu(3)-O(11)	91.8(3)	O(42)-Cu(4)-O(21)	94.1(3)
O(12)-Cu(1)-O(21)	108.7(4)	O(22)-Cu(2)-O(11)	117.4(1)	O(32)-Cu(3)-O(41)	103.2(3)	O(42)-Cu(4)-O(31)	110.3(4)
N(11)-Cu(1)-O(11)	83.9(3)	N(21)-Cu(2)-O(21)	82.6(3)	N(31)-Cu(3)-O(31)	85.4(4)	N(41)-Cu(4)-O(41)	84.1(3)
N(11)-Cu(1)-O(41)	170.4(3)	N(21)-Cu(2)-O(31)	171.1(3)	N(31)-Cu(3)-O(11)	165.7(4)	N(41)-Cu(4)-O(21)	171.6(3)
N(11)-Cu(1)-O(21)	110.2(4)	N(21)-Cu(2)-O(11)	102.2(4)	N(31)-Cu(3)-O(41)	113.3(4)	N(41)-Cu(4)-O(31)	108.5(4)
O(11)-Cu(1)-O(41)	88.0(3)	O(21)-Cu(2)-O(31)	88.6(3)	O(31)-Cu(3)-O(11)	87.3(3)	O(41)-Cu(4)-O(21)	88.1(3)
0(11)-Cu(1)-0(21)	76.7(2)	O(21)-Cu(2)-O(11)	79.2(2)	O(31)-Cu(3)-O(41)	86.0(3)	O(41)-Cu(4)-O(31)	76.2(2)
O(41)-Cu(1)-O(21)	72.9(2)	O(31)-Cu(2)-O(11)	77.4(3)	O(11)-Cu(3)-O(41)	78.5(2)	O(21)-Cu(4)-O(31)	72.8(2)
Cu(1)-O(11)-Cu(2)	106.5(1)	Cu(2)-O(21)-Cu(1)	97.3(1)	Cu(3)-O(31)-Cu(4)	93.4(1)	Cu(4)-O(41)-Cu(3)	104.3(1)
Cu(1)-O(11)-Cu(3)	100.8(1)	Cu(2)-O(21)-Cu(4)	109.8(1)	Cu(3)-O(31)-Cu(2)	104.0(1)	Cu(4)-O(41)-Cu(1)	105.8(1)
Cu(2)-O(11)-Cu(3)	90.7(1)	Cu(1)-O(21)-Cu(4)	89.6(1)	Cu(4)-O(31)-Cu(2)	87.3(1)	Cu(3)-O(41)-Cu(1)	88.7(1)

Table 4. Distances (Å) and angles (°) of atom pairs or triples of which at least one belongs to the Cu4O4 core

<b>Table 5.</b> Copper-copper distances (Å) in complex (2) compared with those in $\beta$ -[{Cu(MeCOCHCMe=NCH ₂ CH ₂ O)} ₄ ]·2C ₆ H ₆ ⁴							
Cu(1)*-Cu(2) Cu(1)-Cu(3) Cu(1)-Cu(4)	[(CuL ² )₄]·9CH₃OH 3.492(2) 3.021(1) 3.198(1)	β- [{Cu(MeCOCHCMe=NCH ₂ ( 3.311(2) 3.064(2) 3.153(2)	CH2O)}4]·2C6H6				
Cu(4)-Cu(3) Cu(4)-Cu(2) Cu(2)-Cu(2) Cu(2)-Cu(3)	3.444(2) 3.252(1) 3.117(1)	3.288(2) 3.172(2) 3.111(2)					
* In ref. 4 the copper atoms are designated in	another way.						
Table 6. Mean Cu-Cu distances (Å)							
[(CuL ² ) ₄ ]·9CH ₃ OH [(CuL ¹ ) ₄ ]·8CH ₃ OH β-[{Cu(MeCOCHCMe=NG α-[{Cu(MeCOCHCMe=NG	CH2CH2O)}4]·2C6H6 CH2CH2O)}4]	3.468 (× 2) 3.481 (× 2) 3.300 (× 2) 3.259 (× 4)	3.147 (× 4) 3.259 (× 4) 3.125 (× 4) 3.006 (× 2)				
Table 7. Hydrogen-bond distances (Å)							
$\begin{array}{c} N(12) \cdots O(8M) \\ N(22) \cdots O(9M) \\ N(32) \cdots O(4M) \\ N(42) \cdots O(6M) \\ O(13) \cdots O(5M) \\ O(23) \cdots O(2M) \\ O(33) \cdots O(1M) \end{array}$	2.729(12) 2.717(11) 2.778(10) 2.737(11) 2.783(12) 2.841(12) 2.745(11)	$O(33) \cdots O(3M)$ $O(43) \cdots O(7M)$ $O(1M) \cdots O(9M)$ $O(2M) \cdots O(6M)$ $O(4M) \cdots O(5M)$ $O(7M) \cdots O(8M)$	2.808(13) 2.721(12) 2.638(12) 2.670(11) 2.698(12) 2.698(14)				



Figure 1. Perspective view of a selected chelate unit of complex (2)

found till now. The differences between the molecular structures of complexes (1) and (2) arise from the different substituents of the iminoalcohol ligand, resulting in  $S_4$  symmetry in (1) and in variations within the Cu₄O₄ cores.

Hydrogen bonding in complex (2) and comparison with that in (1). Nine methanol molecules per tetrameric complex stabilize the crystal structure of (2). Eight of them join the molecules through hydrogen bonds in the following way: each of the four monomeric subunits is involved in two bridges, one from the pyridine nitrogen atom N(n2) (n = 1-4), the other from the oxygen atom O(n3) (Table 7). The bridges are comprised of two methanol hydroxyl groups connecting the pyridine nitrogen with the oxygen atom O(n3) of two different monomeric subunits of neighbouring molecules (Figure 3). In this manner, each tetrameric molecule is joined to four others. The bridges are nearly perpendicular to the monoclinic axis. However the N(n2) and O(n3) atoms of the single subunits have different y co-ordinates and a three-dimensional network of the tetrameric molecules results. For instance, it is possible starting from the molecule in position (x, y, z) to reach the molecule in position (x, 1 + y, z) via the following con-



Figure 2. Projection of the tetrameric unit along the c axis

nected molecules: x, y,  $z \longrightarrow \frac{1}{2} + x$ ,  $\frac{3}{2} - y$ ,  $z \longrightarrow \frac{1}{2} + x$ ,  $\frac{1}{2} + y$ ,  $\frac{1}{2} + z \longrightarrow x$ , 2 - y,  $\frac{1}{2} + z \longrightarrow x$ , 1 + y, z. Thus four of the eight molecules of the unit cell form one part of an infinite network. The other four belong to the corresponding one, however, both networks are not joined together by hydrogen bonds. The ninth methanol molecule is only bonded to one other oxygen atom O(33). It is located approximately between the molecules stacked along the y axis.

Ignoring the ninth methanol molecule, the crystallographic



Figure 3. Schematic representation of the hydrogen-bond bridges between the N(n2) and O(n3) atoms; n is replaced by x for N(2) and by y for O(3). Four such bridges are observed: x = 1, y = 4; x = 2, y = 3; x = 3, y = 1; x = 4, y = 2

Table 8. Experimental and calculated susceptibilities of  $[(CuL^2)_4]^{-1}$  9CH₃OH

10 ⁶ X/cm ³ mol ⁻¹				10 ⁶ X/cm ³ mol ⁻		
<i>T</i> /K	exptl.	calc.	T/K	exptl.	calc.	
4.2	154 043					
6.4	103 005					
10.6	62 719	63 044	78.1	6 480	6 372	
15.3	41 248	41 549	89.6	5 500	5 467	
19.5	32 936	32 322	98.5	4 964	4 922	
25.4	23 427	23 048	112.5	4 305	4 253	
30.6	18 671	18 563	123.5	3 827	3 840	
36.6	14 929	15 092	139.9	3 357	3 355	
42.0	12 562	12 882	161.8	2 883	2 869	
48.8	10 565	10 848	181.8	2 507	2 535	
65.7	7 573	7 739	204.5	2 277	2 239	
70.5	7 285	7 148	215.9	2 084	2 115	

arrangement of the tetrameric molecules and the eight remaining methanol molecules within the monoclinic I2/clattice can be described approximately by a  $P4_2/n$  lattice. With the axis transformations  $a' = b' \approx \left[\left(\frac{a}{2}\right)^2 + \left(\frac{c}{2}\right)^2\right]^{\frac{1}{2}}$ and  $c' \approx \frac{b}{2}$ , lattice dimensions can be obtained for complex (2) which are comparable with those of (1).

The role of the methanol molecules is different in complex (1) [tetragonal, space group  $P4_2/n$ , a = b = 17.226(4) Å, c = 14.667(3) Å]. Four molecules form hydrogen bonds with the four pyridine nitrogen atoms of the tetrameric molecules [O(5)-N(2) 2.80(1) Å]. The remaining four are placed between two tetrameric molecules forming a 16-membered ring perpendicular to the 4 axis. This ring consists of four O(3) atoms of the tetrameric molecules, four methanol oxygen atoms, and eight hydrogen atoms. Consequently the tetrameric units are linked together by the hydrogen-bond bridges along the 4 axis  $[O(3)-O(4) 2.75(1), O(3^1)-O(4) 2.72(1)$  Å,  $O(3^1)$  being in the equivalent position -y, x, -z + 2].

Magnetic Properties.—The magnetic susceptibilities of the crystalline complex in the temperature range from 4.2 to 216 K are shown in Table 8. With increasing temperature the magnetic susceptibility decreases steadily. The magnetic moments first increase with increasing temperature, then reach a maximum at about 15 K, and finally decrease with further increase in temperature. They are higher than those of monomeric copper ions and show a predominant ferromagnetic spin coupling. The susceptibilities and magnetic moments of the amorphous form are slightly different. In contrast to  $[(CuL^1)_m]$ , which shows a weak antiferromagnetic coupling,  $[(CuL^2)_m]$  (3) does not vary significantly in magnetic properties from its crystalline form.



Figure 4. Principal structure of the  $Cu_4O_4$  core with  $S_4$  symmetry and relations between the exchange integrals

Theory and calculations. A quantitative theoretical analysis of the magnetic behaviour is possible for oligomeric copper(II) complexes which are structurally determined. Spin-coupled metal complexes can be described in the simplest case by the isotropic Heisenberg-Dirac-van Vleck (HDvV) model. On the premise of pure spin magnetism (S states or quenched magnetic angular momenta) the exchange interaction can be described by the Hamiltonian (i) where  $J_{ij}$  is the exchange

$$\mathscr{H} = -2\sum_{i < j} J_{ij} S_i S_j \tag{i}$$

integral between the magnetic centres *i* and *j*. Molecular  $C_1$  symmetry implies an effective Hamiltonian with six exchange integrals  $(J_{12}, \ldots, J_{16})$ . However, it is possible to reduce the magnetic behaviour to those of higher symmetrically arranged copper ions. It has been shown in some cases ⁶ that the spin coupling within pseudodimeric units is antiferromagnetic and that perpendicular to them is ferromagnetic. This procedure leads to mean values of exchange parameters. The highest possible molecular symmetry within the Cu₄O₄ core is  $\overline{4}$  (S₄) (Figure 4). The Hamiltonian then becomes as in equation (ii). Evaluation of the energy matrix  $E_{kl} = \langle \psi_k | \mathscr{H} | \psi_l \rangle$  leads to the corresponding energy values. This can be achieved by

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

standard procedures.¹¹ The susceptibility for the tetramer  $\chi_{tet.}$  resulting from the common van Vleck equation is given by equation (iii): where  $u = J_{13}/kT$  and  $v = J_{12}/kT$ .

$$\chi_{tet.} = \frac{N_{A}\beta^{2}g^{2}}{4kT} \cdot \frac{10e^{2u} + 2e^{-2u} + 4e^{-2v}}{5e^{2u} + 3e^{-2u} + 6e^{-2v} + e^{-4v}}$$
(iii)

The experimental susceptibility  $\chi_{exptl.}$  consists of  $\chi_{tet.}$ ,  $\chi_{para.}$  from paramagnetic impurities,  $\chi_{N\alpha}$  from the temperature-independent paramagnetism, and  $\chi_{dia.}$  the diamagnetic susceptibility [equation (iv)]. The contribution  $\chi_{para.}$  is given by the Curie-Weiss law (v) and x is the mole fraction of the

$$\chi_{expil.} = (1 - x)\chi_{tet.} + x\chi_{para.} + \chi_{N\alpha} + \chi_{dla.}$$
 (iv)

$$\chi_{\text{para.}} = N_{\text{A}}\beta^2 g^2 / 4kT \qquad (v)$$

paramagnetic impurity. The exchange integrals  $J_{12}$  and  $J_{13}$ , the g factor, and x are evaluated by fitting equations (iii) and (iv) to the experimental susceptibilities. The function minimized was  $(\chi_{expt1.} - \chi_{cate.})^2 T^2$ . Data at temperatures less than 10 K were omitted since the relative error in temperature measurement becomes important. The following values were obtained:  $J_{12} = -9.9 \pm 3.0 \text{ cm}^{-1}$ ,  $J_{13} = 20.5 \pm$  $3.0 \text{ cm}^{-1}$ ,  $x = 0.019 \pm 0.03$ , and  $g = 2.08 \pm 0.02$ . The excellent agreement between the experimental (circles) and the calculated (full line) values is shown in Figure 5.

Figure 6 shows the energy diagram of the spin states pro-



Figure 5. Temperature dependence of the magnetic susceptibility of complex (2). Experimental values ( $\bigcirc$ ) are compared with values (—) calculated from equations (iii) and (iv) (see text)

duced by the isotropic HDvV model for a  $Cu_4O_4$  core with  $4(S_4)$  symmetry. Assuming that complex (2) can be described with this simplification the diagram demonstrates that one cannot determine whether the spin coupling is ferromagnetic or antiferromagnetic in the ground state. To find the magnetic order in the ground state, measurements at very low temperature are necessary.

Discussion. The calculated exchange integrals of the crystalline complex (2) show the simultaneous presence of a ferromagnetic and an antiferromagnetic exchange interaction within the same tetrameric unit. Such magnetic behaviour is known for a large number of copper(II) complexes.

In case of tetrameric alkoxo-bridged complexes relations were found between the size of the exchange parameters and the structural details.¹² However, recently we were able to show that these relations are not valid for complexes with Schiff bases as ligands.¹⁰

The magnetic behaviour of the amorphous form, derived from the crystalline one by loss of the solvent of crystallization, is quite similar. The magnetic moments show a dominant ferromagnetic spin coupling in the temperature range from 4.2 to 78.1 K. However, an interpretation in molecular terms cannot be made since no structural data are available.

For complexes (1) and (2) the loss of the methanol molecules leads to amorphous forms with completely different magnetic behaviours. The dominant ferromagnetic behaviour of the powder form of complex (2) and the very weak antiferromagnetic coupling observed in the amorphous form of (1) arise from the different molecular structures which in turn are probably due to the different hydrogen-bonding systems present in the crystalline forms.

## Experimental

Preparation of Complex (2).—Pyridoxal base obtained by mixing pyridoxal hydrochloride (0.51 g, 2.5 mmol) and sodium acetate (0.6 g, 5.0 mmol) in methanol (15 cm³) was treated with 2-amino-1-(3',4'-dichlorophenyl)ethanol hydrochloride (0.60 g, 2.5 mmol) in methanol (50 cm³) for 15 min. Copper(II) acetate monohydrate (0.50 g, 2.5 mmol) and methanol (50 cm³) were added. The resulting mixture was stirred vigorously until the copper salt dissolved (*ca.* 20 min). Immediately, the volume was reduced (20 cm³) and Pr¹OH was added to precipitate salts. The filtrate was reduced to a small volume and methanol was added (50 cm³). Upon standing overnight dark green crystals were obtained, m.p. 230—231 °C, yield 0.55 g (60%). In air the crystals easily lose methanol and become powdery.





Figure 6. Schematic energy-splitting diagram for complex (2)

Crystallography.—Crystal data.  $C_{64}H_{56}Cl_8Cu_4N_8O_{12}$  °9CH₃-OH, M = 1 943.36, Monoclinic, space group I2/c (no. 15),¹³ a = 27.062(5), b = 25.062(5), c = 26.390(5) Å,  $\beta = 92.39(1)^{\circ}$ , U = 17 881 Å³,  $D_m = 1.47$  g cm⁻³ (by flotation), Z = 8,  $D_c = 1.461$  g cm⁻³, F(000) = 8 084, graphite monochromatized Mo- $K_{\alpha}$  radiation  $\lambda = 0.710$  69 Å,  $\mu$ (Mo- $K_{\alpha}$ ) = 11.9 cm⁻¹.

Cell constants were obtained by a least-squares fit of 44 strong reflections using a computer-controlled Stoe Stadi 4 four-circle diffractometer. The selection of the I lattice instead of the C lattice was made so that  $\beta \approx 90^{\circ}$ . The systematic absences were *hkl* for h + k + l = 2n + 1 and *h0l* for l = 2n + 1.

Intensity data. A needle-like crystal with the longest dimension b approximately parallel to the fibre axis ( $a \times b \times c \approx 0.30 \times 1.5 \times 0.22$  mm) was sealed in a Lindemann capillary containing methanol to avoid decomposition. Intensity data were collected (scan  $\omega : 2\theta = 1 : 1$ ) in the range  $3 \leq 2\theta \leq 40^{\circ}$  on the Stoe diffractometer. 9 769 *hkl* Reflections were measured, 8 273 of which were symmetry independent. The intensity data were corrected for Lorentz, polarization, and absorption effects. After data processing, 7 045 unique reflections having  $F_o > 2\sigma(F_o)$  were used in the subsequent calculations.

Structure determination. The positions of 114 non-hydrogen atoms per asymmetric unit were to be determined. The positions of the four copper atoms were derived by direct methods. The remaining non-hydrogen atoms could be located after several Fourier syntheses,  $\Delta F$  syntheses, and successive least-squares cycles. Because of the limited computer memory only neighbouring blocks of about 12 atoms were alternately refined. It could be inferred from  $\Delta F$  syntheses that a ninth methanol molecule is present in the asymmetric unit as opposed to the eight originally assumed. Refinement with isotropic thermal parameters for all but the hydrogen atoms allowed R to converge to 0.135. Anisotropic refinement for all non-hydrogen atoms led to a final R value of 0.054 for the observed reflections. When possible, hydrogen atoms were positioned geometrically; the positions of five more hydrogens were obtained by  $\Delta F$  syntheses.

The crystal structure was determined and refined with the aid of a minicomputer program package developed by Stoe, Darmstadt. The computer was a Data General Eclipse S/140 (256 kByte memory) at the application laboratory of Stoe & Cie, Darmstadt.

*Magnetic Measurements.*—The magnetic susceptibilities of the samples were recorded by the Faraday method at *ca*. 10 kG (1 T) in the temperature range from 4.2 to 216 K.¹⁴ To prevent loss of the solvent molecules during measurements on the crystalline sample, methanol was added. Experimental susceptibility data were corrected for underlying diamagnetism and the temperature-independent paramagnetism. Magnetic moments were calculated using the formula (vi). To convert

$$\mu = 2.828 \sqrt{\chi T} \qquad (vi)$$

into S.I. units  $\chi$  should be multiplied by  $4\pi \times 10^{-6}$  and  $\mu$  is then given by  $797.74\sqrt{\chi T}$ . The calculations of the theoretical  $\chi(T)$  curves were performed on an IBM 370/168 computer of the Technische Hochschule Darmstadt.

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