Contribution from the Dipartimento di Chimica and Dipartimento di Scienze della Terra,
Sezione Cristallografia, Università di Perugia, 06100 Perugia, Italy

Exchange Interaction in Multinuclear Transition-Metal Complexes. 8.[1] Structural and Magnetic Studies on $Cu_2L_2(CH_3COO)_2{\cdot}2H_2O$ (LH = *N*-Methyl-*N'*-(5-methoxysalicylidene)-1,3-propanediamine), a Novel "Structural" Ladderlike Compound with "Magnetic" Alternating-Chain Behavior

B. Chiari, J. H. Helms,[†] O. Piovesana,*[‡] T. Tarantelli, and P. F. Zanazzi

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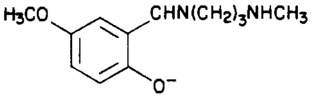
The synthesis, crystal structure, and magnetic properties are reported for the novel compound $Cu_2L_2(CH_3COO)_2{\cdot}2H_2O$, where L^- is the anion of the tridentate Schiff base *N*-methyl-*N'*-(5-methoxysalicylidene)-1,3-propanediamine. The complex, Cu_2-

L^- =



$C_{28}H_{44}O_{10}N_4$, crystallizes in the monoclinic space group *C*2/*c*. Cell dimensions are as follows: a = 17.755 (3), b = 9.208 (3), c = 20.393 (3) Å; β = 105.26 (2)°; Z = 4. The structure was solved by Patterson methods and refined to an R value of 0.051, for 93 parameters and 790 observations. The binuclear molecule exhibits a centrosymmetric parallel-planar structure. Each copper atom shows distorted (4 + 1) square pyramidal coordination. The four short bonds are to the two nitrogens and phenolic oxygen of the L^- ligand and one oxygen atom of an acetato anion. The long, apical bond is to the basal acetate oxygen atom of the other copper atom. In the strictly planar Cu_2O_2 bridging unit the angle at oxygen is 98.1 (3)° and the long Cu–O distance is 2.498 (8) Å. The binuclear molecules are packed along the [110] direction and, as a result of hydrogen-bonding interactions with the water molecules, are connected into infinite ladderlike chains parallel to [110]. Separations between the copper atoms of adjacent binuclear molecules along the chains are in the range 9.097 (2)–11.839 (2) Å. The magnetic susceptibility of the compound has been examined between 2 and 300 K. There is a maximum between 3 and 4 K that indicates the presence of an antiferromagnetic interaction. The exchange interaction in the ladderlike structure of the compound can be reasonably interpreted in terms of an alternating-chain Heisenberg model with J values of -2.26 and -1.54 cm^{-1}. In order to test the acceptability of these results, new magnetic data have been collected for $Cu_2A_2(CH_3COO)_2$ (A^- is the anion of *N*-methyl-*N'*-salicylidene-1,3-propanediamine), whose structure (previously reported by other workers) consists of magnetically dilute dimers with a molecular structure quite similar to that of the binuclear units in the present compound. The magnetic susceptibility data for the A^- derivative, measured down to 2 K, are described precisely by a dimer exchange model with $J = -1.33$ cm^{-1}. The effectiveness of the pathway involving the hydrogen-bonding contacts in propagating magnetic exchange is briefly discussed.

Introduction

The propagation of magnetic information over large distances is a topic that has attracted considerable interest in recent years.[2a,3–7] Presently existing structural data and superexchange data for long-range magnetic exchange have raised several important questions that involve, for example, the existence of a distance-dependent limit to superexchange,[4] or the requirements of the exchange pathway to maximize the exchange interaction at any distance.[2a,3–7] Knowledge in this matter is also relevant to an understanding of the pathways of electron transfer in biological electron transport chains,[8] electron transfer in redox reaction precursors,[9] etc.

The experimental[2b,11] and theoretical[2c,10,11] study of one-dimensional magnetic systems is another research area of intense current interest; however, transition metal ion alternating- or ladderlike-chain compounds are very rare.[2b]

In this article we describe a novel compound, $Cu_2L_2(CH_3COO)_2{\cdot}2H_2O$ (LH = *N*-methyl-*N'*-(5-methoxysalicylidene)-1,3-propanediamine), whose structural and magnetic properties are of interest to both the problems of long-range magnetic exchange and 1-D magnetic systems.

The compound exhibits a rather unique structure built of well-separated ladderlike chains in which parallel-planar dimeric units are connected by weakly hydrogen bonded water molecules. Although the intermolecular Cu···Cu separations along the individual chains are very long, in the range 9.097 (2)–11.839 (2) Å, a significant intermolecular antiferromagnetic coupling, of the order of 2 cm^{-1}, is revealed by the magnetic data. The magnitude of this interaction exceeds the distance-dependent limit to superexchange recently proposed by Coffman and Buettner.[4] In order to substantiate our interpretation of the magnetic data for the title compound, a low-temperature magnetic study has also been carried out on the already known $Cu_2A_2(CH_3COO)_2$ compound (A^- = *N*-methyl-*N'*-salicylidene-1,3-propanediaminato), whose structure consists[12] of magnetically dilute dimers quite similar to those observed in the structure of the L^- derivative.

Experimental Section

Preparation of the Complexes. $Cu_2L_2(CH_3COO)_2{\cdot}2H_2O$. A 15-mL portion of a 0.33 M solution of 2-hydroxy-5-methoxybenzaldehyde in ethanol was added, under nitrogen, to a 10-mL portion of a 0.50 M solution of *N*-methyl-1,3-propanediamine. The resulting yellow solution

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

[†] The University of North Carolina at Chapel Hill.

[‡] Visiting Professor at The University of North Carolina at Chapel Hill, Summer 1984.

(1) Part 7: Chiari, B.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F. *Inorg. Chem.* **1985**, *24*, 4615.
(2) For reviews see: (a) Hendrickson, D. N. In "Magneto-Structural Correlations in Exchange Coupled Systems"; Willett, R. D., Gatteschi, D., Kahn, O., Eds.; D. Reidel: Dordrecht, The Netherlands, 1985; p 523. (b) Hatfield, W. E. *Ibid.*, p 555. (c) Bonner, J. C. *Ibid.*, p 157.
(3) O'Connor, C. J. *Prog. Inorg. Chem.* **1982**, *29*, 203.
(4) Coffman, R. E.; Buettner, G. R. *J. Phys. Chem.* **1979**, *83*, 2387.
(5) Francesconi, L. C.; Corbin, D. R.; Clauss, A. W.; Hendrickson, D. N.; Stucky, G. D. *Inorg. Chem.* **1981**, *20*, 2059 and references therein.
(6) Chiari, B.; Hatfield, W. E.; Piovesana, O.; Tarantelli, T.; ter Haar, L. W.; Zanazzi, P. F. *Inorg. Chem.* **1983**, *22*, 1468.
(7) Chiari, B.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F. *Inorg. Chem.* **1984**, *23*, 2542.
(8) Moore, G. R.; Williams, R. J. P. *Coord. Chem. Rev.* **1976**, *18*, 125.
(9) Reynolds, W. L.; Lumry, R. M. "Mechanism of Electron Transfer"; Ronald Press: New York, 1966. Taube, H. *Adv. Chem. Ser.* **1977**, *No. 162*, 127. See various articles in: Chance, B., De Vault, O. C., Frauenfelder, H., Marcus, R. A., Schrieffer, J. R., Sutin, N., Eds. "Tunneling in Biological Systems"; Academic Press: New York, 1979.
(10) Bonner, J. C. *J. Magn. Magn. Mater.* **1980**, *15–18*, 1003.
(11) Nordio, P. L.; Soos, Z. G.; McConnell, H. M. *Annu. Rev. Phys. Chem.* **1966**, *17*, 237.
(12) Hämäläinen, R.; Ahlgren, M.; Turpeinen, U. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 1577.

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Table I. Fractional Atomic Coordinates in $Cu_2L_2(CH_3COO)_2{\cdot}2H_2O$

atom	*x/a*	*y/b*	*z/c*
Cu	0.0057 (1)	0.1759 (2)	0.0248 (1)
O(1)	0.0084 (5)	0.2250 (8)	−0.0648 (4)
O(2)	0.0846 (5)	0.0265 (9)	0.0258 (4)
O(3)	0.1742 (5)	0.2008 (11)	0.0557 (5)
O(4)	−0.1978 (5)	0.5580 (10)	−0.2555 (4)
O(5)	0.1574 (6)	0.2348 (12)	−0.1092 (6)
N(1)	−0.0602 (6)	0.3428 (10)	0.0325 (4)
N(2)	−0.0037 (6)	0.0852 (10)	0.1126 (5)
C(1)	−0.0454 (4)	0.3087 (8)	−0.1081 (3)
C(2)	−0.0458 (4)	0.3018 (8)	−0.1766 (3)
C(3)	−0.0971 (4)	0.3886 (8)	−0.2241 (3)
C(4)	−0.1481 (4)	0.4823 (8)	−0.2033 (3)
C(5)	−0.1477 (4)	0.4892 (8)	−0.1349 (3)
C(6)	−0.0964 (4)	0.4024 (8)	−0.0873 (3)
C(7)	−0.0954 (6)	0.4230 (12)	−0.0166 (6)
C(8)	−0.0599 (7)	0.3856 (13)	0.1035 (6)
C(9)	−0.0943 (8)	0.2727 (14)	0.1415 (7)
C(10)	−0.0804 (7)	0.1177 (14)	0.1252 (7)
C(11)	0.0612 (8)	0.1076 (16)	0.1743 (7)
C(12)	0.1553 (7)	0.0719 (14)	0.0450 (7)
C(13)	0.2178 (9)	−0.0435 (18)	0.0542 (8)
C(14)	−0.2547 (8)	0.6491 (16)	−0.2382 (7)

was heated at 70 °C for 1 h, under nitrogen. To the clear, hot solution containing the LH ligand was added a 5-mmol quantity of $Cu(CH_3COO)_2{\cdot}H_2O$. The addition was made over a period of 30 min, under nitrogen and with constant stirring. A green solution was obtained. After the solution was allowed to evaporate for 4 days under a slight nitrogen flow, at room temperature, a green crystalline precipitate of the complex was collected by filtration, washed with ethanol, and dried under vacuum: yield 0.6 g (33%); mp 159–162 °C. Anal. Calcd for $C_{28}H_{44}O_{10}N_4Cu_2$: C, 46.47; H, 6.13; N, 7.74; Cu, 17.60. Found: C, 46.79; H, 6.15; N, 7.68; Cu, 17.91.

$Cu_2A_2(CH_3COO)_2$. This compound was prepared by the procedure described in ref 12.

Magnetic Measurements. The magnetic susceptibilities were measured on a Faraday balance between 77 K and room temperature. Measurements between 2 and 80 K were obtained with use of a Princeton Applied Research Model 155 vibrating-sample magnetometer operating at 10 kG, as described elsewhere.[13] Susceptibilities were corrected for the diamagnetism of the ligand system (-168.63×10^{-6} cgsu/Cu atom for $Cu_2L_2(CH_3COO)_2{\cdot}2H_2O$ and -139.16×10^{-6} cgsu/Cu atom for $Cu_2A_2(CH_3COO)_2$) and for the temperature-independent paramagnetism, $N\alpha$, of copper(II) (estimated to be 60×10^{-6} cgsu/Cu atom).

ESR Spectra. These were measured with a Varian E-109 spectrometer operated at X-band frequencies, and with diphenylpicrylhydrazyl (DPPH) as internal reference.

Infrared Spectra. Infrared spectra were recorded with a Perkin-Elmer 521 spectrophotometer. Samples were studied as KBr pellets.

X-ray Data and Structure Solution. A green, short, prismatic crystal with dimensions 0.25 × 0.20 × 0.15 mm was mounted on a computer-controlled Philips PW1100 single-crystal diffractometer, equipped with graphite-monochromatized Mo Kα radiation (λ = 0.710 69 Å). The crystals are monoclinic. The cell dimensions, determined by a least-squares calculation based on the setting angles of 25 reflections with 2ϑ angles ranging between 17 and 25°, are as follows: a = 17.755 (3), b = 9.208 (3), c = 20.393 (3) Å; β = 105.26 (2)°; V = 3216.45 Å^3. The space group is $C2/c$ (from systematic extinctions and intensity statistics). The calculated density for four molecules of $Cu_2(C_{14}H_{20}O_4N_2)_2{\cdot}2H_2O$ (mol wt 723.8) in the unit cell is 1.480 g cm^{-3}; the absorption coefficient for Mo Kα is μ = 13.56 cm^{-1}. The intensities were collected, at room temperature, up to 2ϑ = 40°; the ω–2ϑ scan technique was employed, the scan range being 1.6° and the speed 0.05° s^{-1}. A total of 3045 hkl and $h\bar{k}l$ reflections were measured, and these merged to give 1574 independent reflections, of which 784 having $I < 3\sigma(I)$ were considered as "unobserved" and excluded from the refinement. The agreement factor between equivalent reflections was 0.02. Three standard reflections that were measured periodically showed no apparent variation in intensity during data collection. The data were corrected for Lorentz and polarization factors. An empirical correction was applied during the refinement, according to the method of Walker and Stuart.[14] Correction factors were in the range 1.20–0.98

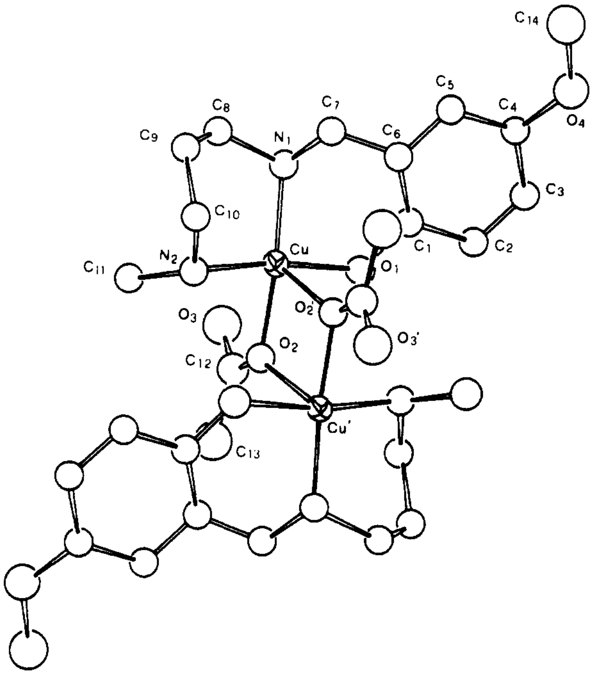

Figure 1. View of the binuclear unit in the structure of $Cu_2L_2(CH_3COO)_2{\cdot}2H_2O$. Hydrogen atoms have been omitted for clarity.

Table II. Bond Lengths (Å) and Angles (deg) in $Cu_2L_2(CH_3COO)_2{\cdot}2H_2O^a$

Cu–O(1)	1.895 (8)	N(1)–C(8)	1.499 (14)
Cu–O(2)	1.960 (8)	N(2)–C(10)	1.481 (12)
Cu–N(1)	1.963 (9)	N(2)–C(11)	1.480 (16)
Cu–N(2)	2.022 (10)	C(6)–C(7)	1.450 (13)
Cu–O(2)′	2.498 (8)	C(8)–C(9)	1.518 (17)
O(1)–C(1)	1.357 (10)	C(9)–C(10)	1.501 (18)
O(2)–C(12)	1.283 (12)	C(12)–C(13)	1.512 (18)
O(3)–C(12)	1.237 (16)	O(5)···O(1)	3.015 (10)
O(4)–C(4)	1.380 (10)	O(5)···O(3)″	2.961 (11)
O(4)–C(14)	1.427 (15)		
N(1)–C(7)	1.269 (14)	Cu···Cu′	3.384 (3)
O(1)–Cu–O(2)	88.7 (3)	Cu–N(2)–C(10)	111.4 (6)
O(1)–Cu–N(1)	93.3 (3)	Cu–N(2)–C(11)	117.9 (6)
O(1)–Cu–N(2)	168.9 (3)	C(10)–N(2)–C(11)	111.7 (7)
O(1)–Cu–O(2)′	87.5 (3)	N(2)–C(10)–C(9)	116.3 (8)
O(2)–Cu–N(1)	171.3 (3)	O(1)–C(1)–C(2)	116.3 (5)
O(2)–Cu–N(2)	85.8 (3)	O(1)–C(1)–C(6)	123.7 (5)
O(2)–Cu–O(2)′	81.9 (3)	O(4)–C(4)–C(3)	114.4 (5)
N(1)–Cu–N(2)	93.6 (3)	O(4)–C(4)–C(5)	125.6 (5)
N(1)–Cu–O(2)′	106.6 (3)	C(1)–C(6)–C(7)	123.0 (5)
N(2)–Cu–O(2)′	82.2 (3)	N(1)–C(7)–C(6)	125.7 (7)
Cu–O(1)–C(1)	124.8 (5)	N(1)–C(8)–C(9)	114.4 (8)
Cu–O(2)–Cu′	98.1 (3)	C(10)–C(9)–C(8)	115.3 (8)
Cu–O(2)–C(12)	114.4 (6)	O(2)–C(12)–O(3)	124.4 (8)
C(14)–O(4)–C(4)	117.2 (7)	O(2)–C(12)–C(13)	115.9 (8)
Cu–N(1)–C(7)	125.0 (6)	O(3)–C(12)–C(13)	119.8 (8)
Cu–N(1)–C(8)	115.6 (5)	O(1)···O(5)···O(3)″	140.9 (3)
C(7)–N(1)–C(8)	119.0 (7)		

[a] Symmetry codes: (′) $-x, -y, -z$. (″) $^1/_2 - x, ^1/_2 - y, -z$.

The structure was solved by Patterson methods and refined with the SHELX-76[15] package of programs. The function minimized was $\sum w(|F_o| - |F_c|)^2$. The phenyl group was refined as a perfect hexagon (C–C = 1.395 Å). The hydrogen atoms, with the exception of those of the methyl groups, were included at the calculated positions (C–H = 1.08 Å) with overall isotropic parameter U = 0.04 Å^2. The methyl groups were refined as rigid groups starting from the staggered position. The overall isotropic thermal parameter for these H atoms was refined to 0.10 Å^2. Several cycles of refinement converged to an R value of 0.051, for 93 parameters (anisotropic thermal factors only for Cu atoms) and 790 observations.

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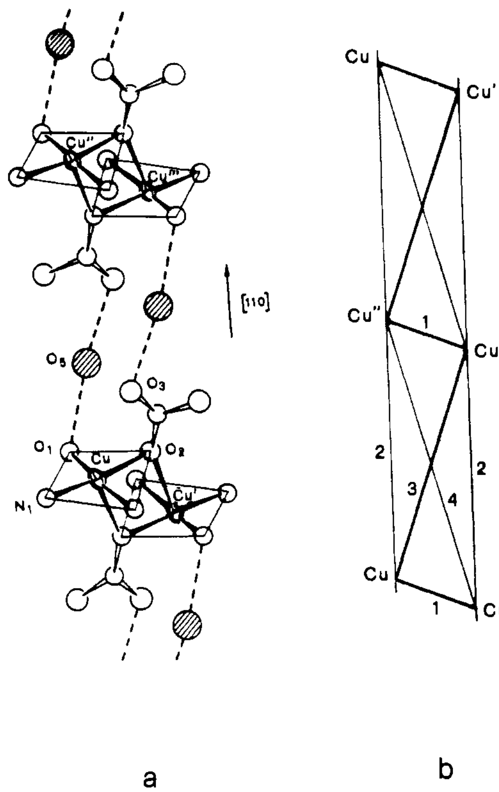
(13) Hall, J. W.; Marsh, W. E.; Weller, R. R.; Hatfield, W. E. *Inorg. Chem.* **1981**, *20*, 1033 and references therein.

(14) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 158.

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



a b

Figure 2. (a) Schematic view of a fragment of the ladderlike chain structure of $Cu_2L_2(CH_3COO)_2{\cdot}2H_2O$. Symmetry code: (′) $\bar{x}, \bar{y}, \bar{z}$; (″) $^1/_2 + x, {}^1/_2 + y, z$; (‴) $^1/_2 - x, {}^1/_2 - y, \bar{z}$. (b) Simplified scheme of the four pathways available for exchange. The thick line represents the "magnetic" alternating-chain approximation that obtains if $J_1, J_3 >> J_2, J_4$ (J subscripts refer to the relative pathways).

R_w was 0.055 ($R_w = \sum(w(|F_o| - |F_c|)^2)^{1/2}/\sum(wF_o^2)^{1/2}$, $w = (\sigma^2(F_o) + 0.0026F_o^2)^{1/2}$). The atomic scattering factors were taken from ref 15 for the O, N, C, and H atoms and from ref 16 for the Cu atom; the correction for anomalous dispersion of Cu was included.

Results and Discussion

Structural Information. Final positional parameters for $Cu_2L_2(CH_3COO)_2{\cdot}2H_2O$ are given in Table I. Figure 1 is a perspective view of the binuclear unit of the complex with the atom-numbering scheme indicated. Intramolecular bond distances and angles are listed in Table II.

The halves of the binuclear units are related by crystallographic inversion symmetry. Each copper atom shows distorted (4 + 1) square pyramidal coordination. The four short bonds are to the two nitrogens (Cu–N(1) = 1.963 (9) Å, Cu–N(2) = 2.022 (10) Å) and the phenolic oxygen (Cu–O(1) = 1.895 (8) Å) of the chelating L^- ligand and one oxygen atom of an acetate anion (Cu–O(2) = 1.960 (8) Å). The N(1), N(2), O(1), O(2), and Cu atoms lie approximately on a plane, the maximum deviation from planarity being 0.14 Å. The long, apical bond is to the basal acetate oxygen atom, O(2)′, of the other copper atom (Cu–O(2)′ = 2.498 (8) Å) and is in the range reported for structures involving parallel-planar units linked by relatively long out-of-plane bonds.[6,12,17-19] The four-membered Cu_2O_2 bridging unit, which is strictly planar owing to inversion symmetry, forms a dihedral angle of 113.2° with the mean basal plane of the copper "square pyramid". The briding angle at oxygen is 98.1 (3)°. The intramolecular Cu⋯Cu separation is 3.384 (3) Å. There are very few structurally characterized precedents[6,12,19] of compounds containing the one-atom acetate bridging observed in the present case. Bond distances and angles of the L^- ligand are normal.

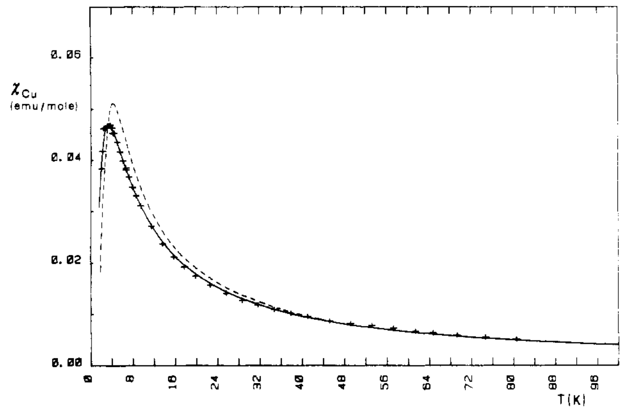


Figure 3. Magnetic susceptibility data for $Cu_2L_2(CH_3COO)_2{\cdot}2H_2O$. The solid line through the data was generated by the expression given in the text for Heisenberg exchange in an alternatingly spaced chain with an exchange coupling constant of -2.26 cm^{-1} and an alternating parameter of 0.68. The dashed line represents the base fit obtained for $\alpha = 0$ (dimeric case), $J = -2.31$ cm^{-1}.

As schematically shown in Figure 2, the binuclear molecules are packed along the [110] direction of the $C2/c$ space group. Adjacent molecules along this axis are connected, in a remote fashion, by two bridges that are related by inversion symmetry. In each bridge the oxygen atom of a water molecule, O(5), is connected to a noncoordinated acetate oxygen atom, O(3), of one dimer, and an L^- phenolic oxygen, O(1)″, of the successive dimer along [110]. The O(3)–O(5)–O(1)″ angle is 140.9 (3)°. The O(5)–O(3) and O(5)–O(1)″ distances are 2.960 (8) and 3.010 (8) Å, respectively. These values are slightly less than twice the van der Waals radius of oxygen as given by Bondi (3.02 Å)[20] but greater than the corresponding value given by Pauling (2.80 Å).[21] Our inability to locate the hydrogen atoms on the water molecule prevents us from using hydrogen–oxygen distances to infer[22] the presence (or absence) of hydrogen bonding. However, convincing evidence that the water molecules are involved in hydrogen-bonding interactions is provided by the infrared spectrum of the compound, which shows, in the O–H stretching region, an intense, broad absorption with peaks at 3420, 3510, and 3600 cm^{-1}. Frequency shift, increase in breadth, and intensity enhancement of the stretching modes of the gaseous water molecule ($\bar{\nu}_s = 3652$ cm^{-1}, $\bar{\nu}_{as} = 3756$ cm^{-1})[23] are characteristic of hydrogen bond formation.

As a result of the hydrogen-bonding interactions with the water molecules the binuclear units are connected into infinite ladderlike chains parallel to [110]. The separations between copper atoms of adjacent binuclear units along the chains are as follows: Cu⋯Cu‴ = 9.097 (2), Cu⋯Cu″ = Cu′⋯Cu‴ = 10.000 (2), Cu′⋯Cu″ = 11.839 (2) Å.

From the interchain contacts, which are longer than the sums of van der Waals radii, it appears that the individual chains in the structure are effectively isolated.

This polymeric structure in which each copper atom is connected to five other copper atoms through one intramolecular (3.384 (3) Å) and four intermolecular distances, in the range 9.097 (2)–11.839 (2) Å, is unique to our knowledge.

Magnetic Properties. The room-temperature X-band ESR spectra of polycrystalline samples of $Cu_2L_2(CH_3COO)_2{\cdot}2H_2O$ show only one broad uninterpretable signal with a pronounced hump at g = ca. 2.10 and apparent g values of 2.17 and 2.06. No additional information could be obtained upon decreasing the temperature of the sample to 77 K.

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(16) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 99.
(17) Hatfield, W. E. *Inorg. Chem.* **1972**, *11*, 216 and references therein.
(18) Brown, J. N.; Trefonas, L. M. *Inorg. Chem.* **1973**, *12*, 1730.
(19) Greenaway, A. M.; O'Connor, C. J.; Overman, J. W.; Sinn, E. *Inorg. Chem.* **1981**, *20*, 1508.
(20) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.
(21) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960.
(22) Hamilton, W. C.; Ibers, J. A. "Hydrogen Bonding in Solids"; W. A. Benjamin: New York, 1968; p 16.
(23) Herzberg, G. "Molecular Spectra and Molecular Structure"; Van Nostrand: New York, 1945; Vol. II, pp 207, 282.

Variable-temperature magnetic susceptibility data for the compound have been collected between 2 and 300 K. The data between 2 and 80 K are given in Figure 3. A maximum between 3 and 4 K clearly indicates the presence of an antiferromagnetic interaction. The μ_{eff}/Cu values range from 1.82 μ_B at 300 K to 0.80 μ_B at 2.1 K. The inverse susceptibility vs. temperature plot obtained for data above ca. 10 K is linear with a slope of 2.44 cgsu^{-1} K^{-1}, and hence there is a Curie constant, C, of 0.41 cgsu K and a calculated g value of 2.10. This g value, and the temperature-independent paramagnetism, $N\alpha$, assigned as previously described, were held constant during all the fitting calculations described below. Also, in these calculations, only the data between ca. 2 and 80 K were considered.

In light of the large intermolecular Cu$\cdots$Cu distances that are observed in the structure of the compound, an attempt was initially made to fit the susceptibility data to a dimer exchange equation corrected, in the molecular field approximation, for the presence of magnetic interactions between neighboring dimers. Since the temperature at which the maximum in susceptibility occurs indicates that the condition $|J| >> g\mu_BH$ ($g\mu_BH$ is ca. 1 cm^{-1} for H = 10 000 G) is not satisfied, the application of the usual Bleaney–Bowers[24] susceptibility expression would be inappropriate in the present case. Consequently, we have used a susceptibility expression that considers the external field,[25] namely eq 1, where

$$\chi_M \text{ (per Cu)} = \frac{Ng\mu_B \sinh(g\mu_BH/kT)}{H[\exp(-2J/kT) + 2\cosh(g\mu_BH/kT) + 1]} + N\alpha \quad (1)$$

the exchange Hamiltonian is given by eq 2 and $\hat{S}$ is the total spin

$$\hat{H}_{ex} = -2J(\hat{S}_A\cdot\hat{S}_B) + g\mu_BH\hat{S} \quad (2)$$

operator (i.e. $\hat{S} = \hat{S}_A + \hat{S}_B$). The molecular field treatment[26] of eq 1 gives eq 3, where z is the number of nearest-neighboring

$$\chi_M' \text{ (per Cu)} = \chi_M/[1 - (4zJ'/Ng^2\mu_B^2)\chi_M] \quad (3)$$

dimers and J' is the lattice interaction parameter. Equation 3 was used to fit the experimental data for $Cu_2L_2(CH_3COO)_2\cdot 2H_2O$. The function that was minimized in curve fitting was $F = \sum_i(\chi_i^{obsd})^{-1}(\chi_i^{obsd} - \chi_i^{calcd})^2$. The best fit to the data yielded $J = -1.92$ cm^{-1} and $zJ' = -1.46$ cm^{-1}. The agreement factor was $F = 3.12 \times 10^{-4}$, for 40 observations. This fit, although precise, is not acceptable since the correction term is nearly equal to the primary interaction parameter.

Clearly, a theoretical approach must be used that employs the intermolecular interactions explicitly in the spin Hamiltonian.

As noted above, a prominent structural feature of the complex is the presence of ladderlike chains parallel to [110], with essentially no interactions between chains. Exact solutions of model Hamiltonians appropriate for the analysis of magnetic data pertaining to compounds with ladderlike structures are not available.[2b,27] Attempts[2b,27,28] at using the cluster approach to model the magnetic properties of $(N_2H_5)CuCl_3$, which has a ladderlike structure with two exchange interactions, have shown that model calculations with either 8 or 10 spins do not converge to the thermodynamic limit and that, therefore, calculations with larger numbers of spins must be carried out to resolve this problem. A rigorous description of the magnetic coupling in the title compound would be even more difficult to attain since the problem involves four superexchange interactions (J values), namely, with reference to Figure 2: Cu$\cdots$Cu′ = Cu″$\cdots$Cu‴ $\neq$ Cu$\cdots$Cu″ = Cu′$\cdots$Cu‴ $\neq$ Cu′$\cdots$Cu″ $\neq$ Cu$\cdots$Cu‴. In this context, we have examined the possibility, suggested by physical intuition, of using a simpler, tractable model.

Inspection of Figure 2 shows that if the exchange pathways connecting Cu to Cu″ (and Cu′ to Cu‴) and Cu′ to Cu″ lead to exchange interactions that are considerably weaker than those propagated by the intramolecular (the shortest one) Cu$\cdots$Cu′ (and Cu″$\cdots$Cu‴) and the intermolecular Cu$\cdots$Cu‴ superexchange pathways, then the magnetic behavior of the "structural" ladder would approximate that of a "magnetic" alternating chain. Such an approach can be justified as follows. The copper atoms have a (4 + 1) square-pyramidal geometry. In this geometry the unpaired electron of the copper ion lies in a mainly $d_{x^2-y^2}$ orbital, and there is very small unpaired electron density on the apical, out-of-plane ligand. Since the Cu$\cdots$Cu‴ superexchange pathway involves in-plane unpaired electron density while the other intermolecular superexchange pathways involve out-of-plane unpaired electron density (and longer distances), the former pathway is likely to be much more effective than the latter pathways in propagating magnetic exchange.

With this in mind, an alternating-chain model was attempted in data fitting. An appropriate Hamiltonian for this approach, in the Heisenberg model, may be written as

$$\hat{H} = -2J\sum_{i=1}^{n/2}(\hat{S}_{2i}\cdot\hat{S}_{2i-1} + \alpha\hat{S}_{2i}\cdot\hat{S}_{2i+1}) \quad (4)$$

where J is the exchange integral between a spin and one of its nearest neighbors and αJ is the exchange interaction of the same spin with the other nearest neighbor in the chain. The case of immediate interest is for $J < 0$ and $0 \leq \alpha \leq 1$. This alternating Heisenberg model cannot be solved exactly at present.[29] However, numerical data for the generation of the magnetic susceptibility have recently been obtained by Hatfield et al.[27,30] The equation is

$$\chi_M \text{ (per Cu)} = (Ng^2\mu_B^2/kT)(A + Bx + Cx^2)(1 + Dx + Ex^2 + Fx^3)^{-1} \quad (5)$$

where $x = -J/kT$ and constants A–F are power series in terms of the alternation parameter α. The best fit of our data to eq 5 yielded $J = -2.26$ cm^{-1} and $\alpha = 0.68$, with F being 3.47×10^{-4}. The theoretical susceptibility curve is drawn in Figure 3 and represents a precise fit to the experimental data.

The problem of testing the acceptability of these results must now be dealt with. The magnetic and structural results that we have recently obtained[6] for $Cu_2D(CH_3COO)_2\cdot 2CH_3OH$ (D^{2-} is the anion of *N*,*N*′-bis(2-((*o*-hydroxybenzhydrylidene)amino)ethyl)-1,2-ethanediamine) have a bearing on this problem. This compound exhibits on alternating-chain structure containing a strictly planar one-atom acetato-bridged Cu_2O_2 moiety (Cu–O–Cu = 98.3 (5)°, Cu–O(basal) = 1.952 (6) Å, Cu–O(out-of-plane) = 2.495 (6) Å) that is identical, within experimental error, with the corresponding moiety observed in the present structure. Also, the coordination geometry of copper is virtually the same in the two compounds. Interpretation of the magnetic susceptibility data for the D^{2-} derivative by alternating-chain theory yielded values for the exchange coupling constants of −7.88 and −1.50 cm^{-1}. The J value of −1.50 cm^{-1} was assigned to the acetato-bridged unit.[6] There is an outstanding agreement between this J value and the αJ value of −1.54 cm^{-1} deduced for the title compound. Since the structures of the two compounds under discussion exhibit one identical ligand bridge, Cu_2O_2, but are otherwise very different, it is only natural to believe that the almost identical J values of −1.50 and −1.54 cm^{-1} obtained for the two compounds arise from the Cu_2O_2 moiety.

Additional evidence of what may be expected for the exchange coupling constant that characterizes exchange through the Cu_2O_2 bridging unit in $Cu_2L_2(CH_3COO)_2\cdot 2H_2O$ can be obtained through the determination of the J value for a system built of magnetically dilute dimers with a molecular structure similar to that found for the binuclear units in the present structure. Recent X-ray studies[12] have shown that $Cu_2A_2(CH_3COO)_2$[31] (A^- = anion of *N*-

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[24] Bleaney, B.; Bowers, K. *Proc. R. Soc. London, Ser. A* **1952**, *214*, 451.

[25] Myers, B. E.; Berger, L.; Friedberg, S. A. *J. Appl. Phys.* **1969**, *40*, 1149.

[26] Smart, J. S. "Effective Field Theories of Magnetism"; W. B. Saunders: Philadelphia, PA, 1966.

[27] Hatfield, W. E. *J. Appl. Phys.* **1981**, *52*, 1985.

[28] Weller, R. R. Ph.D. Dissertation, The University of North Carolina, Chapel Hill, NC, 1980.

[29] Bonner, J. C.; Blote, H. W. J. *Phys. Rev. B: Condens. Matter* **1982**, *25*, 6959.

[30] Hall, J. W.; Marsh, W. E.; Weller, R. R.; Hatfield, W. E. *Inorg. Chem.* **1981**, *20*, 1033.

[31] Tokii, T.; Emori, S.; Muto, Y. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2114.

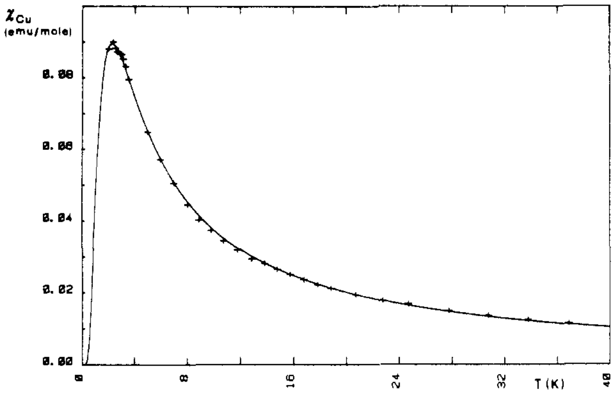

Figure 4. Magnetic susceptibility data for $Cu_2A_2(CH_3COO)_2$. The solid line through the data was generated by the dimer model of eq 3, with $J = -1.33$ cm^{-1} and $zJ' = -0.02$ cm^{-1}.

methyl-*N*′-salicylidene-1,3-propanediamine) has such a structure, with a strictly planar one-atom acetato-bridged Cu_2O_2 moiety characterized by a bridging angle at oxygen of 96.9 (2)° and a bridging, out-of-plane Cu–O distance of 2.512 (5) Å. We have therefore determined the J value for this compound.

Magnetic susceptibility data, between ca. 2 and 40 K, for the A^- derivative are reported in Figure 4. The maximum at ca. 2 K is indicative of antiferromagnetic exchange interaction. The X-band ESR spectra of powdered samples of the compound are axial with $g_{\parallel} = 2.24$ and $g_{\perp} = 2.06$ ($g_{av} = 2.12$). Interpretation of the magnetic susceptibility data by eq 3 yielded $J = -1.33$ cm^{-1}, $zJ' = -0.02$ cm^{-1}, and $F = 2.20 \times 10^{-4}$, for 30 observations, with use of the ESR g value of 2.12 and $N\alpha = 60 \times 10^{-6}$. The best fit is indicated by the solid line in Figure 4 and represents a precise description of the experimental data.

In light of the structural similarity between the Cu_2O_2 bridging units in $Cu_2A_2(CH_3COO)_2$ and $Cu_2L_2(CH_3COO)_2{\cdot}2H_2O$, the J value obtained for the A^- derivative, -1.33 cm^{-1}, represents convincing evidence that the J value that can be assigned to the Cu_2O_2 moiety of $Cu_2L_2(CH_3COO)_2{\cdot}2H_2O$ by alternating-chain theory (-1.54 or -2.26 cm^{-1}; most likely -1.54 cm^{-1}, as previously discussed) is of reliable sign and magnitude. It should be noted that both negative and positive J values have been reported for oxygen-bridged parallel-planar dimers and that the magnitudes of the singlet–triplet splitting for these compounds span a relatively wide range of energy.[17,19,32]

A final point for discussion is the effectiveness of the pathway involving the hydrogen-bonding contacts in propagating magnetic exchange.

It is useful to consider the limit function that Coffman and Buettner[4] have proposed, on the basis of existing structural data and superexchange data, for long-range antiferromagnetic exchange (organic and inorganic biradicals were, however, not considered[2a,5]). This function, assuming an $\hat{H} = -2J\hat{S}_A{\cdot}\hat{S}_B$ Hamiltonian, has the form

$$-2J = 1.35 \times 10^7 \exp(-1.80R) \qquad (6)$$

and gives a limiting magnitude for the J parameter for a given internuclear distance R. The calculated limiting J value for the Cu···Cu‴ separation of 9.097 (2) Å in the present structure is -0.52 cm^{-1}, which is smaller, in absolute value, than both of the J values deduced by our alternating-chain approach.

Thus, although much stronger magnetic interactions propagated by exchange pathways involving hydrogen-bonding contacts have been noted in a number of dimeric complexes[33-38] and hydrated metal salts,[39] the extent of interaction propagated, in the present system, through the weakly hydrogen bonded, uncomplexed water molecules, appears to be rather unique upon consideration of the large distance that is involved. Since the original proposal of Coffman and Buettner in 1979 only a few binuclear metal complexes and organic biradicals[2a,5] have been reported for which the magnitude of the exchange interaction exceeds the limit threshold represented by eq 6.

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Registry No. $Cu_2L_2(CH_3COO)_2{\cdot}2H_2O$, 100020-05-1; $Cu_2A_2(CH_3COO)_2$, 82328-98-1.

Supplementary Material Available: Listings of thermal parameters, hydrogen atom coordinates, and observed and calculated structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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(32) Dixon Estes, E.; Estes, W. E.; Scaringe, R. P.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1975**, *14*, 2564.

(33) Bertrand, J. A.; Helm, F. T. *J. Am. Chem. Soc.* **1973**, *95*, 8184.

(34) Bertrand, J. A.; Black, T. D.; Gary Eller, P.; Helm, F. T.; Mahmood, R. *Inorg. Chem.* **1976**, *15*, 2965.

(35) Duggan, D. M.; Jungst, R. G.; Mann, K. R.; Stucky, G. D.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1974**, *96*, 3443.

(36) Duggan, D. M.; Hendrickson, D. N. *Inorg. Chem.* **1974**, *13*, 2920.

(37) Hendrickson, D. N.; Duggan, D. M. "Extended Interactions Between Metal Ions in Transition Metal Complexes"; Interrante, L. W., Ed.; American Chemical Society: Washington, DC, 1974; ACS Symp. Ser. No. 5, p 76.

(38) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 3988.

(39) Culvahouse, J. W.; Francis, C. L. *J. Chem. Phys.* **1977**, *66*, 1079.