$$-\left(\ln \frac{k_{ex}}{K_0\nu_n\Gamma_\lambda} + \frac{\Delta G^*_{out}}{RT}\right) \text{ vs. } \frac{\Delta G^*_{in}}{RT}$$

is plotted (Figure 7), a nice linear dependence is observed. This plot encompasses self-exchange rates of cobalt complexes, which span 11 (!) orders of mangitude.[10]

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Supplementary Material Available: Listings of anisotropic and isotropic thermal parameters, calculated positional parameters of hydrogen atoms, and intraligand bond distances of $[Co(tacn)_2]I_2{\cdot}2H_2O$ and of $[Co(ttcn)_2](ClO_4)_3$, respectively (5 pages). Ordering information is given on any current masthead page.

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Exchange Interaction in Multinuclear Transition-Metal Complexes. 9.[1] Magnetostructural Correlations in One-Atom Acetato-Bridged Copper(II) Dimers

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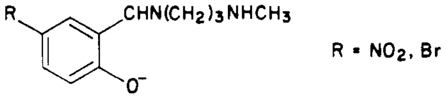
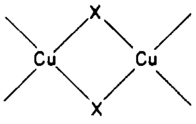
The syntheses, crystal and molecular structures, and magnetic properties are reported for the new complexes $Cu_2(5\text{-}NO_2\text{-}L)_2(CH_3COO)_2$ and $Cu_2(5\text{-}Br\text{-}L)_2(CH_3COO)_2$, where $(5\text{-}NO_2\text{-}L)^-$ and $(5\text{-}Br\text{-}L)^-$ are the anions of *N*-methyl-*N'*-(5-nitrosalicylidene)-1,3-propanediamine and *N*-methyl-*N'*-(5-bromosalicylidene)-1,3-propanediamine, respectively:



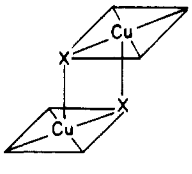
The 5-nitro complex, $Cu_2C_{26}H_{34}N_6O_{10}$, crystallizes in the triclinic space group $P\bar{1}$. Cell dimensions: $a = 9.305$ (3), $b = 9.209$ (3), $c = 8.993$ (3) Å; $\alpha = 94.94$ (2), $\beta = 94.92$ (2), $\gamma = 92.78$ (2)°. $Z = 1$. The structure was solved by Patterson and Fourier methods and refined to an R (unweighted) value of 0.026 (R(weighted) = 0.030) for 208 parameters and 2086 observed reflections. The 5-bromo complex, $Cu_2C_{26}H_{34}N_4O_6Br_2$, crystallizes in the monoclinic space group $P2_1/a$. Lattice parameters: $a = 14.519$ (2), $b = 10.859$ (2), $c = 9.547$ (3) Å; $\beta = 93.35$ (2)°. $Z = 2$. The structure was solved by Patterson and Fourier methods. The final R index was 0.045 for 1674 observations and 113 parameters ($R_w = 0.053$). Both complexes consist of centrosymmetric dimeric units that are well separated from one another. The dimeric units are very similar. Each copper atom shows distorted (4 + 1 + 1) square-bipyramidal coordination. The four short bonds, which lie approximately in a plane, are to the two cis nitrogens and the phenolic oxygen of a tridentate Schiff base ligand, and one oxygen atom of an acetate anion. Each complete fragment so formed is linked via a fifth weak bond to the in-plane coordinated acetate oxygen atom of the other. Therefore, each bridging oxygen simultaneously occupies an in-plane coordination site on one copper(II) ion and an apical site of the other copper(II) ion. The second oxygen atom of each acetate ligand is at a weakly linking distance of only one copper atom and is not involved in any bridging. The four-membered Cu_2O_2 bridging units in the dimers are strictly planar owing to crystallographic inversion symmetry. In the 5-nitro complex the bridging angle at oxygen is 96.1 (1)°, and the long, out-of-plane Cu-O bond distance is 2.577 (2) Å, while the corresponding values in the 5-bromo complex are 96.3 (2)° and 2.665 (4) Å, respectively. The magnetic susceptibilities of powdered samples of the complexes have been examined down to ca. 2 K. The two compounds exhibit antiferromagnetic exchange interactions with the best fit to an appropriate dimer-exchange equation yielding singlet-triplet splittings of -3.02 cm^{-1} for the 5-nitro complex and -3.68 cm^{-1} for the 5-bromo complex. A comparison of the structural and magnetic data obtained for the present compounds with corresponding data for five previously characterized compounds that involve similarly bridged Cu_2O_2 moieties shows that a smooth correlation of $2J$ with the ϕ/R_0 quotient, where ϕ is the bridging angle at oxygen and R_0 is the axial Cu-O bond distance, begins to emerge.

Introduction

Dinuclear copper(II) complexes with planar, I, or parallel-planar, II, geometries have occupied considerable experimental[2a,b,d-f] and theoretical[2c,3-5] work.



I



II

Much of this work has been concerned with the correlation of the structural properties of these complexes with their magnetic properties.

For planar hydroxo-bridged systems of type I it has been possible to establish,[2a,6] and theoretically justify,[2c,3] that the sin-

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(1) Part 8: Chiari, B.; Helms, J. H.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F., *Inorg. Chem.* **1986**, *25*, 870.

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glet–triplet splitting, $2J$, varies linearly with a single structural variable, ϕ, where ϕ is the bridging CuOCu angle. For the few cases that deviate from such a behavior rational explanations have been produced.[7] A correlation between $2J$ and ϕ has also been proposed for chloride-bridged copper(II) dimers.[8]

The structural dependence of the magnetic properties of dimers of type II (in which the bridging framework is not longer in the xy plane of the copper atoms, one bridging ligand being axial to a given copper atom and the other equatorial) is more difficult to elucidate for several reasons. For example, there are changes in structural features (particularly the out-of-plane bond distance) other than the ligand bridge angle, the range of observed J values is much smaller, additional metal orbitals become involved in the exchange mechanism, and it must also be recognized that the energies of the highest occupied MO's are influenced by the ligands that are not primarily involved in the exchange process since the symmetry of the exchange-coupled unit is relatively low.[9]

Results obtained for a wide range of parallel-planar bis(μ-chloro)-[2a,e,9,10] and bis(μ-bromo)-bridged[2a,e,11] copper(II) dimers, and some bis(μ-sulfur)-bridged copper(II) dimers[2a,e,10] have shown that the singlet-triplet splitting is mainly dependent on the magnitude of the angle at the bridge and the bond length in the superexchange pathway.

Hatfield et al. have examined the $2J$ values for these series of compounds in terms of the simple structural parameter ϕ/R_0, where R_0 is the long, out-of-plane bond distance.[2a,e,10] Although calculations would suggest[2a,b] that the $2J$ vs. ϕ/R_0 should be a surface and not one universal curve, almost all available data for the aforementioned series of compounds fall on or near a single line.

The situation is much less clear for parallel-planar systems with oxygen bridges. Magnetostructural correlations for these compounds have not been developed in any detail, in spite of the rather large body of structural and magnetic data that is available.[1,2a,10,12–17] A possible explanation of this seeming inconsistency arises from the observation that most members of this structural class have different bridging groups and/or metal environments. Recent experimental[2b,d,7a,18,19] and theoretical[3] work on various bimetallic systems indicates that the electron density at the bridging atom and the ligand environment of the metal, besides the geometry of the bridging unit, are factors that can enter into determining the extent of exchange coupling.

These observations invite a search for additional parallel-planar oxygen-bridged copper(II) systems having more closely related structural and chemical features, so that the effect of the bridge length and angle can be separated from other effects.

In this paper we report the synthesis and structural and magnetic characterization of two new compounds: $Cu_2(5\text{-}NO_2\text{-}L)_2(CH_3COO)_2$ and $Cu_2(5\text{-}Br\text{-}L)_2(CH_3COO)_2$, where $(5\text{-}NO_2\text{-}L)^-$ and $(5\text{-}Br\text{-}L)^-$ are the anions of *N*-methyl-*N'*-(5-nitrosalicylidene)-1,3-propanediamine and *N*-methyl-*N'*-(5-bromosalicylidene)-1,3-propanediamine, respectively. The structures of both compounds consist of magnetically dilute parallel-planar dimers involving one-atom acetato-bridged Cu_2O_2 moieties. A comparison of the structural and magnetic data obtained for these compounds with corresponding data for five other previously characterized compounds that also involve one-atom carboxylato bridged Cu_2O_2 moieties shows that a smooth correlation of $2J$ with the quotient ϕ/R_0 begins to emerge.

A main problem associated with magnetostructural correlations in transition-metal alternating-chain compounds is the assignment of the exchange-coupling constants (J_1 and J_2) to the relative ligand bridges from which they arise. The data for the present series of compounds have also a bearing on this problem since they aid the assignment of the exchange-coupling constants that we have determined earlier for two magnetic alternating-chain systems.[1,17]

Experimental Section

Preparation of the Complexes. $Cu_2(5\text{-}NO_2\text{-}L)_2(CH_3COO)_2$. A solution of *N*-methyl-1,3-propanediamine (0.44 g, 5 mmol) in anhydrous ethanol (10 mL) was added, under nitrogen, to a solution of 2-hydroxy-5-nitrobenzaldehyde (0.84 g, 5 mmol) in the same solvent (25 mL). The resulting yellow solution was heated at ca. 70 °C for 15 min, under nitrogen, and with constant stirring. To the clear, hot solution containing the 5-NO$_2$-LH 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, under nitrogen, and with constant stirring. A green solution was obtained. After the solution was allowed to evaporate for ca. 3 days, at room temperature, under a slight nitrogen flow, a green microcrystalline precipitate of the complex was collected by filtration and dried under vacuum: yield 1.38 g (80%); mp 210–212 °C. Recrystallization from acetone yielded crystals (mp 210–212 °C) suitable for X-ray analysis. The compound remains unaltered for several months in inert atmosphere but decomposes upon exposure to air. However, the decomposition process takes several days, ca. 5, to become perceptible. Anal. Calcd for $C_{26}H_{34}N_6O_{10}Cu_2$: C, 43.51; H, 4.77; N, 11.71; Cu, 17.70. Found: C, 43.59; H, 4.92; N, 11.70; Cu, 17.81.

$Cu_2(5\text{-}Br\text{-}L)_2(CH_3COO)_2$. *N*-Methyl-1,3-propanediamine (0.44 g, 5 mmol) and 2-hydroxy-5-bromobenzaldehyde (1.00 g, 5 mmol) were dissolved in anhydrous ethanol (50 mL), under nitrogen. The resulting yellow solution was heated, under nitrogen, at ca. 70 °C for 0.5 h. To the clear hot solution containing the 5-Br-LH ligand was added a 5-mmol (1.00-g) quantity of $Cu(CH_3COO)_2\cdot H_2O$. The addition was made over a period of 0.5 h, under nitrogen, and with constant stirring. A dark green solution was obtained, which was heated at ca. 50 °C for ca. 1 h and then allowed to stand at room temperature for ca. 48 h. The few well-shaped, blue-green crystals that formed, suitable for X-ray analysis, were decanted and dried with filter paper. The residual solution was then reduced in volume to ca. 25 mL (on a rotatory evaporator) to yield a further 1.2 g of polycrystalline product, which was washed with ethanol and dried under vacuum: yield 1.2 g (61%); mp 217–220 °C. Anal. Calcd for $C_{26}H_{34}N_4O_6Br_2Cu_2$: C, 39.76; H, 4.36; N, 7.13; Cu, 16.18. Found: C, 39.82; H, 4.40; N, 7.20; Cu, 16.05. The compound is air-stable.

Magnetic Susceptibility Measurements. Variable-temperature magnetic susceptibility studies of the compounds, down to ca 2 K, were carried out on solid polycrystalline samples, with a Princeton Applied Research Model 155 vibrating-sample magnetometer operating at 10 kOe. The apparatus and techniques used to collect the data have been described elsewhere.[20] Susceptibilities were corrected for the diamagnetism of the ligand systems (-146.44×10^{-6} cgsu/Cu atom for $Cu_2(5\text{-}NO_2\text{-}L)_2(CH_3COO)_2$ and -163.21×10^{-6} cgsu/Cu atom for $Cu_2(5\text{-}Br\text{-}L)_2(CH_3COO)_2$) and for the temperature-independent paramagnetism, $N\alpha$, of copper(II) (estimated to be 60×10^{-6} cgsu/Cu atom).

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Table I. Fractional Atomic Coordinates in $Cu_2(5\text{-}NO_2\text{-}L)_2(CH_3COO)_2$

atom	x/a	y/b	z/c
Cu	0.81675 (4)	−0.02056 (4)	0.96626 (4)
O(1)	0.8178 (2)	0.0901 (3)	1.1590 (2)
O(2)	0.9580 (2)	−0.1460 (2)	1.0605 (2)
O(3)	0.7515 (3)	−0.2666 (3)	1.0799 (3)
O(4)	0.5618 (3)	0.6523 (3)	1.4312 (3)
O(5)	0.3963 (3)	0.5865 (3)	1.2533 (3)
N(1)	0.6465 (2)	0.0698 (3)	0.8832 (2)
N(2)	0.8659 (2)	−0.1038 (3)	0.7618 (3)
N(3)	0.5113 (3)	0.5695 (3)	1.3238 (3)
C(1)	0.7462 (3)	0.2039 (3)	1.1909 (3)
C(2)	0.7795 (3)	0.2860 (4)	1.3309 (3)
C(3)	0.7065 (3)	0.4060 (4)	1.3731 (3)
C(4)	0.5925 (3)	0.4452 (3)	1.2768 (3)
C(5)	0.5545 (3)	0.3690 (3)	1.1413 (3)
C(6)	0.6316 (3)	0.2494 (3)	1.0940 (3)
C(7)	0.5833 (3)	0.1736 (3)	0.9491 (3)
C(8)	0.5780 (3)	0.0006 (4)	0.7392 (3)
C(9)	0.6711 (3)	0.0138 (4)	0.6105 (3)
C(10)	0.8315 (4)	−0.0011 (4)	0.6476 (4)
C(11)	0.8224 (4)	−0.2576 (4)	0.7119 (4)
C(12)	0.8843 (4)	−0.2524 (4)	1.1017 (4)
C(13)	0.9658 (5)	−0.3654 (5)	1.1809 (6)

ESR Spectra. These were measured with a Varian E-9 spectrometer operated at X-band frequencies. Spectra at liquid-helium temperatures were measured with use of an Oxford Instruments ESR 9 continuous-flow cryostat.

X-ray Data and Structure Solution. $Cu_2(5\text{-}NO_2\text{-}L)_2(CH_3COO)_2$. A green, tabular crystal with dimensions 0.25 × 0.20 × 0.05 mm was mounted on a computer-controlled Philips PW1100 single-crystal diffractometer equipped with graphite-monochromatized Mo Kα radiation (λ = 0.71069 Å). The crystals are triclinic. 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 a = 9.305 (3) Å, b = 9.209 (3) Å, c = 8.993 (3) Å, α = 94.94 (2)°, β = 94.92 (2)°, γ = 92.78 (2)°. V = 763.7 Å^3. The space group is $P\bar{1}$ (from intensity statistics). Although from a geometrical point of view the lattice could be described according to a C-centered monoclinic cell obtained by applying the matrix 110/1$\bar{1}$0/001 to the triclinic cell, a check of the true symmetry confirmed the $\bar{1}$ Laue group. The calculated density for one dimeric $Cu_2C_{26}H_{34}N_6O_{10}$ molecule (M_r = 717) in the unit cell is 1.559 g cm^{-3}. The absorption coefficient for Mo Kα is μ = 14.3 cm^{-1}.

The intensities were collected at room temperature up to 2θ = 60°; the ω–2θ scan technique was employed, the scan range being 1.4° and the speed 0.05° s^{-1}. A total of 4407 independent reflections were measured, of which 2321, having $I < 3\sigma(I)$ were considered as "unobserved" and excluded from the refinement. 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. During the refinement, an empirical absorption correction was applied, according to the method of Walker and Stuart.[21] The correction factors were in the range 1.11–0.93.

The structure was solved by Patterson and Fourier methods and refined by the full-matrix least-squares method with the SHELX-76 package of programs.[22] The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. Anisotropic thermal parameters were refined for all non-hydrogen atoms. The hydrogen atoms, with the exception of those of the methyl groups, were included at their calculated positions (C–H = 1.08 Å). The overall isotropic parameter U refined to 0.07 Å^2. The methyl groups were refined as rigid groups by starting from the staggered position. The common U of the hydrogen atoms of the methyl groups refined to 0.14 Å^2. The refinement converged at R(unweighted) = 0.026 and R(weighted) = 0.030 ($w = \sigma^{-2}(F_o)$), for 208 parameters and 2086 observed reflections.

Table II. Bond Lengths (Å) and Angles (deg) in $Cu_2(5\text{-}NO_2\text{-}L)_2(CH_3COO)_2$

Cu–O(1)	1.933 (2)	N(1)–C(7)	1.276 (3)
Cu–O(2)	1.976 (2)	N(1)–C(8)	1.472 (3)
Cu–O(3)	2.630 (3)	N(2)–C(10)	1.481 (4)
Cu–N(1)	1.947 (2)	N(2)–C(11)	1.475 (4)
Cu–N(2)	2.028 (3)	N(3)–C(4)	1.454 (4)
Cu–O(2)′	2.577 (2)	C(6)–C(7)	1.449 (4)
O(1)–C(1)	1.294 (3)	C(8)–C(9)	1.514 (4)
O(2)–C(12)	1.268 (4)	C(9)–C(10)	1.517 (4)
O(3)–C(12)	1.233 (4)	C(12)–C(13)	1.509 (6)
O(4)–N(3)	1.223 (4)	Cu···Cu′	3.409 (1)
O(5)–N(3)	1.220 (4)		
O(1)–Cu–O(2)	87.9 (1)	C(7)–N(1)–C(8)	118.1 (2)
O(1)–Cu–O(3)	92.0 (1)	Cu–N(2)–C(10)	110.6 (2)
O(1)–Cu–N(1)	93.1 (1)	Cu–N(2)–C(11)	118.8 (2)
O(1)–Cu–N(2)	164.5 (1)	C(10)–N(2)–C(11)	114.0 (2)
O(1)–Cu–O(2)′	83.7 (1)	O(4)–N(3)–O(5)	123.2 (3)
O(2)–Cu–O(3)	54.9 (1)	O(4)–N(3)–C(4)	118.6 (2)
O(2)–Cu–N(1)	167.3 (1)	O(5)–N(3)–C(4)	118.2 (2)
O(2)–Cu–N(2)	89.3 (1)	O(1)–C(1)–C(2)	119.0 (2)
O(2)–Cu–O(2)′	83.9 (1)	O(1)–C(1)–C(6)	123.4 (2)
O(3)–Cu–N(1)	112.4 (1)	N(3)–C(4)–C(3)	118.8 (2)
O(3)–Cu–N(2)	98.8 (1)	N(3)–C(4)–C(5)	119.6 (2)
O(3)–Cu–O(2)′	138.8 (1)	C(1)–C(6)–C(7)	123.5 (2)
N(1)–Cu–N(2)	93.0 (1)	C(5)–C(6)–C(7)	116.9 (2)
N(1)–Cu–O(2)′	108.7 (1)	N(1)–C(7)–C(6)	125.5 (2)
N(2)–Cu–O(2)′	80.8 (1)	N(1)–C(8)–C(9)	113.3 (2)
Cu–O(1)–C(1)	127.1 (2)	C(8)–C(9)–C(10)	115.6 (2)
Cu–O(2)–C(12)	105.9 (2)	N(2)–C(10)–C(9)	114.2 (2)
Cu–O(3)–C(12)	76.1 (2)	O(2)–C(12)–O(3)	123.1 (3)
Cu–N(1)–C(7)	125.5 (2)	O(2)–C(12)–C(13)	117.2 (3)
Cu–N(1)–C(8)	116.0 (1)	O(3)–C(12)–C(13)	119.6 (3)

Table III. Fractional Atomic Coordinates in $Cu_2(5\text{-}Br\text{-}L)_2(CH_3COO)_2$

atom	x/a	y/b	z/c
Cu	−0.0228 (1)	0.5048 (1)	0.1782 (1)
Br	0.3958 (1)	0.5570 (1)	0.6574 (1)
O(1)	0.1008 (3)	0.4443 (5)	0.2093 (5)
O(2)	−0.0310 (3)	0.3660 (4)	0.0399 (4)
O(3)	−0.0768 (4)	0.2827 (5)	0.2355 (5)
N(1)	−0.0088 (4)	0.6227 (5)	0.3358 (6)
N(2)	−0.1452 (4)	0.5672 (5)	0.0911 (6)
C(1)	0.1624 (2)	0.4727 (4)	0.3108 (4)
C(2)	0.2466 (2)	0.4108 (4)	0.3109 (4)
C(3)	0.3157 (2)	0.4358 (4)	0.4148 (4)
C(4)	0.3005 (2)	0.5228 (4)	0.5185 (4)
C(5)	0.2163 (2)	0.5847 (4)	0.5184 (4)
C(6)	0.1473 (2)	0.5597 (4)	0.4145 (4)
C(7)	0.0637 (4)	0.6301 (7)	0.4196 (7)
C(8)	−0.0838 (5)	0.7100 (8)	0.3648 (8)
C(9)	−0.1336 (7)	0.7546 (10)	0.2360 (9)
C(10)	−0.1914 (6)	0.6721 (9)	0.1519 (10)
C(11)	−0.2174 (6)	0.4704 (8)	0.0613 (9)
C(12)	−0.0539 (4)	0.2735 (7)	0.1133 (7)
C(13)	−0.0486 (5)	0.1492 (8)	0.0477 (8)

$Cu_2(5\text{-}Br\text{-}L)_2(CH_3COO)_2$. A blue-green tabular crystal with dimensions 0.20 × 0.10 × 0.05 mm was mounted on the diffractometer and treated with the procedure described for the 5-nitro compound. Crystals are monoclinic, space group $P2_1/a$ (from systematic extinctions). The lattice parameters are a = 14.519 (2) Å, b = 10.859 (2) Å, c = 9.547 (3) Å, β = 93.35 (2)°. V = 1502.6 Å^3. The calculated density for two dimeric $Cu_2C_{26}H_{34}N_4O_6Br_2$ molecules (M_r = 783) in the unit cell is 1.729 g cm^{-3}. The absorption coefficient is μ = 40.5 cm^{-1}.

A total of 3501 independent intensity data were measured in the 2θ range 4–40°, with the same technique and collection parameters as for the 5-nitro compound. A total of 1377 reflections with $I < 3\sigma(I)$ were considered as "unobserved". The data were corrected for geometrical and absorption factors as in the case of the previous compound (correction factors in the range 1.20–0.87).

The structure was solved and refined with the procedure previously described for the 5-nitro compound. The phenyl group was constrained to a perfect hexagon (C–C = 1.395 Å). The hydrogen atoms (with the exception of those of the methyl groups) were included at their calculated positions (C–H = 1.08 Å), with overall isotropic parameter U = 0.10 Å^2. The methyl groups wer refined as rigid groups by starting from the staggered position. Anisotropic thermal parameters were assigned to the Cu, Br, O, and N atoms. The carbon atoms were refined isotropically. The final R index was 0.045 for 1674 observations and 113 parameters (R_w = 0.053).

The atomic scattering factors were taken from ref 22 for the Br, O, N, C, and H atoms and from ref 23 for the Cu atom. The correction for

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

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

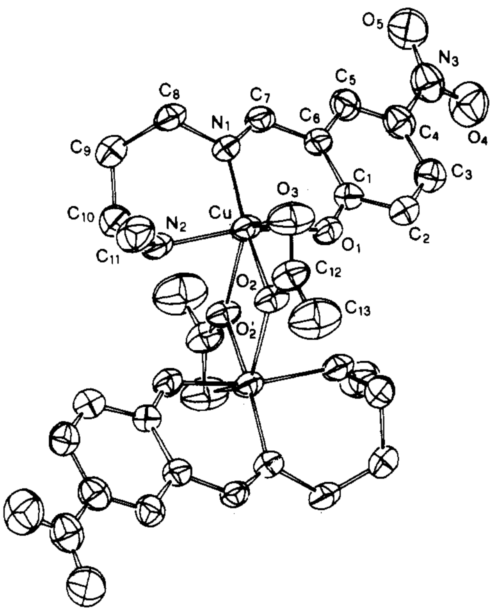

Figure 1. View of the dimeric $Cu_2(5\text{-}NO_2\text{-}L)_2(CH_3COO)_2$ molecule. Hydrogen atoms have been omitted for clarity. Unlabeled atoms are related to labeled atoms by the inversion center.

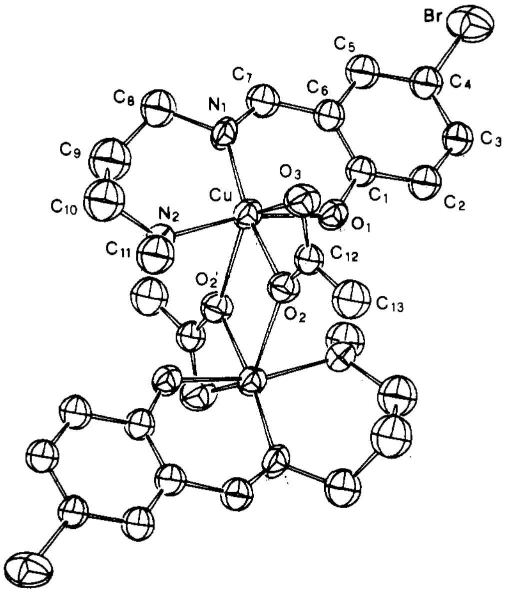

Figure 2. View of $Cu_2(5\text{-}Br\text{-}L)_2(CH_3COO)_2$. Unlabeled atoms are related to labeled atoms by the inversion center.

anomalous dispersion of Cu and Br was included.

Results

Description of the Structures. Both complexes consist of dimeric $Cu_2(5\text{-}R\text{-}L)_2(CH_3COO)_2$ units (R = NO_2, Br) which are well separated from one another. The molecules and labeling schemes are shown in Figures 1 and 2. Final positional parameters and bond lengths and angles are given in Table I–IV.

The dinuclear units in the present structures are very similar to that found in the previously characterized[16] $Cu_2L_2(CH_3COO)_2$ compound, where L^- is the anion of the parent ligand *N*-methyl-*N'*-salicylidene-1,3-propanediamine. In each dimer, the ligand environments of the copper atoms are identical owing to crystallographic inversion symmetry. Each copper atom shows distorted (4 + 1 + 1) square-bipyramidal coordination. The four short bonds are to the two nitrogens, N(1) and N(2), and the phenolic oxygen, O(1), of the tridentate Schiff base ligand and one oxygen atom, O(2), of an acetate anion. The N(1), N(2), O(1), O(2), and Cu atoms lie approximately in a plane (detailed atomic deviations from the least-squares planes supplied as supplementary material). Comparable in-plane bond lengths and angles are similar in the two complexes. The copper atom of the approximately planar fragment so formed is linked via a weak fifth bond to the in-plane coordinated acetate oxygen atom, O(2)', of the other. Therefore, each bridging oxygen simultaneously occupies an in-plane coordination site on one copper(II) ion and an apical site of the other copper(II) ion. The second oxygen atom, O(3), of each acetate ligand is at a weakly linking distance of only one copper atom and is not involved in any bridging. The Cu–O(3) separation is 2.630 (3) Å in the 5-nitro compound and 2.604 (6) Å in the 5-bromo analogue. The four-membered Cu_2O_2 bridging units in both dimers are strictly planar owing to inversion symmetry. The difference in the CuOCu bridging angle, ϕ, is within experimental error for the two dimers (ϕ = 96.1 (1) and 96.3 (2)°), but the out-of-plane, bridging Cu-O(2)' bond distance in the 5-nitro compound, 2.577 (2) Å, is significantly shorter than the corresponding value in the 5-bromo compound, 2.665 (4) Å. In the 5-nitro complex the bridge plane forms a dihedral angle of 92.0° with the mean basal plane of the copper "square bipyramid"; the corresponding value in the 5-bromo complex is 96.6°. The bond lengths and angles in the Schiff base ligands have their usual values within error limits.

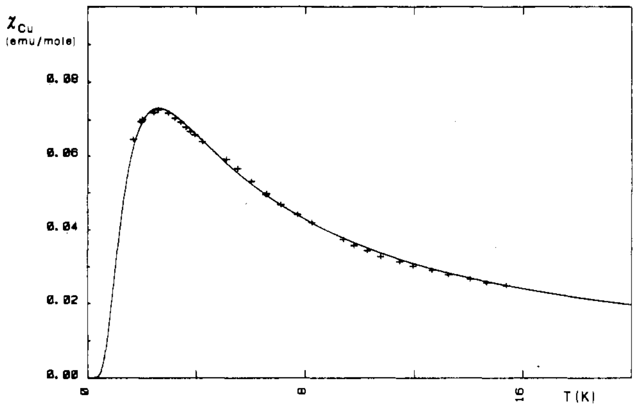

Figure 3. Low-temperature magnetic susceptibility data for $Cu_2(5\text{-}NO_2\text{-}L)_2(CH_3COO)_2$, along with the fit described in the text.

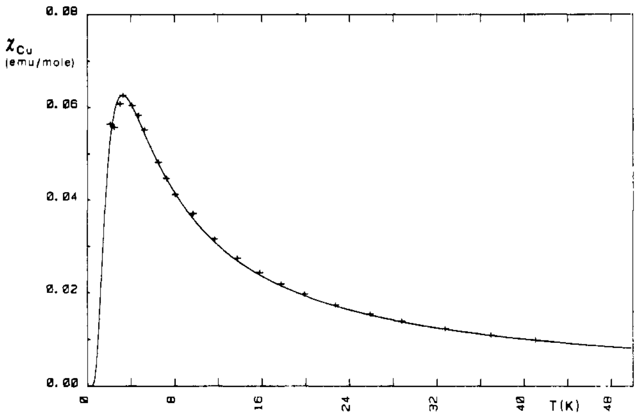

Figure 4. Temperature dependence of the magnetic susceptibility of $Cu_2(5\text{-}Br\text{-}L)_2(CH_3COO)_2$. The best fit described in the text is shown as the full line.

Magnetic Properties. In agreement with the coordination geometry revealed by the X-ray structure, the X-band ESR spectra of powdered samples of $Cu_2(5\text{-}NO_2\text{-}L)_2(CH_3COO)_2$ are axial with $g_\parallel = 2.237$ and $g_\perp = 2.063$ ($g_{av} = 2.121$). There is no appreciable change in the spectrum in changing the temperature of the sample from room temperature to 4.2 K. Only one rather broad, featureless signal (peak-to-peak separation ca. 150 G) centered at g = ca. 2.10 could be observed at 300 K for solid $Cu_2(5\text{-}Br\text{-}L)_2(CH_3COO)_2$.

Corrected magnetic susceptibility data for the two compounds are given in Figures 3 and 4. For both complexes a maximum

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[23] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, p 99.

Table IV. Bond Lengths (Å) and Angles (deg) in $Cu_2(5\text{-}Br\text{-}L)_2(CH_3COO)_2$[a]

Cu–O(1)	1.918 (4)	N(1)–C(7)	1.287 (8)
Cu–O(2)	2.003 (4)	N(1)–C(8)	1.482 (9)
Cu–O(3)	2.604 (6)	N(2)–C(10)	1.459 (11)
Cu–N(1)	1.977 (6)	N(2)–C(11)	1.500 (10)
Cu–N(2)	2.034 (6)	C(6)–C(7)	1.438 (7)
Cu–O(2)′	2.665 (4)	C(8)–C(9)	1.472 (12)
Br–C(4)	1.896 (4)	C(9)–C(10)	1.440 (13)
O(1)–C(1)	1.316 (6)	C(12)–C(13)	1.492 (11)
O(2)–C(12)	1.280 (8)	Cu···Cu′	3.506 (1)
O(3)–C(12)	1.236 (8)		
O(1)–Cu–O(2)	82.1 (2)	Cu–N(1)–C(7)	123.9 (4)
O(1)–Cu–O(3)	86.6 (2)	Cu–N(1)–C(8)	120.8 (4)
O(1)–Cu–N(1)	92.9 (2)	C(7)–N(1)–C(8)	115.3 (5)
O(1)–Cu–N(2)	164.8 (2)	Cu–N(2)–C(10)	120.6 (5)
O(1)–Cu–O(2)′	89.3 (2)	Cu–N(2)–C(11)	115.4 (4)
O(2)–Cu–O(3)	55.6 (2)	C(10)–N(2)–C(11)	106.9 (6)
O(2)–Cu–N(1)	171.3 (2)	O(1)–C(1)–C(2)	116.4 (3)
O(2)–Cu–N(2)	88.0 (2)	O(1)–C(1)–C(6)	123.6 (3)
O(2)–Cu–O(2)′	83.7 (2)	Br–C(4)–C(3)	119.3 (2)
O(3)–Cu–N(1)	117.3 (2)	Br–C(4)–C(5)	120.6 (2)
O(3)–Cu–N(2)	97.3 (2)	C(5)–C(6)–C(7)	116.4 (3)
O(3)–Cu–O(2)′	139.2 (2)	N(1)–C(7)–C(6)	127.4 (5)
N(1)–Cu–N(2)	98.3 (2)	N(1)–C(8)–C(9)	112.6 (6)
N(1)–Cu–O(2)′	103.4 (2)	C(8)–C(9)–C(10)	120.2 (8)
N(2)–Cu–O(2)′	78.1 (2)	N(2)–C(10)–C(9)	116.2 (7)
Cu–O(1)–C(1)	128.5 (3)	O(2)–C(12)–O(3)	123.1 (5)
Cu–O(2)–C(12)	103.7 (3)	O(2)–C(12)–C(13)	117.3 (5)
Cu–O(3)–C(12)	77.0 (4)	O(3)–C(12)–C(13)	119.5 (5)

[a] Primed atoms: $-x$, $1 - y$, $-z$.

in the χ_M vs. T curve is observed, which is indicative of antiferromagnetic coupling between the two copper(II) centers in the dimeric units. From the very low temperatures (2–3 K) at which the maxima in susceptibility occur, it appears that the condition $J \gg g\mu_BH$ ($g\mu_BH$ is ca. 1 cm^{-1} for H = 10000 G) is not satisfied in the present cases and that, therefore, the application of the usual Bleaney–Bowers[24] susceptibility expression would be inappropriate. Consequently, we have used a susceptibility expression that considers the external field,[25] namely eq 1, where the exchange

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

Hamiltonian is given by eq 2 and $\hat{S}$ is the total spin operator (i.e.

$$H_{ex} = -2J(\hat{S}_A \cdot \hat{S}_B) + g\mu_BH\hat{S} \tag{2}$$

$\hat{S} = \hat{S}_A + \hat{S}_B$). Equation 1 was corrected, in the molecular field approximation, for the presence of possible magnetic interactions between neighboring dimers. The molecular field treatment[26] of eq 1 gives eq 3, where z is the number of nearest-neighboring

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

dimers and J' is the lattice interaction parameter. Equation 3 was used to fit the experimental data for the two complexes. The function that was minimized in curve fitting was $F = (\chi_i^{\text{obsd}})^{-1}(\chi_i^{\text{obsd}} - \chi_i^{\text{calcd}})^2$. The best fit to the data for $Cu_2(5\text{-}NO_2\text{-}L)_2(CH_3COO)_2$ yielded $J = -1.51 \pm 0.01$ cm^{-1}, $zJ' = -0.33$ cm^{-1}, and $F = 3.48 \times 10^{-4}$, for 32 observations, using the ESR g value of 2.121 and $N\alpha = 60 \times 10^{-6}$ cgsu/Cu atom. The best fit is indicated by the solid line in Figure 3 and represents a precise description of the experimental data.

The experimental and theoretical temperature dependence of the magnetic susceptibility for $Cu_2(5\text{-}Br\text{-}L)_2(CH_3COO)_2$ are shown in Figure 4. The best fit led to values of $g = 2.10$, $J = -1.84 \pm 0.01$ cm^{-1}, $zJ' = -0.03$ cm^{-1}, and $F = 6.10 \times 10^{-4}$, for 23 observations, using, as before, $N\alpha = 60 \times 10^{-6}$ cgsu/Cu atom. It can be seen from Figure 4 that eq 3 is in excellent agreement with experiment.

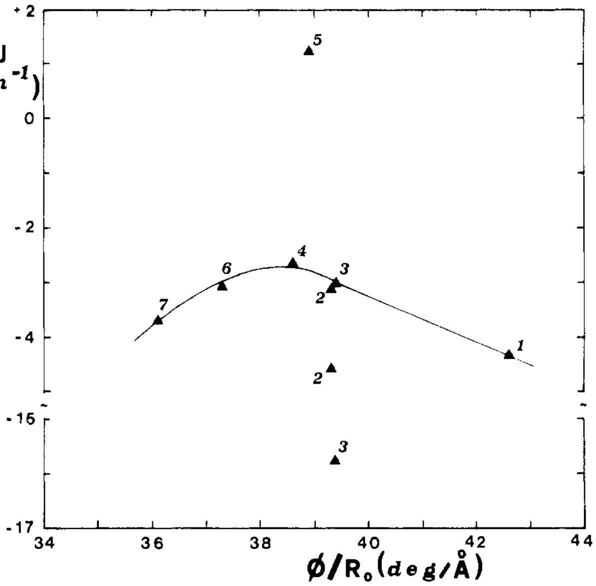

Figure 5. Dependence of the singlet–triplet splitting, $2J$, on ϕ/R_0 for the copper(II) compounds containing one-atom carboxylato-bridged Cu_2O_2 units. The data points are keyed by number to the data in Table V. For the alternating-chain compounds, **2** and **3**, the two values of $2J$ that characterize alternating-chain magnetic exchange are reported.

Discussion

There are now six completely characterized examples of compounds containing one-atom acetate-bridged (in an axial–equatorial way) Cu_2O_2 moieties.

Magnetic and structural data for this series are summarized in Table V.

Compounds **4**–**7** have structures built of magnetically dilute dimers, compound **3** exhibits an alternating-chain structure and attendant magnetic properties, and compound **2** is a "structural" ladderlike system with "magnetic" alternating-chain behavior. Table V also reports data for the $[Cu(R\text{-}CH_2COO)_2(H_2O)_2]_2 \cdot 4H_2O$ dimer (**1**) (R = C_6H_5CONH, the ligand is hippurate), in which the copper atoms are bridged, in an axial–equatorial way, by two monodentate carboxylate groups of the hippurate anions.[13] It is tentatively assumed that the small differences in electron density and electronic structure between the acetate and hippurate bridging oxygens have negligible magnetic consequences.

The dinuclear units in the compounds under discussion, besides being all of the out-of-plane type and having the same bridge ligand (with the just mentioned exception of the hippurate derivative) are structurally related in showing quite similar copper coordination geometries: distorted (4 + 1) square pyramidal or (4 +1 + 1) square bipyramidal, with atomic deviations from the least-squares basal planes (supplementary material) of comparable magnitude. In addition, the chemical nature of the in-plane coordination is identical for compounds **2**–**4**, **6**, and **7** (CuN_2O_2) and not radically different for compounds **5** ($CuNO_3$) and **1** (CuO_4). If it is further considered that the in-plane Cu–O(bridging) bond distances are nearly constant at 1.96 ± 0.04 Å, it appears that these complexes are well suited for observing how the singlet–triplet splitting depends on the angle at the bridge and the out-of-plane Cu–O bond distance, R_0.

A plot of $2J$ vs. the ϕ/R_0 structural parameter for this series is shown in Figure 5, where it may be seen that a smooth correlation, which appears to follow the trends established for the above-mentioned parallel-planar chloro-, bromo-, and sulfur-bridged complexes, begins to emerge.

The following features deserve attention.

For all the compounds in Table V the exchange interaction is weak, as expected. With square-pyramids and square-bipyramids,

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(24) Bleaney, B.; Bowers, K. *Proc. R. Soc. London, 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*; Saunders: Philadelphia, PA, 1966.

Table V. Structural and Magnetic Parameters for Copper(II) Compounds Containing One-Atom Carboxylato-Bridged Cu_2O_2 Units

compd	R_i,[a] Å	R_o,[b] Å	CuOCu, deg	ϕ/R_o, deg/Å	$2J$, cm^{-1}	ref
$Cu_2A_4(H_2O)_4\cdot 4H_2O$[c] (**1**)	1.93 (1)	2.37 (1)	101.0 (5)	42.6	−4.30	13, 15
$Cu_2(5\text{-}CH_3O\text{-}L)_2(CH_3COO)_2\cdot 2H_2O$[d] (**2**)	1.960 (8)	2.498 (8)	98.1 (3)	39.3	−3.08, −4.52[i]	1
$Cu_2G(CH_3COO)_2\cdot 2CH_3OH$[e] (**3**)	1.952 (6)	2.495 (6)	98.3 (5)	39.4	−3.00, −15.76[i]	17
$Cu_2L_2(CH_3COO)_2$[f] (**4**)	1.978 (3)	2.512 (5)	96.9 (2)	38.6	−2.66	1, 16
$Cu_2X_2(CH_3COO)_2\cdot H_2O\cdot C_2H_5OH$[g] (**5**)	1.952 (1)	2.446 (2)	95.7 (1)	39.8[h]	+1.26	14
	1.952 (1)	2.651 (1)	102.6 (1)			
$Cu_2(5\text{-}NO_2\text{-}L)_2(CH_3COO)_2$ (**6**)	1.976 (2)	2.577 (2)	96.1 (1)	37.3	−3.02	this work
$Cu_2(5\text{-}Br\text{-}L)_2(CH_3COO)_2$ (**7**)	2.003 (4)	2.665 (4)	96.3 (2)	36.1	−3.68	this work

[a] R_i = in-plane Cu–O bond distance. [b] R_o = out-of-plane Cu–O bond distance. [c] A^- = $(C_6H_5)CONHCH_2COO^-$, hippurate anion. [d] $(5\text{-}CH_3O\text{-}L)^-$ = *N*-methyl-*N'*-(5-methoxysalicylidene)-1,3-propanediaminate anion. [e] G^{2-} = anion of *N*,*N'*-bis(2-((*o*-hydroxybenzhydrylidene)amino)ethyl)-1,2-ethanediamine. [f] L^- = anion of *N*-methyl-*N'*-salicilydene-1,3-propanediamine. [g] X^- = anion of *N*-(1,1-dimethyl-2-hydroxyethyl)salicylaldimine. [h] Mean value. [i] Alternating-chain magnetism.

the unpaired electron of the copper(II) 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 in all the present compounds the superexchange pathways involve out-of-plane unpaired electron density, a weak exchange interaction may be anticipated.

Differences in $2J$ between the compounds in this series, although small, are significant due to both the high sensitivity of the magnetic susceptibility to very small changes in the value of the exchange parameter, J, in the temperature region where the maximum susceptibility is observed and the excellent agreement between theory and experiment obtained in each case.

The data for compound **5** represent a serious deviation from the apparent correlation. In addition, compound **5** is the only one, among those considered here, for which a triplet ground state is observed. It has been suggested that the value of 95.7 (1)° of one CuOCu bridging angle in the structure of this compound is responsible for the presence of a triplet ground state.[14] The data for compounds **6** and **7** do not provide support for this view since both of these compounds exhibit bridging angles (96.1 (1) and 96.3 (2)°, respectively) that are not significantly different from 95.7 (1)° and a singlet ground state. The fact that compound **5** is the only one-atom acetato-bridged copper(II) dimer in the series in which there is no center of symmetry and the two principal ligand planes are not parallel (being tilted at an angle of 19.6° to each other) might be indicative that the orientation of the magnetic planes rather than the value of the bridging angle induces the presence of a triplet ground state. Additional research will hopefully provide the necessary data to resolve the interesting question of the influence of the angle between planes on exchange coupling.

The relative magnetic coupling in compounds **4**, **6**, and **7** is also of interest since the fact that the structures of these compounds show virtually identical ϕ angles affords the opportunity of observing that the magnitude of the singlet–triplet splitting increases as the axial Cu–O separation increases. This trend does not conform to predictions of current orbital models for superexchange. According to these models, which are described extensively elsewhere,[3-5,27] the singlet–triplet splitting for a copper(II) dimer is expressed as the sum of a ferromagnetic term ($2J_F > 0$) and an antiferromagnetic contribution ($2J_{AF} < 0$):

$$E_{ST} = 2J = 2J_F + 2J_{AF} \tag{4}$$

In essence, the J_F term is assumed to be small and virtually constant in a series of chemically related compounds, and J_{AF} is related to the energy separation between the two highest occupied molecular orbitals containing the unpaired electrons. The larger the energy separation is, the stronger the antiferromagnetic interaction should be. From orbital-overlap considerations alone it would therefore be expected that an increase in bond distance should be accompanied by a decrease in exchange coupling.[2a,e,4,27] Further theoretical inspection, including higher order contributions to the singlet–triplet splitting (such as those that have been considered recently by de Loth et al.[28] in an ab initio calculation on dimeric copper(II) acetate hydrate), appears to be required in order to better understand the relative magnetic coupling in compounds **4**, **6**, and **7**.

A final comment concerns the alternating-chain compounds, **2** and **3**. These complexes have identical Cu_2O_2 moieties but quite different overall structures. It may be noted that, for both **2** and **3**, one of the two J values that characterize alternating-chain magnetic exchange follows the $2J$ vs. ϕ/R_o correlation while the other does not. If it is further considered that the two J values that follow the correlation are virtually identical (1.52 ± 0.02 cm^{-1}), it is logical to assign these J values to the Cu_2O_2 bridging units in the two chains. This appears to provide evidence that the correlation between $2J$ and ϕ/R_o may be usefully applied to extended systems.

To conclude, the results of the present study confirm the view that magnetic exchange interactions in copper(II) compounds of type II geometry can be examined in terms of the ϕ/R_o structural parameter but, on the other hand, clearly indicate that this is only possible when series of compounds having strongly related chemical and structural features are considered. Attempts are now being made to obtain additional members of this series of oxygen-bridged copper(II) compounds in order to refine the relationship between structure and exchange coupling.

Acknowledgment. O.P. thanks Professor William E. Hatfield for his hospitality during his stay at The University of North Carolina at Chapel Hill.

Registry No. **6**, 101835-60-3; **7**, 101858-56-4; *N*-methyl-1,3-propanediamine, 6291-84-5; 2-hydroxy-5-nitrobenzaldehyde, 97-51-8; 2-hydroxy-5-bromobenzaldehyde, 1761-61-1.

Supplementary Material Available: Listings of atomic displacements from mean planes, thermal parameters, and hydrogen atom coordinates (5 pages). Ordering information is given on any current masthead page.

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