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First Example of a Cu^{II} Polymeric Complex Having a Tetranuclear Repeating Unit with a $S = 2$ Ground State. Crystal Structure of $[Cu_4(dpk\cdot CH_3O)_2Cl_6]_n$ ($dpk\cdot CH_3OH$ = Unimethylated Diol of Di-2-pyridyl Ketone)

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The synthesis, crystal structure and properties of the compound $[Cu_4(dpk\cdot CH_3O)_2Cl_6]_n$ ($dpk\cdot CH_3OH$ = unimethylated diol of di-2-pyridyl ketone) (**1**), the first example of a copper(II) polymer having a tetrameric repeating unit with $S = 2$ ground state is reported. The synthesis of compound **1** has been achieved via the reaction of $CuCl_2$ with dpk in methanol. The base-catalyzed addition results in the formation of a unimethylated diol which may deprotonated. Crystal structure data: $[C_{12}H_{11}N_2O_2Cl_3Cu_2]$, $M_r = 448.68$; triclinic; space group $P\bar{1}$; $a = 7.800(1)$ (Å); $b = 8.946(1)$ (Å); $c = 13.383(1)$ (Å); $\alpha = 118.964(3)°$; $\beta = 92.693(3)°$; $\gamma = 66.824(3)°$; $Z = 2$. Variable temperature magnetic susceptibility measurements indicate the presence of a ferromagnetic behavior with antiferromagnetic coupling below 15 K. The best fit parameters obtained from this model are $J_1 = 71.32$ cm^{-1}, $J_2 = 1.43$ cm^{-1}, $J_3 = 0.07$ cm^{-1}, $J_4 = 0$ (fixed), $zJ = -0.553$ cm^{-1}, and $g = 2.1$ (fixed). The energy levels obtained from the fitting procedure show a $S = 2$ ground state. The polycrystalline powder EPR spectra at 4.1 K, show an intense broad signal spread over 3900 G with $g = 2.34$, indicative of a bulk concentration of copper ions having strong ferromagnetic interaction.

Introduction

Structural and magnetic properties of copper(II) halide complexes have long been of interest.[1] Structurally, the coordination geometry of the copper(II) ions has a very diverse range. In addition, the halide ion is an effective bridging ligand, which imposes few steric constraints upon the coordination geometry. In extended systems with stacking[2−5] or polymeric[6−20] patterns two copper(II) ions may be bridged by one, two or three halide ions with four general structure types: (i) the alternating chain(bibridged chain of dimers); (ii) uniform chain with planar bridging units; (iii) uniform chain with folded bridging units; (iv) tribridged chain. However, for polymeric structures alternating Cu_2O_2 and Cu_2Cl_2 bridging units[20] only the first one has been observed thus far. Extended structures

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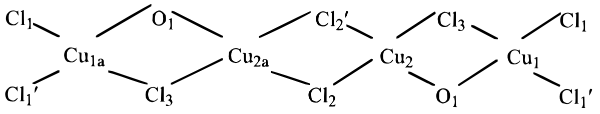
containing binuclear units with two nonsimilar bridging ligands of the type shown in structure **I** have not been reported till now.



I

The Cu_2ClO binuclear unit has attracted a great deal of attention as it is related with the dioxygen-binding protein hemocyanin in the “oxy”, “met”, and “half-met” derivatives[21−23] and the various multicopper oxidases.[24] Binuclear model Cu(II) compounds that contain various ligands, X, in the exogenous bridging site have been reported, and in some cases the magnetic properties have also been investigated.[25−32] Di-2-pyridyl ketone (dpk) forms complexes in which undergoes hydration on complex formation.[33]

Studies for extended systems on the relationship between structure and magnetic behavior have shown that i and ii structure types favor antiferromagnetic behavior while iii and iv favor ferromagnetic behavior.[8d] Especially for “molecular” insulating solids, structure−magnetism relationships[32a] have demonstrated that in such compounds several factors can complement the role of the distance apart (R) in determining superexchange interactions (J), a feature that potentially allows superexchange at longer range than conceivable from results for ionic lattices. Studies on “molecular” long-range superexchange have produced several systems[32b−d] in which appreciable exchange coupling is propagated up to distances of 6−12 Å.

The title compound is the first example having a tetrameric repeating unit and alternating folding and planar bridging subunits.

Table 1. Crystallographic Data for $[Cu_2(dpk)Cl_3]_n$

chem formula: $C_{12}H_{11}N_2O_2Cl_3Cu_2$	fw = 448.68
$a = 7.800(1)$ Å	space group: $P\bar{1}$
$b = 8.946(1)$ Å	$T = 23$ °C
$c = 13.383(1)$ Å	$\lambda = 0.7107$ Å
$\alpha = 118.964(3)°$	$\rho_{obsd} = 1.99$ g cm^{-3}
$\beta = 92.693(3)°$	$\rho_{calcd} = 2.016$ g cm^{-3}
$\gamma = 66.824(3)°$	$\mu = 34.40$ cm^{-1}
$V = 739.05$ Å^3	$R^a = 0.0261$
$Z = 2$	$R_w{}^b = 0.0372$

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|^2))^{1/2}$.

Experimental Section

The following abbreviations are used throughout the text: dpk = di-2-pyridyl ketone, DMF = dimethylformamide, DMSO = dimethyl sulfoxide.

Materials. The chemicals for the synthesis of the compounds were used as purchased. Acetonitrile (CH_3CN) was distilled from calcium hydride (CaH_2) and CH_3OH from magnesium (Mg) and were stored over 3 Å molecular sieves. Diethyl ether, anhydrous grade and absolute ethanol were used without any further purification. Di-2-pyridyl ketone and $CuCl_2\cdot 4H_2O$ were purchased from Aldrich Co. All chemicals and solvents were reagent grade.

Physical Measurements. Infrared spectra (200−4000 cm^{-1}) were recorded on a Perkin-Elmer 467 infrared spectrometer with samples prepared as KBr pellets. UV−vis spectra were recorded on a Perkin-Elmer Lambda-5 dual beam spectrophotometer. Solution and solid state EPR spectra were recorded in the 295−5.0 K temperature range, on a Bruker ER 200D-SRC X-band spectrometer equipped with an Oxford ESR 9 cryostat. DPPH was used as an external standard. ZnO was used as a diamagnetic substance for powder solution in order to minimize the spin−spin interactions. Room temperature magnetic measurements were carried out by Faraday’s method using mercury tetrathiocyanatocobaltate(II) as a calibrant. Magnetic susceptibility measurements were carried out on powdered samples of **(1)** in the range 5.0−300 K temperature using a Quantum Design Squid susceptometer by applying magnetic fields of 1000 and 6000 G. The correction for the diamagnetism of the complex was estimated from Pascal constants, a value of 60×10^{-6} cm^3 mol^{-1}, was used for the TIP of the Cu(II) ion. Electric conductance measurements were carried out with a WTW Model LF 530 conductivity outfit and a type C cell, which had a cell constant of 0.996. This represents a mean value calibrated at 25 ºC with potassium chloride. All temperatures were controlled with an accuracy of ± 0.1 °C using a Haake thermoelectric circulating system. C, H, and N elemental analyses were performed on a Perkin-Elmer 240B elemental analyzer.

Preparation of the Compound. A 10.0 mmol (1.84 g) sample of dpk and 10.0 mmol (0.61 g) ethanolamine was added to a solution of 10 mmol (1.70 g) of $CuCl_2$ in 100 mL of MeOH. The resulting mixture was refluxed for 1 h. After the reaction mixture was cooled to room temperature, it was exposed to air and left for slow evaporation. A green crystalline solid was deposited in a couple of days. The crystalline product was characterized by elemental analysis with the formula $C_{12}H_{11}N_2O_2Cl_3Cu_2$. Yield: 70%. Anal. Calcd for (M_r = 449): C, 32.10; H, 2.40; N, 6.20; Cl, 23.70; Cu, 28.30 Found: C, 31.95; H, 2.50; N, 6.05; Cl, 23.15; Cu, 27.80 IR (KBr pellet, cm^{-1}): ν(C=N) 1592 (vs); ν(C−O) 1035 (vs); ν(Cu−Cl) 275 (m), 295 (m). UV−Vis (λ (ϵ)), CH_3CN): 465 nm (220); 780 nm (190).

Collection and Reduction of X-ray Data. A blue prismatic crystal of $[Cu_4(dpk\cdot CH_3O)_2Cl_6]_n$ **(1)** with approximate dimensions 0.51 × 0.31 × 0.08 mm, was mounted in air. Complete crystal data and parameters for data collection are reported in Table 1. Diffraction measurements were made on a Syntex P2$_1$ diffractometer upgraded by Crystal Logic using Zr filtered Mo Kα radiation. The space group was determined by preliminary Weissenberg and precession photographs. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the range of $11° < 2\theta < 24°$. Intensity data were recorded using a $\theta-2\theta$ scan to 2θ(max) = 51° with scan speed 3.0 deg/min and scan range 2.5 plus $\alpha_1\alpha_2$ separation. Three standard reflections, measured every 97 reflections, showed less than <3.0% intensity fluctuation and no decay. Lorentz−

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Scheme 1

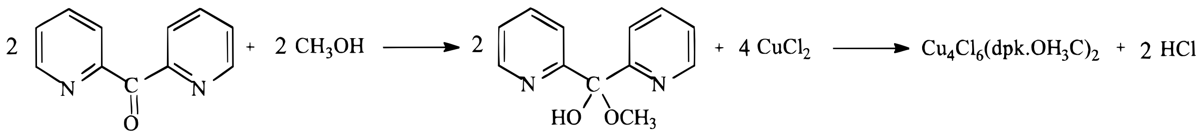

Table 2. Selected Bond Distances (Å) and Angles (deg)

Bonds

Cu(1)···Cu(2)	2.940(1)	Cu(1)−N(1)	1.988(2)
Cu(1)···Cu(1*)	3.659(1)	Cu(1)−Cl(1*)	2.242(2)
Cu(1)···Cu(2*)	6.474(1)	Cu(2)−Cl(2)	2.255(1)
Cu(1*)···Cu(2)	6.474(1)	Cu(2)−Cl(3)	2.328(1)
Cu(2)···Cu(2*)	3.687(1)	Cu(2)−O(1)	1.947(2)
Cu(1)−Cl(1)	2.751(1)	Cu(2)−N(2)	2.004(2)
Cu(1)−Cl(3)	2.325(1)	Cu(2)−Cl(2*)	2.734(2)
Cu(1)−O(1)	1.968(2)	O(1)−C(6)	1.397(3)

Angles

Cu(2)−Cu(1)−Cl(1)	132.1(1)	Cu(1)−O(1)−Cu(2)	97.3(1)
Cu(2)−Cu(1)−Cl(3)	50.9(1)	Cu(1)−O(1)−C(6)	116.7(1)
Cl(1)−Cu(1)−Cl(3)	109.7(1)	Cu(2)−O(1)−C(6)	118.1(1)
Cu(2)−Cu(1)−O(1)	41.1(1)	Cu(1)−N(1)−C(1)	125.5(2)
Cl(1)−Cu(1)−O(1)	101.3(1)	Cu(1)−N(1)−C(5)	114.7(2)
Cl(3)−Cu(1)−O(1)	82.1(1)	Cl(1)−Cu(1)−Cl(1*)	86.4(1)
Cu(2)−Cu(1)−N(1)	106.6(1)	Cl(1*)−Cu(1)−N(1)	97.0(3)
Cl(1)−Cu(1)−N(1)	90.4(1)	Cu(1)−Cu(2)−Cl(2*)	130.2(1)
Cl(3)−Cu(1)−N(1)	156.5(1)	Cl(2*)−Cu(2)−Cl(2)	85.2(1)
O(1)−Cu(1)−N(1)	82.1(1)	Cl(2*)−Cu(2)−Cl(2)	98.9(2)
Cu(1)−Cu(2)−Cl(2)	134.6(1)	Cu(2)−N(2)−C(7)	114.5(2)
Cu(1)−Cu(2)−Cl(3)	50.8(1)	Cu(2)−N(2)−C(11)	126.7(2)
Cl(2)−Cu(2)−Cl(3)	95.4(1)	Cu(2)−Cu(1)−Cl(1*)	133.1(1)
Cu(1)−Cu(2)−O(1)	41.6(1)	Cl(3)−Cu(1)−Cl(1*)	96.4(1)
Cl(2)−Cu(2)−O(1)	175.9(1)	Cl(1*)−Cu(1)−O(1)	172.2(4)
Cl(3)−Cu(2)−O(1)	82.5(1)	Cl(2*)−Cu(1)−Cl(3)	109.1(1)
Cu(1)−Cu(2)−N(2)	102.8(1)	Cl(2*)−Cu(2)−N(2)	97.3(3)
Cl(2)−Cu(2)−N(2)	98.7(1)	Cu(1)−Cl(1)−Cu(1*)	93.7(1)
Cl(3)−Cu(2)−N(2)	151.1(1)	Cu(2)−Cl(2)−Cu(2*)	94.8(1)
O(1)−Cu(2)−N(2)	81.8(1)	Cu(1)−Cl(1*)−Cu(1*)	93.7(3)
Cu(1)−Cl(3)−Cu(2)	78.4(1)	Cu(2)−Cl(2*)−Cu(2*)	94.8(1)

Dihedral Angles

O(1)−Cu(2)−Cl(3)/Cl(2*)−Cu(2)−Cl(2)	71.6
O(1)−Cu(2)−Cl(3)/O(1)−Cu(1)−Cl(3)	134.6
O(1)−Cu(2)−Cl(3)/Cl(1)−Cu(1)−Cl(1*)	52.7
O(1)−Cu(2)−Cl(3)/Cu(2)−O(1)−Cu(1)	35.7
O(1)−Cu(2)−Cl(3)/Cu(2)−Cl(3)−Cu(1)	150.0
Cl(2*)−Cu(2)−Cl(2)/O(1)−Cu(1)−Cl(3)	51.5
Cl(2*)−Cu(2)−Cl(2)/Cl(1)−Cu(1)−Cl(1*)	45.5
Cl(2*)−Cu(2)−Cl(2)/Cu(2)−O(1)−Cu(1)	35.9
Cl(2*)−Cu(2)−Cl(2)/Cu(2)−Cl(3)−Cu(1)	77.3
O(1)−Cu(1)−Cl(3)/Cl(1)−Cu(1)−Cl(1*)	71.5
O(1)−Cu(1)−Cl(3)/Cu(2)−O(1)−Cu(1)	35.7
O(1)−Cu(1)−Cl(3)/Cu(2)−Cl(3)−Cu(1)	29.7
Cl(1)−Cu(1)−Cl(1*)/Cu(2)−O(1)−Cu(1)	35.8
Cl(1)−Cu(1)−Cl(1*)/Cu(2)−Cl(3)−Cu(1)	78.3
Cu(2)−O(1)−Cu(2)/Cu(2)−Cl(3)−Cu(1)	131.7

Table 3. Positional and Equivalent Thermal Parameters (×10^4) of the Non-H Atoms[a]

atom	x	y	z	U
Cu(1)	1969.9(5)	4114.5(5)	3879.0(3)	280
Cu(2)	4348.6(4)	1778.8(4)	1561.0(3)	229
Cl(1)	−1858(1)	6361(1)	4632(1)	431
Cl(2)	6606(1)	−1205(1)	546.1(6)	283
Cl(3)	2472(1)	1089(1)	2424(1)	396
O(1)	2436(3)	4347(2)	2539(2)	221
N(1)	2506(3)	6377(3)	4719(2)	271
N(2)	5923(3)	3145(3)	1669(2)	248
C(1)	2374(5)	7385(5)	5881(3)	385
C(2)	2410(5)	9116(5)	6422(3)	385
C(3)	2524(5)	9887(4)	5773(3)	383
C(4)	2644(5)	8875(4)	4575(3)	324
C(5)	2678(4)	7099(4)	4078(2)	215
C(6)	2888(4)	5832(4)	2763(2)	222
C(7)	4945(4)	5031(4)	2177(2)	225
C(8)	5749(5)	6158(5)	2188(3)	357
C(9)	7655(5)	5341(5)	1727(3)	444
C(10)	8680(5)	3437(6)	1258(3)	402
C(11)	7771(4)	2360(5)	1216(3)	338
O(2)	1626(3)	7051(3)	2418(2)	276
C(12)	1751(5)	6325(5)	1195(3)	386

[a] Esd's are in parentheses. $U_{eq} = {}^{1}/_{3}(U_{11} + U_{22} + U_{33})(10^4)$.

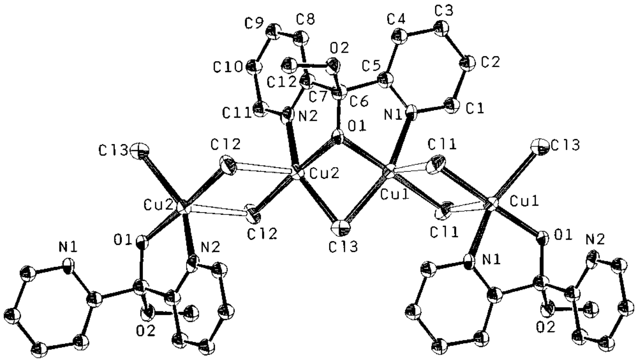

Figure 1. ORTEP view of the tetrameric repeat unit of **1** with 50% thermal ellipsoids showing the atom-labeling scheme.

polarization, *Lp*, and ψ-scan absorption corrections were applied using Crystal Logic software. Scattering factors were taken from ref 34a.

Solution and Refinement of the Structure. Symmetry equivalent data of **1** were averaged with $R = 0.0184$ to give 2745 independent reflections from a total 2873 collected. The structure of **1** was solved with direct methods using the programs SHELX86[34b] and refined by full-matrix least-squares techniques with SHELX76[35] using only 2366 reflections with $F > 6\sigma(F_o)$ and refining 234 parameters. All hydrogen atoms were located by difference maps and their positions were refined isotropically. All non-hydrogen atoms were refined anisotropically. The final values for R and R_w for observed data are in Table 1, for all data are 0.0343 and 0.0433, respectively. The maximum and minimum residual peaks in the final difference map were 0.487 and −0.346 e/Å^3. The largest shift/esd in the final cycle was 0.018.

Results and Discussion

Synthesis. The synthesis of compound **1** can be achieved via the reaction of $CuCl_2$ with dpk in methanol. The reaction involves carbonyl addition in methanolic solution in the presence of aminoalcohols. The base-catalyzed addition (in MeOH) results in the formation of a unimethylated diol which may deprotonated (Scheme 1).

Compound **1** is a green crystalline solid that appears to be air and moisture stable. It is soluble in Me_2SO, DMF, and MeOH.

Description of the Structure. The complex consists of tetrameric $[Cu_4(dpk{\cdot}CH_3O)_2Cl_6]_n$ repeating units having alternating Cu_2Cl_2 and Cu_2ClO bridging subunits. The bond distances and angles for the complex are listed in Table 2 and positional and equivalent thermal parameters in Table 3. A view of the tetrameric repeating unit is shown in Figure 1. The bridging Cu(1)−Cu(1)*−Cl(1)−Cl(1)* and Cu(2)−Cu(2)*−Cl-

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(34) (a) *International Tables for X-ray Crystallography*; Vol. IV, Birmingham, Kynoch Press: Birmingham, England, 1974; Vol. IV. (b) Sheldrick, G. M., SHELX 86. Universitaet Goettingen, Germany, 1986.

(35) Sheldrick, G. M., SHELX 76, Program for Crystal Structure determination. University of Cambridge, England, 1976.

(2)−Cl(2)* units are constrained to be planar by the presence of a crystallographic inversion center in the middle of the dimeric unit. The Cu_2ClO bridging unit is folded across the Cl(3)−O(1) and Cu(1)−Cu(2) lines. This is defined by the dihedral angles between the two O(1)−Cu(2)−Cl(3) and O(1)−Cu(1)−Cl(3) planes of 134.65° and between the Cu(1)−O(1)−Cu(2) and Cu(1)−Cl(3)−Cu(2) planes of 131.71°. The folding leads to a shortening of the intrachain Cu(1)···Cu(2) distance to 2.940(2) Å as compared to the neighboring Cu_2Cl_2 planar units (Cu(1)···Cu(1)* = 3.569(1) Å and Cu(2)···Cu(2)* = 3.687(1) Å) while the Cu(1)···Cu(2)* and Cu(2)···Cu(1)* distances are the same (6.474(1) and 6.472(1) Å). It is noted that this extended structure is the first example of alternating folding and planar bridging units. In the folding Cu_2ClO unit the angle Cu(1)−O(1)−Cu(2) = 97.3(1)° is consistent with those observed in binuclear complexes having Cu_2O_2[20] or Cu_2ClO bridging units,[25−30] but the Cu(1)−Cl(3)−Cu(2) angle of 78.4(1)° is in extremely low compared with values observed for Cu_2Cl_2 [10,20] or Cu_2ClO[25−30] planar or folding units. This compound is the first example of an extended structure having Cu_2ClO repeating units.

The geometry at each copper(II) center is best described as a distorted tetragonal pyramid, as can be determined by examining the angles subtended at copper with the axial bond substantially longer than the basal bonds. As can be seen in Figure 1, each copper(II) center is surrounded by two *cis* chloride ions, a nitrogen atom and an oxygen atom on the basal plane and a chloride ion that occupies the axial coordination site. Using the trigonality index, $\tau = (\varphi_1 - \varphi_2)$ /60, where φ_1 and φ_2 the largest angles in the coordination sphere, $\tau = 0$ perfect square pyramid, and $\tau = 1$ perfect trigonal bipyramid, for Cu(1) a $\tau = 172.2-156.5/60 = 0.26$ and for Cu(2) $\tau = 175.9-151.1/60 = 0.41$ can be calculated showing a different degree of distortion for the two Cu(II) ions.

The Cu(1)−N(1), Cu(2)−N(2) and Cu(1)−O(1), and Cu(2)−O(1) distances observed in this complex of 1.988(2), 2.004(2), 1.968(2), and 1.947(2) Å, respectively, are consistent with the distances reported for related complexes[4,8,36−39]. The basal Cu−Cl distances are 2.325(1) and 2.242(2) Å with the distance to the bridging Cl(3) of the folded Cu_2ClO unit being longer than to the bridging Cl(1*) of the planar Cu_2Cl_2 one. Within the basal planes, the *trans* Cl(2)−Cu(2)−O(1) and N(2)−Cu(2)−Cl(3) angles are 175.9(1) and 151.1° for Cu(2) and O(1)−Cu(1)−Cl(1)* and N(1)−Cu(1)−Cl(3) angles are 172.2(4) and 156.5(1)° for Cu(1), respectively. Considering the three types of chain compounds with square−pyramidal coordination environment which have been reported; the alternating chain (bibridged chain of dimers), the uniform chain with planar bridging units and the uniform chain with folded bridging units, the present compound is best suited to the first type but it keeps characteristics of the other two.

Magnetic Properties. The results of magnetic susceptibility measurements for $[Cu_4(dpk\cdot CH_3O)_2Cl_6]_n$ are given in Figure 2, in the form χ_M(4Cu), and the inset is a μ_{eff} /copper vs T plot. When the temperature is lowered from 300 to 5.0 K the plot reveals two domains. (i) The magnetic susceptibility increases from a value of μ_{eff}/copper = 1.90 μ_B steadily with decreasing temperature until it reaches a maximum at about 50 K, with μ_{eff}/copper of about 2.06 μ_B showing a ferromagnetic behavior. (ii) Below 50 K μ_{eff}/copper decreases slowly to 2.0 μ_B at 15 K below which there is a large decrease to μ_{eff}/copper = 1.85 μ_B at 5 K, indicating the existence of intermolecular interaction. Such an unusual behavior of μ_{eff}, along with the postulate of intercluster antiferromagnetic coupling to explain it, was first reported by Lines *et al.*[40] and several authors[41] have observed it since then. More specifically Lines *et al.* have shown that using a simple Heisenberg exchange process assuming an isotropic exchange interaction a plot of μ_{eff} vs T does not exhibit a maximum. By allowing for an antiferromagnetic interaction between tetramers the μ_{eff} vs T plot passes through a maximum at low T.[40,41] These intermolecular interaction are important[40] only for the tetramers which saturate into spin-aligned $S = 2$ states at low T.

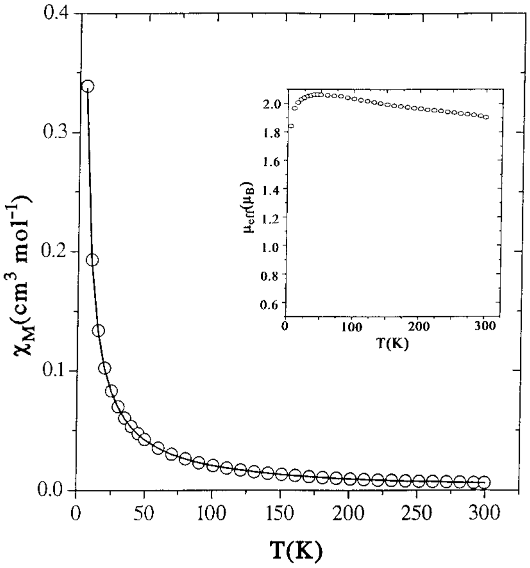

Figure 2. Temperature dependence (300−5 K) of χ_M(4Cu) and showing inset μ_{eff}/copper vs T for **1**. The solid line represents the fitting using the fourth set of parameters.

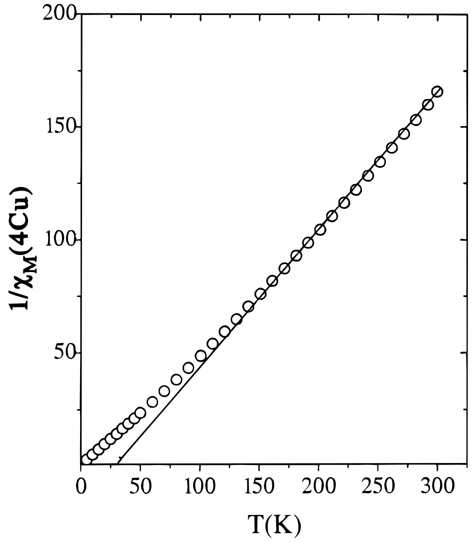

Figure 3. Temperature dependence (300−5 K) of $\chi^{-1}(T)$ vs T for **1**.

In Figure 3 the $\chi^{-1}(T)$ vs T plot shows a systematic curve throughout higher-T data, as expected from the nonconstancy

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of μ_{eff}. The higher-T data can be extrapolated to yield an effective θ of 31.2, which confirms the significant ferromagnetic exchange.

The Fitting Procedure and Magnetic Discussion. In the relatively simple case of four copper(II) ions, where four $S = {}^1/_2$ states are coupled to give a quintet, three triplet, and two singlet electronic levels, many difficulties have been encountered, and still much controversy is present in the literature concerning the relative order of the various multiplets and especially the correct determination of the ground state.[31a,42a]

By virtue of crystallographic criteria, the spin problem for the tetrameric repeating unit involves four exchange-coupling constants and a Hamiltonian of the form shown in eq 1, where we have adhered to the numbering scheme of structure **I**.

$$\boldsymbol{H} = -2J_1(S_1{\cdot}S_2 + S_{1a}{\cdot}S_{2a}) - 2J_2(S_2{\cdot}S_{2a}) - 2J_3(S_1{\cdot}S_{2a} + S_{1a}{\cdot}S_2) - 2J_4(S_1{\cdot}S_{1a}) \quad (1)$$

J_1 describes the nearest neighbor interaction between the outer pairs of copper atoms, J_2 is the central exchange constant, J_3 describes the next-nearest neighbor interaction, and J_4 is the exchange constant between the terminal copper atoms of the tetrameric unit. The eigenvalues of the Hamiltonian have been obtained by using standard techniques and are as follows:

spin state	eigenvalues
$S = 2$	$E_1 = -J_1 - 0.5J_2 - J_3 - 0.5J_4$
$S = 1$	$E_2 = J_1 - 0.5J_2 + J_3 - 0.5J_4$
$S = 1$	$E_3 = 0.5(J_2 + J_4) + [(J_2 - J_4)^2 + (J_3 - J_1)^2]^{1/2}$
$S = 1$	$E_4 = 0.5(J_2 + J_4) - [(J_2 - J_4)^2 + (J_3 - J_1)^2]^{1/2}$
$S = 0$	$E_5 = J_1 + J_3 + 0.5(J_2 + J_4) + [4(J_1^2 + J_3^2) + J_2^2 + J_4^2 - 2J_1(J_2 + 2J_3 + J_4) - 2J_2(J_3 - J_4) - 2J_3J_4]^{1/2}$
$S = 0$	$E_6 = J_1 + J_3 + 0.5(J_2 + J_4) - [4(J_1^2 + J_3^2) + J_2^2 + J_4^2 - 2J_1(J_2 + 2J_3 + J_4) - 2J_2(J_3 - J_4) - 2J_3J_4]^{1/2}$

The magnetic data were fitted to the susceptibility equation which has the form

$$\chi = \frac{\chi_{\mathrm{M}}}{\left(1 - \dfrac{2zJ\chi_{\mathrm{M}}}{N\mu_{\mathrm{B}}{}^2g^2}\right)}$$

where the χ_{M} is the molar susceptibility of the tetramer unit and zJ is the mean field correction.

$$\chi_{\mathrm{M}} = \frac{Ng^2\mu_{\mathrm{B}}{}^2}{3\kappa_{\mathrm{B}}T} \times \frac{\sum_i S_i(S_i + 1)(2S_i + 1)\exp\left(-\dfrac{E_i}{\kappa_{\mathrm{B}}T}\right)}{\sum_i (2S_i + 1)\exp\left(-\dfrac{E_i}{\kappa_{\mathrm{B}}T}\right)} + 4N\alpha$$

Table 4. Magnetic Sets of Parameters[43]

first set	second set	third set	fourth set
$J_1 = 73.247$	$J_1 = 74.288$	$J_1 = 73.211$	$J_1 = 71.32$
$J_2 = 1.014$	$J_2 = -2.245$	$J_2 = 1.638$	$J_2 = 1.43$
$J_3 = 0.35$	$J_3 = -0.787$	$J_3 = 0$ (fixed)	$J_3 = 0.07$
$J_4 = 0$ (fixed)	$J_4 = 0$ (fixed)	$J_4 = 0$ (fixed)	$J_4 = 0$ (fixed)
$zJ = -0.56$		$zJ = -0.557$	$zJ = -0.553$
$g = 2.1$ (fixed)	$g = 2.08$ (free param)	$g = 2.1$ (fixed)	$g = 2.1$ (fixed)
$R = 4.2 \times 10^{-7}$	$R = 6.7 \times 10^{-7}$	$R = 4.4 \times 10^{-7}$	$R = 4.8 \times 10^{-7}$

The fitting procedure revealed four sets of parameters with good R-values. We used

$$R = \sum_n |\chi_{\mathrm{M,exp}} - \chi_{\mathrm{M,calc}}|^2$$

having the g parameter fixed to the value 2.1 according to the EPR experiments and we found the sets of parameters given in Table 4. The tetrameric model described by the Hamiltonian in eq 1, was used with all four sets of parameters, but for the second set, the mean field correction was not included. This second set was rejected for the following reasons: (a) From structural data we feel quite sure that J_2 cannot be negative (see below). (b) The values of these parameters gave an energy scheme inconsistent with the magnetic behavior of the tetramer[40] and the EPR results. Using the mean field correction, we were able to improve the fitting, get a reliable value for $J_2 = 1.3(3)$ cm^{-1}, and obtain an energy scheme with $S = 2$ ground state which is consistent with EPR results. Mean field correction has been used successfully to effect a fit for tetrameric clusters by other authors.[40−42] This small intermolecular exchange parameter $zJ = -0.5(1)$ cm^{-1} dominates the bulk susceptibility at low temperatures, something that has been noticed earlier by several researchers[40,41]. Dickinson *at al.*[42a] showed that an intermolecular exchange of $zJ = -0.31(2)$ cm^{-1} was responsible for the drastic decrease of μ_{eff} below 20 K while an $S = 2$ ground state was confirmed by EPR experiments as well as the fitting of the magnetic susceptibility data which revealed a ferromagnetic behavior with $J = 47.3(2)$ cm^{-1}.

Lines *at al.*[40] studied several tetramers whose the ferromagnetic behavior revealed that $S = 2$ was the ground state and the drastic decrease of μ_{eff} below 40−60 K was due to small intermolecular exchange. More recently Fujii *at al.*[42b] studied an analogous $S = 2$ antiferromagnetic linear chain of tetramers and they noticed a more drastic drop of μ_{eff} at low T. The reason for that drastic decrease seems to be the more effective intermolecular exchange between those tetramers ($J/k = -2.6$ K) which at low T dominates the large ferromagnetic behavior ($J/k = 50$ K).

In order to investigate the influence of J_3 on the energy scheme, we at first kept it constant at zero, which is very reasonable considering the large distances between the coppers Cu(1)−Cu(2a) and Cu(2)−Cu(1a). This produced the third set of parameters and an energy scheme (Table 6) with $S = 2$ as the ground state. Taking J_3 as a free variable but restricting it to values smaller than J_2 and positive we obtained the first and fourth sets of parameters. We tend to reject the first set because of its large J_3 value relative to J_2. We have no way of choosing between the third and fourth sets. In any case sets one, three, and four give energy schemes with $S = 2$ ground states and reliable J_2 values. The energy difference between the ground state and the first exited states is less than 3 cm^{-1} (Table 6). This small difference between the ground state and the first excited has been used as an important key to fit the magnetic susceptibility data but unfortunately no EPR evidence was given to confirm this assumption.[32d]

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(43) We used the multidimensional minimization package MERLIN/MCL[44] and after a session of optimization with it, and by using many optimization teqniques such as the BFGS algorithm, the Simplex algorithm or the Conjugate Gradient algorithm, we arrived at an optimum determination of the five parameters, where the value of the agreement factor is $R = 0.62 \times 10^{-6}$. At first we considered the interactions within the two dimers and between them and the best fit was made on J_1, J_2 as variables with $J_3 = J_4 = 0 = zJ$. Then we kept J_1 and J_2 constant and fit the J_3 and zJ. This procedure was continued until self-consistent values for all parameters were found.

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Table 5. Selected Bond Distances (Å) and Angles (deg) for some Polymeric and Binuclear Cu(II) Complexes Having Cu_2Cl_2, Cu_2O_2, or Cu_2OCl Bridging Units[a]

	1 for Cu(2)	**1** for Cu(1)	**2**[37]	**3**[38]	**4**[39]	**5**[36]	**6**[4b]	**7**[4b]	**8**[8d]	**9**[8d]	**10**[8d]	**11**[8d]	**12**[50,51]	**13**[52]	**14**[49]
Cu···Cu′	2.940	2.940	3.003	2.950	2.981	2.956	3.063	3.060	3.084	3.138	3.405	3.419	3.167	3.265	3.255
Cu−X′(polym)	2.734	2.751	3.660	2.979	2.851	2.846	3.127	2.905	2.576	2.564	2.468	2.473			
Cu−O−Cu′	97.3	97.3	103.9	100.9	101.5	101.0	103.9	104.2					105.9	111.4	113.4
Cu−Cl−Cu′	78.4	78.4							84.10	85.62	94.35	95.11	87.0	89.6	86.1
trigonality index	0.41	0.26	0.23	0.18	0.42	0.43	0.18	0.22							
$2J$ (cm^{-1})							−1.065	−1.020	+45	+45	−48	−55	−84	−335	−443

[a] Key: **1**, as earlier defined in this paper; **2**, β-bromo(2-diethylaminoethanolato)copper(II); **3**, (2-(dimethylamino)ethanolato)isothiocyanatocopper(II); **4**, (2-(diethylamino)ethanolato)isothiocyanatocopper(II); **5**, (2-(dipropylamino)ethanolato)isothiocyanatocopper(II); **6**, β-bromo(2-(dimethylamino)-propan-1-olato)copper(II); **7**, β-chloro(2-(dimethylamino)propan-1-olato)copper(II); **8**, cyclopentylammonium trichlorocuprate(II); **9** cyclohexylammonium trichlorocuprate(II); **10** 4-methyl-2-aminopyridinium trichlorocuprate(II); **11**, 6-methyl-2-aminopyridinium trichlorocuprate(II); **14**, [2,6-bis(4-(2-benzimidazolyl)2-thiabutyl)-4-methylphenolato]trichlorodicopper(II).

Table 6. Energy Levels of the Tetrameric Repeating Unit

	SET 1	*SET 2*	*SET 3*	*SET 4*
	S = 0 (219.7 cm⁻¹)	*S = 0 (222.9 cm⁻¹)*	*S = 0 (219.6 cm⁻¹)*	*S = 0 (213.75 cm⁻¹)*
	S = 1 (73.40 cm⁻¹)	*S = 1 (75.40 cm⁻¹)*	*S = 1 (74.04 cm⁻¹)*	*S = 1 (71.91 cm⁻¹)*
E	*S = 1 (73.09 cm⁻¹)*	*S = 1 (73.20 cm⁻¹)*	*S = 1 (72.40 cm⁻¹)*	*S = 1 (70.60 cm⁻¹)*
	S = 0 (-71.52 cm⁻¹)	*S = 2 (-73.15 cm⁻¹)*	*S = 0 (-71.57 cm⁻¹)*	*S = 0 (-69.69 cm⁻¹)*
	S = 1 (-72.38 cm⁻¹)	*S = 1 (-75.45 cm⁻¹)*	*S = 1 (-72.41 cm⁻¹)*	*S = 1 (-70.48 cm⁻¹)*
	S = 2 (-74.10 cm⁻¹)	*S = 0 (-76.56 cm⁻¹)*	*S = 2 (-74.03 cm⁻¹)*	*S = 2 (-72.03 cm⁻¹)*

At this point we should mention that when a simple Bleaney−Bowers expression was used to fit the data (with g treated as a variable) it resulted in a g value of 1.87. Such unusual g values-(1.7−1.89) have been observed in dimeric copper complexes with interdimer interaction.[31b] This led us to use the more complex Hamiltonian in eq 1, which takes into account this interaction.

According to Kahn's theory,[45] it is possible to decompose the observed interaction between the Cu(1)−Cu(2) or/and Cu-(1a)−Cu(2a) into contributions arising from each of the Cu−O−Cu and Cu−Cl−Cu linkages. Hatfield *at al.*[46] for hydroxy-bridged copper(II) dimers and Merz *at al.*[47] for alkoxo-bridged copper(II) complexes have proposed linear relationships between the Cu−O−Cu′ angle Φ and the observed exchange constant. Both linear relationships have almost the same slope, $\delta J_{12}/\delta\Phi$, but the crossover angle is slightly different due to the different electronegativities of the bridging ligands. This effect was also studied theoretically by Hay *et al.*[48] An interesting feature can be observed by comparing the distances and angles involving the copper atoms in (1) with the corresponding ones in polymeric Cu(II) complexes derived from N and O or Cl donor ligands[8d,4b,36−39,49−52] (Table 4). The Cu−Cu′ and Cu−X′ (polym) distances and the Cu−O−Cu′ or Cu−Cl−Cu′ angles show marked differences. The trigonality index shows that the distortion from an ideal square-pyramidal coordination is not related to the Cu−O−Cu′ angle, which is related to the magnetic behavior of the complexes. Considering the Merz straight line for the relationship between $2J$ and the Cu−O−Cu′ bridging angle[47] for alkoxo-bridged copper(II) complexes, an antiferromagnetic behavior in the order of $2J = -120$ cm^{-1} is expected for compound **1**. However, compound **1** shows a ferromagnetic behavior with exchange constant $2J = +73$ cm^{-1}.

Since the copper−oxygen distances do not differ from related distances[8,36−39,49−52] the reason for the difference in expected and observed exchange constants must be found in the influence (a) of the chloro bridge into the Cu_2OCl dimeric unit and (b) of the chloro bridges of the Cu_2Cl_2 units which transform the idealized system of noninteracting dimers in a many-spin system.

The Cu_2Cl_2 units are planar while the Cu_2OCl unit is folded across the Cl−O line as it is defined by the dihedral angle δ = Cu(2)−O(1)−Cu(1)/Cu(2)−Cl(3)−Cu(1) = 131.7°. The Cu-(2)−Cl(3)−Cu′(1) angle of 78.4° is the lowest angle observed for dimeric or polymeric structures with folded units.

Bencini and Gatteschi[53] considered the folding of a dimer with square-pyramidal coordination environment around the Cu atoms, but kept Φ fixed as the dimer was folded, while Willett[8d] using extended Hückel calculation for dimeric planar or folding units of extended structures have proposed a plot for the relationship between J/k and Φ. Using this plot[8d] an antiferromagnetic behavior in the order of $J/k = -45$ (K) is expected for the Cu_2Cl_2 units while for the folding Cu_2OCl unit a ferromagnetic behavior may be calculated. For dimeric compounds with planar Cu_2OCl units a net antiferromagnetic coupling has been observed[49−52] except one[54] but without crystal structure data.

As has been shown for dimers[19] with the same linkages the exchange coupling constants might be expected to show a simple relationship with the quantity φ/R, where R is the longer Cu−Cl separation. This value for the Cu(2a)−Cl−Cu(2) unit is 34.67 which corresponds to $2J \sim 1.0$ cm^{-1} a value well calculated from the fitting procedure, showing that we can use these empirical formulas as a guide for polynuclear complexes having dimeric units in them.

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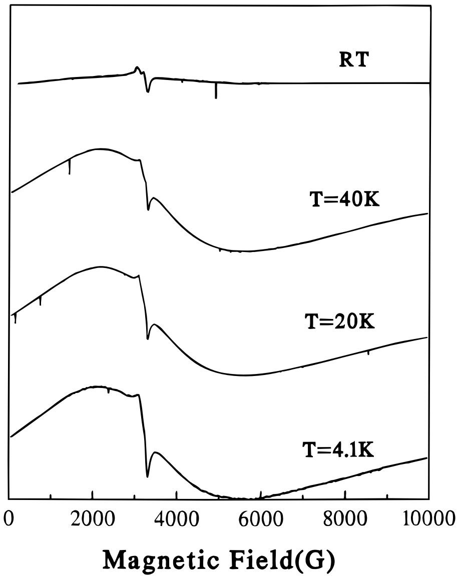

Figure 4. Polycrystalline powder EPR spectra of **1** in the range 4.1–300 K at X-band frequency (9.42 GHz).

EPR Study. The polycrystalline powder EPR spectra at 4.1, 20.0, and 40.0 K and room temperature are shown in Figure 4. At 4.1 K an intense broad signal spread over 3900 G (2000–5900) with $g = 2.34$ and a weak axial signal with $g_{\perp} = 2.16$, $g_{\|} = 2.059$ appear. The equation $g = (2g_{\perp} + g_{\|})/3 = 2.09(1)$ has been used as a fixed parameter in the fitting procedure. The broad signal is indicative for a bulk concentration of copper ions having strong ferromagnetic interaction.[55,56] The broad signal disappears at room temperature showing only the presence of a paramagnetic impurity. By diluting the sample with ZnO no improvement in the resolution of the broad signal was observed. A noteworthy feature of the EPR spectra was that their intensities increase in going from 40 to 4.1 K. More specifically the intensity of the spectrum at 20 K is 0.8 times the intensity at 4.1 K and the intensity at 40 K is 0.45 times the intensity at 4.1 K. This confirms that the ground state manifold is paramagnetic and that the intracluster exchange interaction is primarily ferromagnetic; $J > 0$. In addition, no $\Delta M = +2$ transitions were observed and no hyperfine structure was evident except as a possible contribution to the broadening of the line.

This compound may be a possible candidate to examine the Haldane gap problem. Haldane[57] predicted that for one-dimensional Heisenberg $S \geq 1$ antiferromagnets the ground state should be a singlet, separated from the first triplet excited state by an energy gap (Haldane gap). As the temperature is reduced to zero, the effective moment of integer spin systems was predicted to vanish. Although this Haldane gap has now been well confirmed theoretically[58] and experimentally for $S = 1$ systems of Ni^{2+} chains, the problem of the existence or not of this gap for systems with integer spin $S = 2$ still remain unsolved. Investigation of the magnetic susceptibility below 4 K and EPR experiments at 2 K are in progress.

In conclusion the ferromagnetic behavior of **1** is dictated by the Cu–Cl–Cu′ of the Cu_2OCl unit and the mean field correction was successfully used to interpret the magnetic behavior of **1** at low T and it produced an energy scheme consistent with the EPR results.

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Supporting Information Available: Tables giving anisotropic thermal parameters of the non-H atoms for $[Cu_4(dpk{\cdot}CH_3O)_2Cl_6]_n$ (Table 1S), positional and isotropic thermal parameters of the H atoms (Table 2S), complete tables of bond distances and angles (Table 3S), and complete crystal and data statistics (Table 4S), figures giving a complete numbering scheme for all atoms (Figure $1S_F$), and a stereoview (Figure $2S_F$), and a table of magnetic data for $[Cu_4(dpk{\cdot}CH_3O)_2Cl_6]_n$ (Table 5S) (7 pages). Ordering information is given on any current masthead page.

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