4834 Inorg. Chem. 1993, 32, 4834–4838

Further Neighbor Magnetic Exchange Interaction in a Novel Pseudolinear Tetramer of Copper(II)

B. Chiari, O. Piovesana,* T. Tarantelli, and P. F. Zanazzi

Dipartimento di Chimica and Dipartimento di Scienza della Terra, Sezione Cristallografia,
Università di Perugia, 06100 Perugia, Italy

Received September 11, 1992⊗

The synthesis, crystal structure, and magnetic properties are reported for the novel compound $Cu_4L_2(CH_3COO)_6$, where LH = 1-(5-bromosalicylaldimino)-3-(2-methylpiperidino)propane. The compound, $Cu_4C_{44}H_{62}N_4O_{14}Br_2$, crystallizes in the monoclinic space group $P2_1/n$. Cell dimensions are as follows: $a = 11.627(3)$ Å, $b = 22.442(3)$ Å, $c = 9.693(3)$ Å, $\beta = 94.46(2)°$, and $Z = 2$. The structure was refined to an R(unweighted) value of 0.076. The tetranuclear unit of the complex is centrosymmetric and has an almost linear geometry. The separation between the "central" Cu(2) and Cu(2)′ atoms is 2.63 Å and that between the end Cu(1) and Cu(1)′ atoms is 11.81 Å. The Cu(1)–Cu(2) and Cu(2)–Cu(2)′ directions form an angle of 164.5°. Cu(2) and Cu(2)′ have a square pyramidal environment and are bridged by four acetate groups in a syn–syn conformation, as in the well-known copper(II) acetate monohydrate dimer. Two additional acetate groups bridge, by adopting a syn–anti conformation, from the axial position of a central copper atom to a pseudo-basal position of the adjacent terminal copper atom. The end copper atoms have a (4 + 1) coordination geometry that is intermediate between square pyramidal and capped tetrahedral. The X-ray analysis of the compound does not reveal any bonding interactions between tetramers. The magnetic susceptibility of the compound has been measured between 2 and 290 K. At room temperature the $\chi_M(4Cu)T$ value is slightly lower than expected for four uncoupled $S = {}^1/_2$ spins (1.29 vs 1.50 emu·mol^{-1}·K). When the temperature is lowered, $\chi_M T$ first decreases, reaching a value appropriate for two uncorrelated $S = {}^1/_2$ spins (0.8 emu·mol^{-1}·K) at about 80 K, then remains quite constant until ca. 10 K, and ultimately tends to zero as the temperature approaches zero. These properties can be nicely accounted for by a model in which there is very weak magnetic exchange between the outer pairs of copper atoms, strong antiferromagnetic exchange ($-2J_2 \sim 300$ cm^{-1}) between the central pair, and an individual antiferromagnetic coupling ($-2J_4 = 3.5$ cm^{-1}) between the terminal copper atoms. An orbital mechanism for the end–end interaction is proposed.

Introduction

A characteristic property of exchange interactions is their lack of additivity with respect to the interaction energy between *isolated* pairs of atoms or ions.[1] In 1934, Kramers[2] was the first to anticipate that, owing to this property, superexchange may have a considerably longer range than direct exchange interactions. Since then the problem of relating the strength of superexchange interactions (J) to the distance apart (R) of the interacting spins has received considerable interest.[3]

Knowledge in this matter has traditionally developed in solid state physics, through studies on magnetic insulators with ionic lattices, typically transition metal oxides or fluorides. For these systems, in general, $J(R)$ can be approximated by empirical relationships of which an R^{-n} dependence[4] (the "magnetic Gruneisen law", where n is typically ≥ 10) or an $e^{-\alpha R}$ dependence (α = constant)[5] are the most common. The widespread practice of assuming only nearest-neighbor interactions in the spin Hamiltonian counts on this remarkable sensitivity of J to R. The above models, however, rely on chemically simple systems that have relatively high symmetries.

In the past two decades, chemists have shown that "molecular" insulating solids, owing to their chemical and structural flexibility, provide a quite different domain for investigation.

In particular, structure–magnetism relationships[6-8] have demonstrated that in such compounds several factors can contend the role of R in determining J, a feature that potentially allows superexchange of longer range than conceivable from results for ionic lattices. Actually, studies on "molecular" long-range superexchange have produced several systems[9-22] in which significant exchange coupling is propagated up to distances in excess of 6–10 Å. Examples include binuclear transition-metal compounds bridged by suitable organic ligands,[9,17,18,21] organic

---

* To whom correspondence should be addressed at the Dipartimento di Chimica.

⊗ Abstract published in *Advance ACS Abstracts*, August 15, 1993.

(1) Block, R.; Jansen, L. In *Quantum Science*; Plenum: New York, 1976; p 123 and references therein.

(2) Kramers, A. *Physica* **1934**, *1*, 182.

(3) de Jongh, L. J.; Block, R. *Physica 79B* **1975**, 568 and references therein.

(4) Bloch, D. *J. Phys. Chem. Solids* **1966**, 881.

(5) Harris, E. A. *J. Phys. C: Solid State Phys.* **1972**, *5*, 338. Mason, E. A.; Monchick, L. *Adv. Chem. Phys.* **1967**, *12*, 338.

(6) (a) See various articles in: *Magneto-Structural Correlations in Exchange Coupled Systems*; Willett, R. D., Gatteschi, D., Kahn, O., Eds.; Reidel: Dordrecht, The Netherlands, 1985. (b) Kahn, O. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 834 and references therein.

(7) (a) Moreland, J. A.; Doedens, R. J. *Inorg. Chem.* **1978**, *17*, 674 and references therein. (b) Melnik, M. *Coord. Chem. Rev.* **1982**, *42*, 259. (c) Doedens, R. J. *Prog. Inorg. Chem.* **1976**, *21*, 209. (d) Kato, M.; Muto, Y. *Coord. Chem. Rev.* **1988**, *92*, 45.

(8) Hatfield, W. E. *Comments Inorg. Chem.* **1981**, *1*, 105.

(9) Hendrickson, D. N. In Ref 6a, p 523.

(10) Chiari, B.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F. *Inorg. Chem.* **1984**, *23*, 2542.

(11) Chiari, B.; Hatfield, W. E.; Piovesana, O.; Tarantelli, T.; ter Haar, L. W.; Zanazzi, P. F. *Inorg. Chem.* **1983**, *22*, 1468.

(12) Chiari, B.; Helms, J. H.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F. *Inorg. Chem.* **1986**, *25*, 870.

(13) Chiari, B.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F. *Inorg. Chem.* **1990**, *29*, 1172.

(14) Tinti, F.; Verdaguer, M.; Kahn, O.; Savariault, J. M. *Inorg. Chem.* **1987**, *26*, 2380.

(15) Felthouse, T. R.; Dong, T. Y.; Hendrickson, D. N.; Shieh, H. S.; Thompson, M. R. *J. Am. Chem. Soc.* **1986**, *108*, 8201.

(16) Cogne, A.; Grand, A.; Rey, P.; Subra, R. *J. Am. Chem. Soc.* **1989**, *111*, 3230.

(17) Girerd, J. J.; Jeannin, S.; Jeannin, Y.; Kahn, O. *Inorg. Chem.* **1978**, *17*, 3034.

(18) Veit, R.; Girerd, J. J.; Kahn, O.; Robert, F.; Jeannin, Y.; El Murr, N. *Inorg. Chem.* **1984**, *23*, 4448.

(19) Benelli, C.; Caneschi, A.; Gatteschi, D.; Pardi, L.; Rey, P. *Inorg. Chem.* **1990**, *29*, 4223.

(20) Chaudhuri, P.; Winter, M.; Birkelbach, F.; Fleischhauer, P.; Haase, W.; Florke, U.; Haupt, H. J. *Inorg. Chem.* **1991**, *30*, 4293.

(21) Chaudhuri, P.; Oder, K.; Wieghardt, K.; Gehring, S.; Haase, W.; Nuber, B.; Weiss, J. *J. Am. Chem. Soc.* **1988**, *101*, 3657.

(22) Coffman, R. E.; Buettner, G. R. *J. Phys. Chem.* **1979**, *83*, 2387.

0020-1669/93/1332-4834$04.00/0

Table I. Crystallographic Data for $Cu_4L_2(CH_3COO)_6$

$Cu_4C_{44}H_{62}N_4O_{14}Br_2$	fw = 1284
cryst class: monoclinic	$T = 20$ °C
space group: $P2_1/n$	$\lambda = 0.7107$ Å
$a = 11.627(3)$ Å	$\rho = 1.691$ g·cm^{-3}
$b = 22.442(3)$ Å	$\mu = 28.4$ cm^{-1}
$c = 9.693(3)$ Å	trans coeff = 0.88–0.99
$\beta = 94.46(2)°$	$R = 0.076$
$V = 2521.6$ Å^3	$R_w{}^a = 0.075$
$Z = 2$	

^{a} $R_w = (\sum(w|F_o| - |F_c|)^2)^{1/2}/(\sum wF_0{}^2)^{1/2}$; $w = (\sigma^2(F_0))^{-1}$.

biradicals bridged by metal–metal bonded complexes,[15,16] linear-chain gadolinium(III) nitroxyl–nitroxide compounds,[19] extended copper(II) systems bridged by hydrogen bonds.[12] The different nature of these compounds suggest that a variety of mechanisms might be available to support long-range superexchange in molecular aggregates. Studies on such interactions, besides being of magnetic interest, are relevant to several areas of chemistry, physics, and biology.[23]

In the present paper we report the synthesis, X-ray structure, and magnetic properties of the novel pseudo-linear tetramer $Cu_4L_2(CH_3COO)_6$ (LH = 1-(5-bromosalicylaldimino)-3-(2-methylpiperidino)propane).

The compound provides the interesting possibility of testing the potential of a marginally explored way to propagate long-range interactions, i.e. individual exchange coupling between necessarily far apart further neighboring spins in magnetic systems with linear geometry.

The tetramer affords the direct observation of an appreciable antiferromagnetic interaction ($J \sim -2$ cm^{-1}) between the terminal copper atoms that are separated by a distance of ~12 Å.

Experimental Section

Synthesis. A 0.36-g (1.25-mmol) quantity of 5-bromo-2-hydroxybenzaldehyde was dissolved in absolute ethanol (60 mL). This solution was added to a solution of 1-(3-aminopropyl)-2-methylhexahydropyridine (0.195 g, 1.25 mmol) in the same solvent (25 mL), at room temperature. The resulting yellow solution was heated at ca. 50 °C for 4 h. To the clear, hot solution containing the ligand was added a 5 mmol quantity of $Cu(CH_3COO)_2{\cdot}H_2O$. The addition was made over a period of 0.5 h, with constant stirring. A green solution was obtained. The solution was filtered. After the filtrate was allowed to evaporate for about 3 days, at room temperature, small deep-green crystals were collected by filtration, washed with 1:1 ethanol–ligroin, and dried under vacuum: yield 0.35 g (22%); mp 210–212 °C. Anal. Calcd for $C_{44}H_{62}N_4O_{14}Br_2Cu_4$: C, 41.12; H, 4.87; N, 4.36; Cu, 19.78. Found: C, 41.31; H, 4.78; N, 4.25; Cu, 19.90. The product could not be recrystallized unaltered from organic solvents.

Magnetic Susceptibility Measurements. Variable-temperature magnetic susceptibility measurements were performed, on samples from different preparations, in the range 2.0–290 K, with use of a Faraday type magnetometer equipped with a helium continuous-flow cryostat built by Oxford Instruments. Susceptibilities were corrected for the diamagnetism of the ligand system, estimated as -540×10^{-6} emu·mol^{-1}. Our analyses used a temperature-independent paramagnetic term, $N\alpha$, of 60 × 10^{-6} emu/Cu atom and did not include any zero-field splitting.

Table II. Positional Parameters (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for $Cu_4L_2(CH_3COO)_6$

	x/a	y/b	z/c	U(eq)^a
Cu(1)	160(3)	2487(1)	1985(3)	36(2)
Cu(2)	243(3)	520(1)	578(3)	38(2)
Br	1291(3)	5244(1)	−1719(4)	79(3)
O(1)	1187(13)	2000(7)	3209(16)	32(4)
O(2)	1361(4)	3041(8)	1873(18)	46(5)
O(3)	−1436(16)	652(8)	354(18)	50(5)
O(4)	356(16)	792(8)	−1305(20)	59(5)
O(5)	631(4)	1369(7)	1537(17)	42(5)
O(6)	1822(16)	245(8)	568(19)	54(5)
O(7)	33(16)	70(8)	2305(19)	55(5)
N(1)	−543(15)	2672(8)	161(19)	26(5)
N(2)	−1375(16)	2326(8)	2831(20)	35(5)
C(1)	−338(23)	3119(11)	−559(28)	41(7)
C(2)	495(13)	3587(6)	−121(17)	32(6)
C(3)	516(13)	4090(6)	−962(17)	48(7)
C(4)	1333(13)	4536(6)	−658(17)	44(7)
C(5)	2129(13)	4478(6)	488(17)	49(7)
C(6)	2107(13)	3975(6)	1329(17)	44(7)
C(7)	1290(13)	3529(6)	1024(17)	42(7)
C(8)	−1381(20)	2218(11)	−487(26)	37(7)
C(9)	−2330(23)	2142(12)	402(26)	46(7)
C(10)	−2088(20)	1904(10)	1881(24)	32(7)
C(11)	−2012(22)	2937(12)	2963(28)	46(7)
C(12)	−1257(28)	3290(15)	3880(31)	70(9)
C(13)	−3265(26)	2864(14)	3323(31)	63(8)
C(14)	−1177(30)	3033(14)	5393(33)	81(10)
C(15)	−577(25)	2423(13)	5242(30)	62(8)
C(16)	−1241(22)	2053(11)	4198(26)	41(7)
C(17)	2142(23)	−286(11)	132(26)	36(7)
C(18)	3394(24)	−427(12)	272(28)	52(8)
C(19)	−216(21)	−462(12)	2353(28)	40(7)
C(20)	−370(24)	−709(12)	3752(29)	49(7)
C(21)	1235(22)	1504(11)	2614(27)	39(7)
C(22)	2078(21)	1039(10)	3275(26)	36(7)

^{a} The equivalent isotropic U for anisotropically refined atoms is defined as one-third of the trace of the U_{ij} tensor.

Table III. Selected Bond Lengths (Å) and Angles (deg)

Cu(1)–O(1)	1.951(15)	Cu(2)–O(4)	1.939(19)
Cu(1)–O(2)	1.879(17)	Cu(2)–O(5)	2.152(16)
Cu(1)–O(5)	2.612(16)	Cu(2)–O(6)	1.938(18)
Cu(1)–N(1)	1.934(18)	Cu(2)–O(7)	1.986(18)
Cu(1)–N(2)	2.035(18)	Cu(1)–Cu(2)	4.623(3)
Cu(2)–O(3)	1.970(18)	Cu(2)–Cu(2)′	2.631(3)
O(1)–Cu(1)–O(2)	89.0(6)	O(3)–Cu(2)–O(4)	89.3(7)
O(1)–Cu(1)–O(5)	55.7(5)	O(3)–Cu(2)–O(5)	95.0(7)
O(1)–Cu(1)–N(1)	150.6(7)	O(3)–Cu(2)–O(6)	168.1(7)
O(1)–Cu(1)–N(2)	99.7(6)	O(3)–Cu(2)–O(7)	89.1(7)
O(2)–Cu(1)–O(5)	117.4(6)	O(4)–Cu(2)–O(6)	87.8(7)
O(2)–Cu(1)–N(1)	93.9(7)	O(4)–Cu(2)–O(7)	167.2(7)
O(2)–Cu(1)–N(2)	144.7(7)	O(5)–Cu(2)–O(6)	96.7(7)
O(5)–Cu(1)–N(1)	97.7(6)	O(5)–Cu(2)–O(7)	97.0(7)
O(5)–Cu(1)–N(2)	95.6(6)	O(6)–Cu(2)–O(7)	91.2(7)
N(1)–Cu(1)–N(2)	94.8(7)	Cu(1)–O(5)–Cu(2)	152.0(7)

Crystallographic Data Collection and Structure Determination. A deep green prismatic crystal with dimensions 0.15 × 0.10 × 0.05 mm^3 was mounted on a computer-controlled Philips PW1100 single-crystal diffractometer equipped with a graphite-monochromatized Mo Kα radiation. Cell parameters were determined by a least-squares calculation based on the setting angles of 25 reflections with 2Θ angles ranging between 10 and 15°. Cell dimensions and additional crystal data are listed in Table I. The space group resulted from systematic extinctions. The reflection intensities were measured up to 2Θ = 40°; the ω–2Θ scan technique was employed, the scan range being 2.0° and the speed 0.06° s^{-1}. A total of 2500 reflections were measured. Due to the rather small volume of our crystals, only 955 reflections had $I > 3\sigma(I)$, were considered as observed and were used in the refinement. Three standard reflections that were measured periodically showed no apparent variation in intensity during the data collection. The data were corrected for Lorentz and polarization factors. During the refinement, an empirical absorption correction was applied, according to the method of North et al.[24]

The structure was solved by Patterson and direct methods and refined by the full-matrix least-squares method with use of the SHELX-76 package of programs.[25] Anisotropic thermal parameters were refined for the Cu and Br atoms only. The phenyl group was refined as a rigid group, assuming a perfect hexagonal geometry (C–C bond lengths were considered equal to 1.39 Å). The contribution of the hydrogen atoms at the calculated positions (where possible) was included in the calculation. The refinement was carried out with use of 141 parameters and 955 independent reflections. Atomic scattering factors were taken from ref

---

(23) Moore, G. R.; Williams, R. J. P. *Coord. Chem. Rev.* **1976**, *18*, 125. Reynolds, W. L.; Lumry, R. M. *Mechanisms of Electron Transfer*; Ronald Press: New York, 1966. Taube, H. *Adv. Chem. Ser.* **1977**, *No. 162*, 127. Solomon, E. I. In *Metal Clusters in Proteins*; Que, L., Jr., Ed.; American Chemical Society: Washington, DC, 1988; p 116. Kahn, O. *Struct. Bonding (Berlin)* **1987**, *68*, 89.

(24) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1986**, *A24*, 351.

(25) Sheldrick, G. M. *SHELX-76, Program for Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1976.

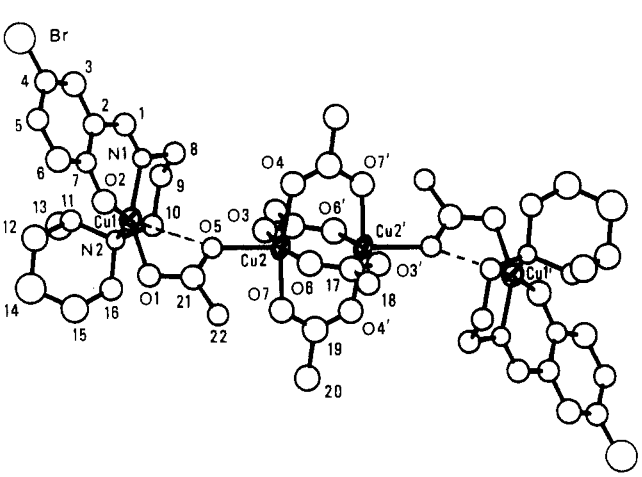

Figure 1. View of the tetranuclear $Cu_4L_2(CH_3COO)_6$ molecule. Hydrogen atoms have been omitted for clarity. Unlabeled atoms are related to labeled atoms by the inversion center.

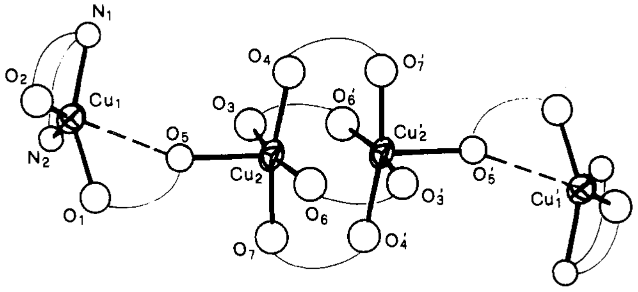

Figure 2. Schematic view of the bridging framework in $Cu_4L_2(CH_3COO)_6$.

25 for O, N, C, and Br atoms and from ref 26 for Cu; the correction for anomalous dispersion was included. Final positional parameters are given in Table II.

Results

Description of the Structure. The crystal structure is composed of discrete tetranuclear units of formula $Cu_4L_2(CH_3COO)_6$. Representative bond distances and angles are compiled in Table III. The structure of the compound is presented in Figures 1 and 2.

The molecule has a crystallographic center of inversion located between the two central copper atoms. These two atoms are bridged by four acetate groups in a syn–syn conformation, as in the well-known copper(II) acetate monohydrate dimer.[27] Two additional acetate groups bridge from the axial position of a central copper atom to a pseudo-basal position of the adjacent terminal copper atom by adopting a syn–anti conformation, as can easily be seen in Figure 2. This bridging arrangement gives rise to a Cu(1)–Cu(2) distance, 4.623(3) Å, substantially longer than that of 2.631(3) Å associated with the $Cu_2(CH_3COO)_4$ core. The Cu(1)–Cu(2)′ and Cu(1)–Cu(1)′ separations are 7.197(3) and 11.806(3) Å, respectively. The angle between the Cu(2)–Cu(2)′ and Cu(1)–Cu(2) axes is 164.5°.

In the central portion of the molecule, the axial acetate oxygen atoms, O(5) and O(5)′, are collinear with the Cu–Cu axis of the $Cu_2(CH_3COO)_4$ core (Cu(2)′–Cu(2)–O(5) = 179.5(4)°) at a distance from the Cu atoms (2.152(16) Å) that is not significantly different from the corresponding distance, 2.156(4) Å, for $Cu_2(CH_3COO)_4{\cdot}2H_2O$.[27] This is also the case for the displacement (0.21 Å) of the copper atoms out of the equatorial planes of the four acetate oxygen atoms toward the axial oxygen atoms and for the bond distances and angles in the $Cu_2(CH_3COO)_4$ fragment.

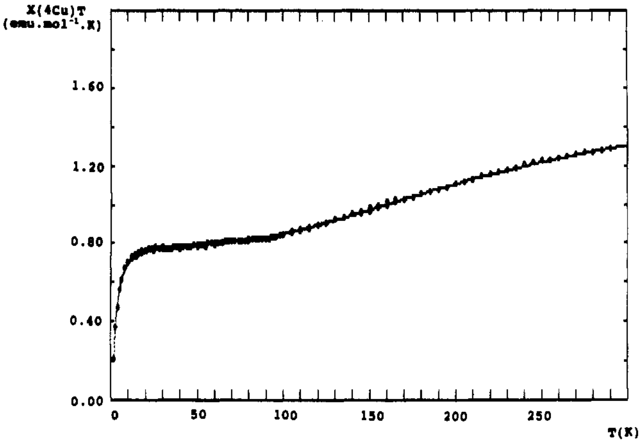

Figure 3. Experimental and theoretical (see text) temperature dependence of $\chi_M(4Cu)T$ for $Cu_4L_2(CH_3COO)_6$ between 2 and 290 K.

The two end copper atoms have a CuN_2O_3 ligand environment and adopt a (4 + 1) coordination mode. The long bond is Cu(1)–O(5), 2.612(16) Å. The coordination geometry of Cu(1) and Cu(1)′ is intermediate between square pyramidal and capped tetrahedral, as indicated by the trans angles N(1)–Cu(1)–O(1) and N(2)–Cu(1)–O(2) of 150.6(7) and 144.3(7)°, respectively. This distorted geometry is due to the constraints of the tridentate L^- and acetate ligand geometries. The distortion is particularly severe for the acetate ligand, where the O(1)–Cu(1)–O(5) angle is 55.7(5)°.

There are four Cu(1)···Cu(1) intermolecular separations that are shorter than the intramolecular one. These repeating distances are as follows: (i) 7.274(3) Å, related to the *n*-glide translation; (ii) 7.853(3) Å, along the direction defined by $x + {}^1/_2, -y + {}^1/_2, z + {}^1/_2$ and $x + 1, y, z$ or $x, y, z + 1$; (iii) 9.693(3) and 11.627(3) Å, corresponding to unit cell translations in *z* and *x*, respectively.

The shortest intermolecular Cu(1)–L separations involve Br($-x, 1 - y, -z$), 5.364 Å, and N(1) ($x + {}^1/_2, -y + {}^1/_2, z + {}^1/_2$), 5.672 Å.

Magnetic Properties. The results of magnetic susceptibility measurements for $Cu_4L_2(CH_3COO)_6$ are given in Figure 3, in the form of the χ_M (4Cu) *T* vs *T* plot. Upon lowering the temperature from 290 to 2 K the plot reveals three domains.

(i) From 290 to about 80 K, $\chi_M T$ decreases from a value of 1.29 emu·mol⁻¹·K, that is slightly lower than that calculated for four uncorrelated $S = {}^1/_2$ spins (1.50 emu·mol⁻¹·K for $g = 2$), to a value of about 0.8 emu·mol⁻¹·K, appropriate for two independent $S = {}^1/_2$ spins.

(ii) Between approximately 80 and 10 K, the latter value of $\chi_M T$ remains practically constant.

(iii) Below 10 K, $\chi_M T$ tends to zero as the temperature approaches zero.

Discussion

Magneto–Structural Correlation. Studies of the structural and magnetic properties of acetate-, substituted-acetate-, and carbonate-bridged complexes of copper(II) have shown that the spin interaction in this series of compounds is largely determined by the conformation of the bridge. In copper acetate hydrate ($J = -143$ cm⁻¹)[27,28] and related complexes,[7] where the copper atoms are bridged in a syn–syn manner, the exchange coupling is always large and antiferromagnetic in nature. Complexes that contain syn–anti bridges are instead characterized by feeble magnetic interactions that can be either ferromagnetic with *J* values[29–33] ranging from ca. 0.5 to 7 cm⁻¹ or, in two cases, antiferromagnetic,

---

(26) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 99.

(27) Meester de, P.; Fletcher, S. R.; Skapsky, A. C. *J. Chem. Soc., Dalton Trans.* **1973**, 2575.

(28) Martin, R. L.; Waterman, R. *J. Chem. Soc.* **1957**, 2545. Lewis, J.; Mabbs, F. E.; Royston, L. K.; Smail, W. R. *J. Chem. Soc. A* **1969**, 291. Gudel, H. U.; Stebler, A.; Furrer, A. *Inorg. Chem.* **1979**, *18*, 1021.

(29) Inoue, M.; Kubo, M. *Inorg. Chem.* **1970**, *9*, 2310.

(30) Kolks, G.; Lippard, S. J.; Waszczack, J. V. *J. Am. Chem. Soc.* **1980**, *102*, 4832.

(31) Corvan, P. J.; Estes, W. E.; Weller, R. R.; Hatfield, W. E. *Inorg. Chem.* **1980**, *19*, 1297.

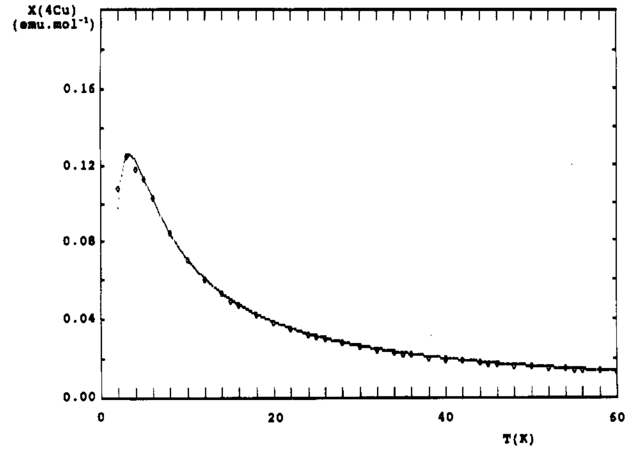

Figure 4. Low-temperature magnetic susceptibility data, χ(4Cu), for $Cu_4L_2(CH_3COO)_6$, along with the fit described in the text.

with J values of -1.0[34] and $-3.0\ cm^{-1}$.[35] The magnetic interactions in these complexes have also been rationalized on an orbital basis.[35,36]

In the tetramer, according to these results, Cu(2) and Cu(1) may be expected to be weakly coupled (syn–anti). In contrast, a strong antiferromagnetic interaction (syn–syn) should occur between Cu(2) and Cu(2)′. The magnetic behavior of $Cu_4L_2(CH_3COO)_6$ between 290 and 10 K is explicable in terms of these concepts.

Clearly, if upon lowering the temperature from 290 to 80 K the singlet ground state becomes the only populated state of the "central dimer", a weak magnetic interaction between the outer pairs of copper atoms cannot be observed below that temperature and the virtually independent spins of the two terminal copper atoms dominate the magnetic response of the compound.

The approach of $\chi_M T$ to zero as the temperature is decreased below 10 K is interpreted accordingly: the terminal copper atoms interact antiferromagnetically, leading to a spin-singlet ground state for the pair.

Other factors to consider here are intercluster interactions. These, however, are unlikely to determine the observed low-temperature magnetic behavior. The structure consists of distinct tetranuclear units held together by van der Waals forces only and, in particular, the several Cu(1)···Cu(1) distances between tetramers that are less than the Cu(1)···Cu(1)′ intramolecular distance are not related to any apparent intercluster superexchange pathway. Additionally, the experimental susceptibility data below 80 K are precisely described by a dimer exchange model[37] with $g = 2.11$ and $J = -1.87(2)\ cm^{-1}$, as shown in Figure 4. There is no reason why weak extended magnetic interactions between tetramers within the crystal lattice should conform to the above dimer model.

Despite prior several studies on copper(II) trimers[38] and tetramers[39,40] with linear or almost linear geometry, the present compound appears to be the first example in which an appreciable, individual magnetic interaction between the terminal copper atoms can be observed. This prompted us to analyze the magnetic structure of the tetramer in more detail.

Table IV. Best-Fit Parameters[a] (cm^{-1}) and Agreement Factors

fit	J_1	J_2	J_3	J_4	10^4F[b]	$E_4 - E_6$
1	c	−156.4	c	−1.75	7.34	3.50
2	−20.37	−144.0	c	c	7.45	3.50
3	+27.88	−172.3	c	c	7.35	3.50
4	+4.52	−164.2	+8.84	−1.70	7.31	3.50
5	−2.18	−153.7	−1.97	−1.75	7.34	3.50
6	−0.19	−156.0	c	−1.75	7.32	3.50

[a] J values denoted by "c" were arbtrarily held constant to zero. [b] F was calculated as described in the text, for 126 observations.

Heisenberg Model. By virtue of the crystallographically imposed inversion symmetry, the spin problem for the present tetramer involves four exchange-coupling constants and a Hamiltonian of the form shown in eq 1, where we have adhered to the

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

numbering scheme of Figure 1. J_1 describes the nearest neighbor (nn) interactions between the outer pairs of copper atoms, J_2 is the central exchange constant, J_3 describes the next-nearest neighbor (nnn) interactions, and J_4 is the exchange constant between the terminal copper atoms. This model has been solved exactly by standard techniques. The energy levels and spin quantum numbers are as follows:

$$\begin{array}{ll}
S_1 = 2 & E_1 = -J_1 - (1/2)J_2 - J_3 - (1/2)J_4 \\
S_2 = 1 & E_2 = J_1 - (1/2)J_2 + J_3 - (1/2)J_4 \\
S_3 = 1 & E_3 = (1/2)(J_2 + J_4) + [(J_2 - J_4)^2 + (J_3 - J_1)^2]^{1/2} \\
S_4 = 1 & E_4 = (1/2)(J_2 + J_4) - [(J_2 - J_4)^2 + (J_3 - J_1)^2]^{1/2} \\
S_5 = 0 & E_5 = J_1 + J_3 + (1/2)(J_2 + J_4) + [4(J_1^2 + J_3^2) + \\
 & \quad J_2^2 + J_4^2 - 2J_1(J_2 + 2J_3 + J_4) - 2J_2(J_3 - J_4) - 2J_3J_4]^{1/2} \\
S_6 = 0 & E_6 = J_1 + J_3 + (1/2)(J_2 + J_4) - [4(J_1^2 + J_3^2) + \\
 & \quad J_2^2 + J_4^2 - 2J_1(J_2 + 2J_3 + J_4) - 2J_2(J_3 - J_4) - 2J_3J_4]^{1/2}
\end{array}$$

Assuming a Boltzmann distribution for the population of the quintet, triplet, and singlet states, and, in addition, equal g values for the various multiplets, the molar susceptibility per tetrameric unit is given by eq 2. The rather crude approximation[41] of

$$\chi_M(4Cu) = (N\mu_B^2g^2/kT)[10\exp(-E_1/kT) + 2\exp(-E_2/kT) + 2\exp(-E_3/kT) + 2\exp(-E_4/kT)]/[5\exp(-E_1/kT) + 3\exp(-E_2/kT) + 3\exp(-E_3/kT) + 3\exp(-E_4/kT) + \exp(-E_5/kT) + \exp(-E_6/kT)] + 4N\alpha \quad (2)$$

attributing the same g value to all the spin states has been used in order to prevent eq 2 from providing too many parameters for evaluation. Indeed, in the absence of adequate information about the g values of the individual copper ions, the g values for the various spin states (that are related to the former through coefficients that are functions of the J values)[41] should be treated as adjustable parameters.

The experimental susceptibility data were fit to eq 2 by holding $g = 2.10$ and letting two to four coupling constants vary (the remaining ones being held equal to zero). The function that was minimized in curve fitting was $F = (\chi_i^{obsd} - \chi_i^{calcd})^2(\chi_i^{obsd})^{-1}$. Best-fit parameters and F values are collected in Table IV, where it can be seen that any set of parameters describe equally well the experimental data. Fit 1 is shown in Figure 3.

All the fitting calculations produce four states grouped around the energy $-2J_2$, with $J_2 = -159 \pm 14\ cm^{-1}$, and two low-lying

---

(32) Towle, D. K.; Hoffmann, S. K.; Hatfield, W. E.; Singh, P.; Chaudhuri, P. *Inorg. Chem.* **1988**, *27*, 394.

(33) Colacio, E.; Dominguez-Vera, J. M.; Costes, J. P.; Kivekas, R.; Laurent, J. P.; Ruiz, J.; Sundberg, M. *Inorg. Chem.* **1992**, *31*, 774.

(34) Coughlin, P. K.; Lippard, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 2328.

(35) Carlin, R. L.; Kopinga, K.; Kahn, O.; Verdaguer, M. *Inorg. Chem.* **1986**, *25*, 1786 and references therein.

(36) Albonico, C.; Bencini, A. *Inorg. Chem.* **1988**, *27*, 1934 and references therein.

(37) Chiari, B.; Helms, J. H.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F. *Inorg. Chem.* **1986**, *25*, 2408.

(38) Chiari, B.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F. *Inorg. Chem.* **1985**, *24*, 4615 and references therein. Woo, L. K.; Maurya, M. R. *Inorg. Chem.* **1992**, *30*, 4671 and references therein.

(39) Halvorson, K. E.; Grigereit, T.; Willett, R. D. *Inorg. Chem.* **1987**, *26*, 1716 and references therein. Willett, R. D.; Geiser, U. *Inorg. Chem.* **1986**, *25*, 4558 and references therein.

(40) Gojon, E.; Greaves, S. J.; Latour, J. M.; Povey, D. C.; Smith, G. W. *Inorg. Chem.*, **1987**, *26*, 1457.

(41) Bencini, A.; Gatteschi D. *EPR of Exchange Coupled Systems*; Springer-Verlag: Berlin, Heidelberg, Germany, 1990.

states, a singlet (E_6) and a triplet (E_4) above it. For all models $E_4 - E_6 = 3.50(1)$ cm^{-1}. Since it is this energy gap which is responsible for the nice fit of the low-temperature susceptibility data, it is of some interest to examine the contribution of J_4 (the exchange constant between the terminal copper atoms) to $E_4 - E_6$ (denoted Δ hereafter).

(i) Model 1 considers the tetramer as composed of two independent dimers and, of course, J_4 is the only determinant of Δ.

(ii) Models 2 and 3 are nn models. In order to fit the low temperature data, J_1 must assume an abnormally large value that can be either positive or negative. Therefore, it can be suspected that the J_1 values obtained from these fits are actually artifacts, due to the neglect of further neighbor interactions.

(iii) In models 4 and 5, where all the four J parameters were included, J_1 and J_3 (the nn and nnn interactions, respectively) have the same sign and a similar magnitude and are much smaller in absolute value than J_2. Each terminal copper atom would be magnetically frustrated for its spin is under the opposing influence of the antiparallel spins of Cu(2) and Cu(2)′. Spin frustration for the end copper atoms determined by J_1, J_2, and J_3 clearly suggests that Δ be fundamentally determined by J_4.

(iv) Model 6 superimposes the nn and the independent dimers models. The calculation indicates a small nn contribution, and as before, J_4 is virtually the only determinant of Δ.

We are thus again led to conclude, by elimination, that the singlet ground state of the tetramer is mainly determined by an individual antiferromagnetic coupling between the end copper atoms.

It is worthy of note that an interaction strength of 3.50 cm^{-1} (or, from the above mentioned dimer model, 3.74 cm^{-1}) is far beyond the limiting value of 8×10^{-3} cm^{-1} deduced for $R = 11.81$ Å (the observed Cu(1)–Cu(1)′ separation) from eq 3, the limit

$$-2J = 1.35 \times 10^7 \exp(-1.80R) \qquad (3)$$

function for long-range superexchange proposed by Coffman and Buettner[22] in 1979 (a $H = -2JS_A \cdot S_B$ Hamiltonian is assumed; J is given in cm^{-1} and R in Å). Actually, the present interaction represents one of the two strongest deviations from eq 3 so far observed, the other being that in the $[Cu_2(tren)_2(BZD)](NO_3)_4$ dimer.[42]

Such an efficient coupling across the tetramer invites speculation about the underlying orbital mechanism.

Orbital Considerations. Ab initio theoretical studies[43] on $Cu_2(CH_3COO)_4 \cdot 2H_2O$, on account of the striking similarity between this dimer and the "central" dimer of the tetramer, allow one to conclude that the only copper orbitals involved in the strong Cu(2)···Cu(2)′ coupling are the $x^2 - y^2$ orbitals. The almost ideal C_{4v} site symmetry at Cu(2) and Cu(2)′ ($x^2 - y^2$ transforms as B_1 and z^2 as A_1 in C_{4v}) precludes any significant delocalization of spin density from these atoms to the bridging apical ligands, O(5) and O(5)′. This implies weak superexchange between the outer pairs of copper atoms, as observed, and, likewise, a negligible role of the $x^2 - y^2$-like magnetic orbitals of Cu(2) and Cu(2)′ in determining the Cu(1)···Cu(1)′ coupling. Thus, the end-end interaction most likely involves filled levels of the O(5)–Cu(2)–$(CH_3COO)_4$–Cu(2)′–O(5)′ manifold.

Before describing a tentative model, we note the strong radical–radical coupling in compounds where nitroxyl radicals are coordinated through the axial positions of the diamagnetic dirhodium(II) tetracarboxylates.[15,16]

In the tetramer, the (4 + 1) ligand environment around Cu(1) (and Cu(1)′) has pseudo-C_{2v} symmetry and the magnetic orbital of this atom is expected to be a mixture of $x^2 - y^2$ (A_1) and z^2 (A_1), with a nonzero spin density on the farthest ligand, O(5).

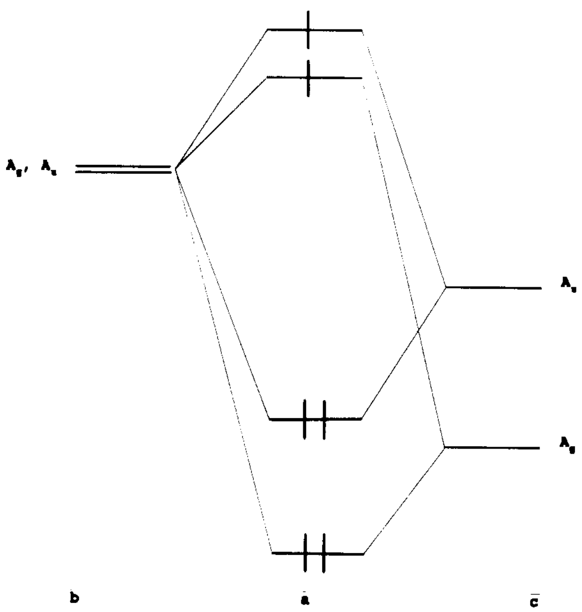

Figure 5. Qualitative interaction diagram showing the splitting (a) of the A_g and A_u combinations (b) of the singly occupied orbitals of Cu(1) and Cu(1)′ as a consequence of their interaction with the doubly filled bonding and antibonding MO's (c) formed by the z^2-like orbitals of Cu(2) and Cu(2)′.

The symmetry of the tetramer in its whole is C_i. The two linear combinations of the above orbitals transform as A_g and A_u in C_i, and because of the absence of any direct overlap at a M···M distance of ca. 12 Å, they will have the same energy.

A splitting in energy between these two MO's (and hence an antiferromagnetic Cu(1)···Cu(1)′ coupling)[44] can arise from their interaction with filled MO's of the central fragment. At first sign, complex patterns arise since in C_i symmetry all the MO's transform as A_g or A_u. However, the "central dimer" has strict D_{4h} geometry and each Cu(2)···Cu(2)′ level has a distinct symmetry in D_{4h}.[45,46] This helps us to decompose the interaction between the Cu(1)···Cu(1)′ and Cu(2)···Cu(2)′ levels into components. It may easily be seen that the most effective interaction involves the antisymmetric (A_{2u} in D_{4h}) and symmetric (A_{1g}) combinations of the z^2-like orbitals (delocalized on the apical ligands) of Cu(2) and Cu(2)′. These are the highest filled MO's[45,46] of the central fragment and the most favorably oriented to give overlap with the corresponding combinations of the magnetic orbitals of Cu(1) and Cu(1)′. A qualitative interaction diagram is given in Figure 5.

In conclusion, the tetramer studied here provides an interesting example of a linear system in which significant coupling of fourth neighboring spins can be observed. The exchange mechanism in the cluster is explicable in terms of orbital symmetry arguments that may assist in the design of other systems.

In a subsequent paper we will report on a similarly explicable direct observation of antiferromagnetic coupling between next-nearest neighboring Mn(II) ions in a linear bimetallic chain of Mn(II) and Cu(II).[47]

Acknowledgment. The financial support of the CNR, of the Progetto Finalizzato "Materiali Speciali per Tecnologie Avanzate", and of MURST is gratefully acknowledged.

Supplementary Material Available: Tables giving bond lengths, bond angles, anisotropic and isotropic thermal parameters, and hydrogen atom locations (4 pages). Ordering information is given on any current masthead page.

---

(42) Felthouse, T. R.; Hendrickson, D. N. *Inorg. Chem.* **1978**, *17*, 2636.

(43) de Loth, P.; Cassoux, P.; Daudey, J. P.; Malrieu, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 4007.

(44) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884.

(45) Forster, L. S.; Ballhausen, C. J. *Acta Chem. Scand.* **1962**, *16*, 1385.

(46) Jotham, R. W.; Kettle, S. F. A. *J. Chem. Soc. A* **1969**, 2816.

(47) Chiari, B.; Cinti, A.; Piovesana, O.; Zanazzi, P. F. Manuscript in preparation.