the extent that the outer-sphere reorganization energy is separable into contributions from the two reactants, as is assumed in the Marcus theory, the self-exchange of the cobalt complex should not be required to fit poorly just because it is calculated from a ferrocene cross-reaction. However, the assumption that the reorganization processes are separable is much less likely to hold for the outer-sphere than for the inner-sphere term, since the reactants must significantly influence each other's solvation in the transition state, and the optimal conformation of the transition state is by definition a function of both partners as well as the solvent.

A pattern is emerging in the solvent-dependence studies that relates the linearity of the solvent-dependence plot and the activation parameters. The best behaved systems, in terms of the linearity of the ln k vs. $((1/D_{op}) - (1/D_s))$ plot, show much less variation in the entropy of activation, while those systems that are poorly behaved show erratic and highly negative activation entropies. This pattern is consistent with the deviations from theory originating in variation in precursor complex stability and structure and changes in electron-transfer probability.

In conclusion, we have shown that electron-transfer reactivity for a system with no charge–charge interactions required in forming the precursor complex is sensitive to ion pairing and the solvent. The solvent dependence is not well predicted by the Marcus theory, which assumes a dielectric continuum model for the solvent, and a solvent-invariant precursor complex structure. Important factors that contribute to the rate variation probably include changes in transition-state structure, electron-transfer distance, and the particulate nature of the solvent. The dielectric continuum model may be adequate for those cases in which the transition-state structure is not changed by solvation effects, as in intervalence compounds, but when more structural flexibility is available, the transition-state conformation is clearly sensitive to solvation factors.

Acknowledgment. The authors are pleased to acknowledge the financial assistance of the National Science Foundation through Grant CHE 8204102 and of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. Fe(Cp)$_2$, 102-54-5; Co(dmg)$_3$(BF)$_2^+$, 34248-47-0; CH$_3$CN, 75-05-8; (CH$_3$)$_2$CO, 67-64-1; C$_6$H$_5$NO$_2$, 98-95-3; (CH$_2$Cl)$_2$, 107-06-2.

Supplementary Material Available: Tables of concentration dependence, temperature dependence, second-order rate constant dependence on added electrolyte, and $\Delta E_{1/2}$ vs. temperature data (16 pages). Ordering information is given on any current masthead page.

Contribution from the Dipartimento di Chimica and Istituto di Mineralogia e Cristallografia,
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Exchange Interaction in Multinuclear Transition-Metal Complexes. 5.[1] Through-Bond Exchange Coupling in $Cu_2A(CH_3COO)_2\cdot 2CH_3OH$ (A^{2-} = Anion of *N*,*N'*-Bis(2-((*o*-hydroxybenzhydrylidene)amino)ethyl)piperazine)

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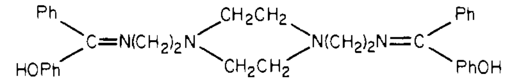
The synthesis, crystal structure, and magnetic properties are reported for the novel compound $Cu_2A(CH_3COO)_2\cdot 2CH_3OH$, where A^{2-} is the hexadentate anion of *N*,*N'*-bis(2-((*o*-hydroxybenzhydrylidene)amino)ethyl)piperazine:



The complex crystallizes in the triclinic space group $P\bar{1}$. Cell dimensions are a = 10.034 (3) Å, b = 14.057 (3) Å, c = 6.897 (2) Å, α = 92.93 (2)°, β = 97.47 (2)°, and γ = 89.64 (2)°. The structure was solved by the Patterson method and refined by full-matrix least-squares techniques to a conventional R value of 0.062. The unit cell comprises one $Cu_2A(CH_3COO)_2$ dinuclear molecule and two uncoordinated methanol molecules of solvation. There are no short intermolecular contacts between the dinuclear units. The coordination sphere of each copper atom is distorted square planar and contains two cis nitrogens and one phenolic oxygen of hexadentate A^{2-} and one oxygen atom of an acetate anion. The second oxygen of each carboxylate ligand is at a very weakly linking distance (2.795 (9) Å) of only one copper atom. The two copper atoms are bridged by a "chair"-shaped piperazine fragment of A^{2-}. The Cu–Cu separation is 6.881 (5) Å. The ESR spectrum of the compound indicates a predominantly $d_{x^2-y^2}$ ground state for the copper(II) ion. The angle formed by the Cu–N-(piperazine) bonds with the C–C bonds of piperazine is only 1.9°. The Cu_2(piperazine) bridging unit, therefore, has an almost ideal symmetry for propagating magnetic exchange between the copper atoms through a dominant through-bond mechanism. The magnetic susceptibility of the compound has been examined in the liquid helium to ~100 K range. A maximum in the susceptibility at ~18 K is indicative of an antiferromagnetic exchange interaction. The best fit to the Van Vleck equation derived from the $H = -2J(\hat{S}_A\cdot\hat{S}_B)$ Hamiltonian yielded $J = -10.42$ cm^{-1}. The efficiency of the piperazine bridge in propagating magnetic exchange between the copper(II) ions is discussed.

Introduction

Rapidly increasing efforts have been directed toward obtaining an adequate understanding of the viability of extended polyatomic bridging units to support magnetic exchange interactions between paramagnetic metal centers.[2] This problem has important implications to topics such as the nature of orbital interactions,[3] electron transfer in redox reaction precursors,[4] and biological electron-transport chains.[5] The ex-

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(1) Part 4: Chiari, B.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F. *Inorg. Chem.* **1983**, *22*, 2781.

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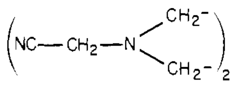
istence of a distance-dependent limit to superexchange has been recently debated.[6,7]

Relative to the exchange mechanism in multiatom-bridged cluster compounds, an important question involves the efficiency of σ-orbital pathways in propagating the exchange interactions. An analysis of this problem is complicated by the fact that in most reported complexes of this type the polyatomic bridges have both σ and π frameworks, with generally low local symmetries that prevent σ–π separability. On the other hand, magnetic susceptibility data for the relatively few characterized examples of dinuclear compounds having extended bridges without π systems are difficult to interpret with regard to the "mechanisms" that lead to the superexchange effect. For example, dinuclear copper(II) or vanadyl complexes bridged by Dabco (1,4-diazabicyclo[2.2.2]octane), which are expected from theory[3] to exhibit an appreciable antiferromagnetic exchange interaction, do not show any signs of an interaction in their susceptibility data down to 4.2 K.[8,9] Hendrickson, Stucky, and others, in a series of notable recent papers.[7,10,11] have reported significant magnetic exchange interaction ($-J \leq 2.8$ cm^{-1}) propagated between two titanium(III) metallocene units via bridges with saturated carbon atoms, over distances of ~6–~10 Å. However, the interpretation of the magnetic susceptibility data for these compounds was complicated by the possible presence of intermolecular interactions and the absence of information on what conformations the complexes assume in the solid state. Similar problems have been encountered in various studies[12-20] of organic biradicals where significant, although very small (order of magnitude $-J \sim 10^{-3}$ cm^{-1}), magnetic exchange interactions appear to be propagated by chains of σ bonds up to distances in excess of 20 Å. As a further example, we have recently reported[21] structural and magnetic information on $Cu_2L(CH_3COO)_2 \cdot 2CH_3OH$ (L^{2-} = anion of *N*,*N'*-bis(2-((*o*-hydroxybenzhydrylidene)amino)ethyl)-1,2-ethanediamine). This compound has a polymeric one-dimensional structure with alternate Cu_2O_2 and Cu_2(1,2-ethanediamine) bridging units. The latter fragment has the correct symmetry to interact via through-bond coupling; however, the extent of exchange interaction propagated by this bridging unit (Cu–Cu separation = 7.352 (2) Å) could be only tentatively assigned ($J = -7.88$ cm^{-1}) due to the need for alternating chain theory in the interpretation of the magnetic susceptibility data.

Such considerations indicate the need for studying systems that allow an independent and reliable determination of both the mechanism of the σ superexchange and the strength of the interaction. One such system is described in the present paper.

Experimental Section

Syntheses. AH_2. 1,4-Piperazinediylbis(ethanenitrile)



$$\left(NC\text{—}CH_2\text{—}N\begin{matrix}CH_2\text{-}\\ CH_2\text{-}\end{matrix}\right)_2$$

was prepared from piperazine and chloroethanenitrile, according to literature methods.[22] The ethanenitrile compound was then reduced to the corresponding amino derivative with use of a modified version of the procedure originally described by Mull et al.[23] An 8.5-g (0.05 mol) portion of 1,4-piperazinediylbis(ethanenitrile) was added to 75 mL of *N*-ethylmorpholine.[24] The mixture was heated under reflux in order to favor the dissolution of the solid and was then cooled to ~10 °C. Dry nitrogen was bubbled in the solution; then, a 4.5-g quantity of $LiAlH_4$ was added. The addition was made over a period of 1 h, with constant stirring and, as all subsequent manipulations, in a dry-nitrogen atmosphere. The reaction mixture was heated under reflux for ~1 h, with stirring, and then cooled at ~0 °C. To the cold solution were added, dropwise, 5 mL of water, 15 mL of a 5 M solution of NaOH in water, and then an additional 5 mL of water. A granular, white solid separated[25] that was easily filtered off. To the clear filtrate was added a 250-mL portion of diethyl ether. A yellow oil separated. After the mixture was kept at ~5 °C for ~12 h, the oil was decanted and dried under vacuum, at room temperature. The yellow, gummy mass, 8.5 g, was found to contain approximately 60% of the diamino derivative, by titration with HCl, in ethanol. The gummy mass was dissolved in 50 mL of anhydrous ethanol. To this solution was added, with stirring, a 60-mL portion of a 1 M solution of *o*-hydroxybenzophenone in the same solvent. After the mixture stood for ~12 h at room temperature, the new, yellow crystalline AH_2 was collected by filtration and dried under vacuum: yield 9.5 g (1.8×10^{-2} mol) (60%); mp 193–195 °C. The compound can be recrystallized from ethanol. Anal. Calcd for $C_{34}H_{36}N_4O_2$: C, 76.66; H, 6.81; N, 10.52. Found: C, 76.68; H, 6.58; N, 10.64.

$Cu_2A(CH_3COO)_2 \cdot 2CH_3OH$. A 0.3-g (1.50 mmol) quantity of $Cu(CH_3COO)_2 \cdot H_2O$ was added to a warm suspension of 0.4 g (0.75 mmol) of AH_2 (previously recrystallized from ethanol) in 65 mL of methanol. The addition was made over a period of 20 min, with constant stirring. A green solution was obtained. The warm solution was filtered; then, the flask containing the filtrate was placed in a Dewar containing hot water, in order to allow a slow cooling. After the mixture was allowed to stand for ~48 h, blue-green crystalline $Cu_2A(CH_3COO)_2 \cdot 2CH_3OH$ was collected by filtration in a dry-nitrogen atmosphere and dried under vacuum: yield 0.4 g (63%); mp 257–259 °C. Anal. Calcd for $C_{40}H_{48}N_4O_8Cu_2$: C, 57.20; H, 5.76; N, 6.67; O, 15.24; Cu, 15.13. Found: C, 57.25; H, 5.78; N, 6.61; O, 15.14; Cu, 15.25.

The compound is air sensitive and almost insoluble in common organic solvents. All solutions decompose rather rapidly, even when carefully dried and deoxygenated solvents are employed.

Chemical Analyses. These were performed by Mikroanalytisches Laboratorium, Elbach, West Germany.

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

Magnetic Measurements. The magnetic susceptibility measurements, in the liquid-helium to ~100 K range, were carried out on solid polycrystalline samples of about 20 mg, with a Faraday type magnetometer equipped with a continuous-flow cryostat designed by

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Cu_2A(CH_3COO)_2 \cdot 2CH_3OH$

atom	x/a	y/b	z/c	U, Å^2
Cu	0.3473 (1)	0.1393 (1)	0.3327 (2)	*a*
O(1)	0.2575 (7)	0.1869 (5)	0.5433 (10)	*a*
O(2)	0.1753 (7)	0.0773 (5)	0.2264 (9)	*a*
O(3)	0.2639 (8)	−0.0461 (6)	0.3825 (12)	*a*
N(1)	0.4972 (7)	0.2264 (5)	0.4084 (10)	*a*
N(2)	0.4580 (8)	0.0813 (5)	0.1263 (10)	*a*
C(1)	0.2951 (6)	0.2560 (4)	0.6744 (8)	0.029 (2)
C(2)	0.2060 (6)	0.2735 (4)	0.8118 (8)	0.044 (3)
C(3)	0.2359 (6)	0.3431 (4)	0.9628 (8)	0.042 (3)
C(4)	0.3549 (6)	0.3953 (4)	0.9763 (8)	0.046 (3)
C(5)	0.4439 (6)	0.3778 (4)	0.8389 (8)	0.033 (2)
C(6)	0.4140 (6)	0.3081 (4)	0.6879 (8)	0.024 (2)
C(7)	0.5158 (8)	0.2895 (6)	0.5549 (12)	0.022 (2)
C(8)	0.6434 (5)	0.3444 (4)	0.5931 (9)	0.023 (2)
C(9)	0.7457 (5)	0.3144 (4)	0.7337 (9)	0.040 (3)
C(10)	0.8628 (5)	0.3684 (4)	0.7795 (9)	0.048 (3)
C(11)	0.8776 (5)	0.4523 (4)	0.6847 (9)	0.054 (3)
C(12)	0.7752 (5)	0.4823 (4)	0.5441 (9)	0.052 (3)
C(13)	0.6581 (5)	0.4283 (4)	0.4982 (9)	0.040 (3)
C(14)	0.6046 (9)	0.2092 (7)	0.2838 (14)	0.034 (2)
C(15)	0.5446 (9)	0.1639 (6)	0.0917 (13)	0.032 (2)
C(16)	0.5412 (9)	−0.0009 (6)	0.2102 (13)	0.033 (2)
C(17)	0.3788 (9)	0.0472 (7)	−0.0576 (13)	0.036 (3)
C(18)	0.1646 (11)	−0.0057 (8)	0.2932 (16)	0.043 (3)
C(19)	0.0310 (13)	−0.0522 (9)	0.2569 (18)	0.066 (3)
O(4)	0.9692 (11)	0.2114 (7)	0.1522 (15)	0.093 (3)
C(20)	0.9624 (13)	0.2731 (9)	0.3168 (19)	0.070 (4)

[a] Anisotropic temperature factors given in the supplementary material.

Oxford Instruments. Magnetic inductions of about 9 kG were used. Mercury tetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard.[26] The absolute accuracy on temperature is estimated at ±0.1 K, and the relative accuracy on the apparent change in weight of the sample when the magnetic field is applied is better than 1%. All data were corrected for diamagnetism (-146×10^{-6} cgsu/mol per copper ion, as calculated from Pascal's constants) and for temperature-independent paramagnetism, $N\alpha$, of copper(II) (estimated to be 60×10^{-6} cgsu/Cu atom).

X-ray Data and Structure Solution. The X-ray measurements were done with a computer-controlled Philips PW 1100 single-crystal diffractometer, with graphite-monochromatized Mo Kα radiation. A crystal with dimensions 0.4 × 0.2 × 0.1 mm was selected and sealed into a glass capillary under nitrogen. The determination of the cell parameters was made by a least-squares method applied to the setting angles of 25 reflections. Crystals are triclinic, space group $P\bar{1}$ (as confirmed by the structural analysis). Lattice dimensions are a = 10.034 (3) Å, b = 14.057 (3) Å, c = 6.879 (2) Å, α = 92.93 (2)°, β = 97.47 (2)°, and γ = 89.46 (2)°. There is one $C_{38}H_{40}N_4O_6Cu_2 \cdot 2CH_3OH$ unit in a cell of 960.8 Å^3. The molecular weight is 839, the calculated density is 1.450 g cm^{-3}, the linear absorption coefficient is μ = 11.4 cm^{-1}. The intensity data were collected in the range $2° \le \vartheta \le 20°$ by the $\omega/2\vartheta$ scan technique (scan speed 0.04° s^{-1}; scan width 1.3°). Weaker reflections (integrated intensity lower than 1000 counts) were measured two times. To check the experimental conditions, three reflections were monitored every 180 min, their intensities oscillated within 3%.

The intensities of 1779 independent reflections were corrected for Lorentz–Polarization factors. An absorption correction was applied on the basis of the variation in intensity during the azimuthal scans of some reflections (method of North et al.[27]); transmission factors were in the range 0.95–0.81. A total of 595 reflections having $I \le 3\sigma(I)$ were omitted from further computation. The structure was solved by the Patterson method and refined by full-matrix least-squares methods with use of the program SHELX-76.[28] The phenyl groups were constrained to perfect hexagons (C–C = 1.395 Å) and refined as rigid groups. The hydrogen atoms, except for those pertaining to the methyl groups, were included at their calculated positions (C–H = 1.08 Å). The overall isotropic thermal parameter was U = 0.08 Å^2 for the hydrogen atoms of the phenyl groups and U = 0.06 Å^2 for the others. Anisotropic thermal parameters were refined for Cu, O, and N atoms. The refinement converged at R(unweighted) = 0.062 and R(weighted) = 0.064, for 1204 observed reflections and 120 parameters ($R_w = [\sum w(|F_o| - |F_c|)^2]^{1/2}/(\sum w F_o^2)^{1/2}$; $w = 1/(\sigma^2(F_o)$

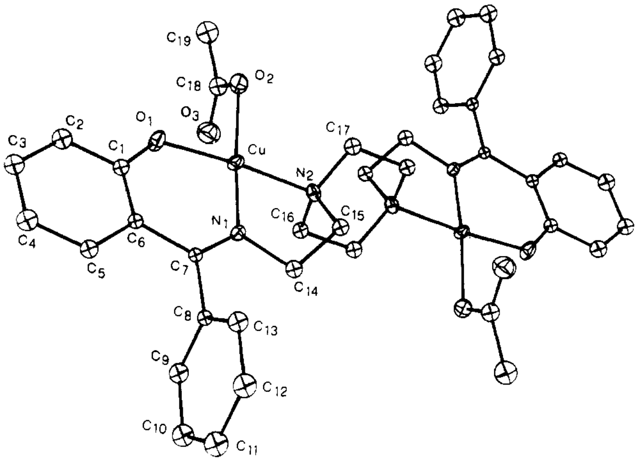

Figure 1. Molecular structure of $Cu_2A(CH_3COO)_2 \cdot 2CH_3OH$. The solvent molecules and hydrogen atoms are not shown for clarity.

Table II. Bond Lengths (Å) for $Cu_2A(CH_3COO)_2 \cdot 2CH_3OH$[a]

Cu–O(1)	1.895 (6)	O(2)–C(18)	1.286 (12)
Cu–O(2)	1.974 (6)	C(18)–O(3)	1.205 (13)
Cu–N(1)	1.945 (7)	C(18)–C(19)	1.482 (16)
Cu–N(2)	2.048 (7)	N(2)–C(16)	1.515 (12)
O(1)–C(1)	1.314 (8)	N(2)–C(17)	1.464 (11)
C(6)–C(7)	1.471 (10)	C(16)–C(17)′	1.520 (12)
C(7)–C(8)	1.485 (10)	C(20)–O(4)	1.399 (15)
C(7)–N(1)	1.304 (11)	Cu···O(3)	2.795 (9)
N(1)–C(14)	1.473 (12)	Cu···Cu′	6.881 (5)
C(14)–C(15)	1.492 (13)	O(2)···O(4)″	2.804 (10)
C(15)–N(2)	1.502 (12)		

[a] Symmetry code: (′) $1 - x, -y, -z$; (″) $1 - x, y, z$.

Table III. Bond Angles (deg) in $Cu_2A(CH_3COO)_2 \cdot 2CH_3OH$[a]

O(1)-Cu-O(2)	86.3 (3)	C(7)-N(1)-Cu	129.3 (6)
O(1)-Cu-N(1)	91.8 (3)	C(7)-N(1)-C(14)	119.3 (7)
O(1)-Cu-N(2)	174.1 (3)	Cu-N(1)-C(14)	111.3 (6)
O(2)-Cu-N(1)	166.5 (3)	N(1)-C(14)-C(15)	108.8 (8)
O(2)-Cu-N(2)	96.7 (3)	C(14)-C(15)-N(2)	109.6 (7)
N(1)-Cu-N(2)	86.4 (3)	C(15)-N(2)-Cu	101.8 (5)
C(1)-O(1)-Cu	128.3 (5)	C(15)-N(2)-C(16)	111.7 (7)
O(1)-C(1)-C(2)	114.1 (4)	C(15)-N(2)-C(17)	110.4 (7)
O(1)-C(1)-C(6)	125.8 (4)	C(16)-N(2)-Cu	109.8 (5)
C(1)-C(6)-C(7)	122.7 (4)	C(17)-N(2)-Cu	114.7 (6)
C(5)-C(6)-C(7)	117.2 (4)	C(16)-N(2)-C(17)	108.4 (6)
C(6)-C(7)-C(8)	117.9 (6)	N(2)-C(16)-C(17)′	110.8 (6)
C(6)-C(7)-N(1)	122.0 (7)	N(2)-C(17)-C(16)′	115.2 (7)
C(8)-C(7)-N(1)	120.1 (7)	O(2)-C(18)-O(3)	121.1 (10)
C(7)-C(8)-C(9)	119.4 (4)	O(3)-C(18)-C(19)	121.3 (11)
C(7)-C(8)-C(13)	120.5 (4)	O(2)-Cu-O(3)	51.8 (3)

[a] For symmetry code see Table II.

Table IV. Deviations of Atoms from the Least-Squares Plane through the Square around Cu[a]

atom	Δ	atom	Δ
Cu	0.05	N(1)	−0.18
O(1)	0.16	N(2)	0.14
O(2)	−0.17		

[a] Esd's are less than 0.02 Å. [b] Equation of the plane (in the form $Ax + By + Cz = D$) in direct space is $2.654x - 10.717y + 4.036z = 0.718$.

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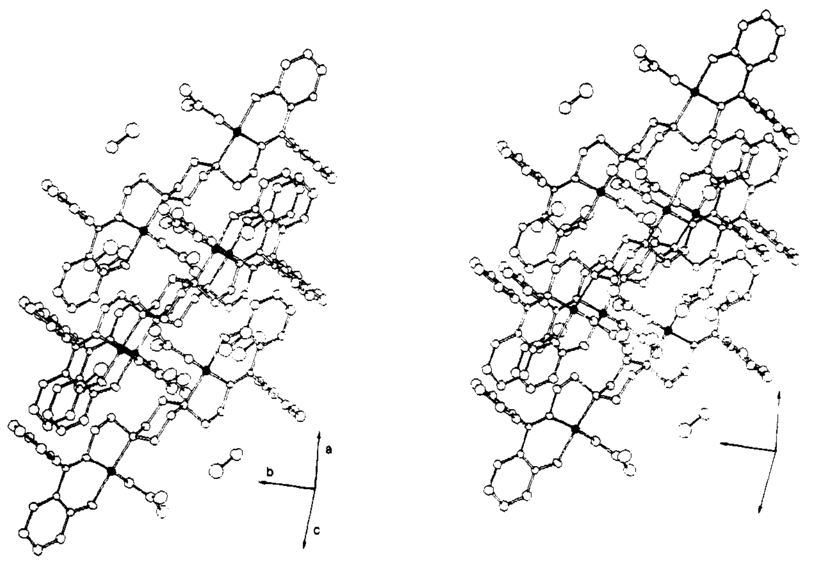

Figure 2. Stereoview of the molecular environment in the structure of $Cu_2A(CH_3COO)_2 \cdot 2CH_3OH$. The view is approximately down [101].

$+ 0.0134F_o^2$)). The atomic scattering factors were taken from ref 29 for Cu and from ref 28 for O, N, C, and H. The correction for anomalous dispersion was included.

Results

Description of the Structure. Structural information about $Cu_2A(CH_3COO)_2 \cdot 2CH_3OH$ is reported in Figure 1 and Tables I–IV. The unit cell comprises one $Cu_2A(CH_3COO)_2$ binuclear molecule and two uncoordinated methanol molecules of solvation. The halves of the binuclear complex are related by crystallographic inversion symmetry.

The coordination spheere of each copper atom contains two cis nitrogens (Cu–N(1) = 1.945 (7) Å, Cu–N(2) = 2.048 (7) Å) and one phenolic oxygen (Cu–O(1) = 1.895 (6) Å) of hexadentate A^{2-} and one oxygen atom of an acetate anion (Cu–O(2) = 1.974 (6) Å). The second oxygen atom of each carboxylate ligand is at a very weakly linking distance of only one copper atom (Cu–O(3) = 2.795 (9) Å). The N(1), N(2), O(1), O(2), and Cu atoms lie only approximately in a plane (Table IV). The dihedral angle between the CuO(1)N(1) and CuO(2)N(2) planes, τ, that is 14° indicates a distortion from planarity toward a tetrahedral environment around the copper atom. A rather loose O···O contact of 2.804 (10) Å between the coordinated acetate oxygen, O(2), and the oxygen atom, O(4), of a methanol molecule may be indicative of some hydrogen-bonding interaction.

The two copper atoms are bridged by a "chair"-shaped piperazine fragment of A^{2-}. The Cu–N(piperazine) directions, when viewed along an N–C bond, form an angle of only 1.9° with the piperazine C–C bonds. There is a dihedral angle of 58° between the best coordination plane and the plane formed by the four piperazine carbons. Bond distances and angles of the A^{2-} ligand are normal. The Cu···Cu separation is 6.881 (5) Å. The N(2)···N(2)′ separation is 2.98 (1) Å.

In the crystal, since there is only one molecule per unit cell, the molecules are packed along the three crystallographic axes. A stereoscopic packing diagram showing how the binuclear molecules are related by the two shorter translations, *a* and *c*, is given in Figure 2. Intermolecular contacts between non-hydrogen atoms of the dinuclear units are always longer than the sums of van der Waals radii by more than 1.5 Å. The shortest intermolecular contacts to the copper atoms involve the uncoordinated acetate oxygens, O(3), and are in a plane that extends along the [101] direction. The distance between O(3) and Cu″ (at $1 - x, \bar{y}, 1 - z$) is 4.360 (9) Å. The Cu–O(3)–Cu″ angle is 114°, and the Cu···Cu″ distance, that is the shortest M–M separation in the crystal, is 5.381 (5) Å.

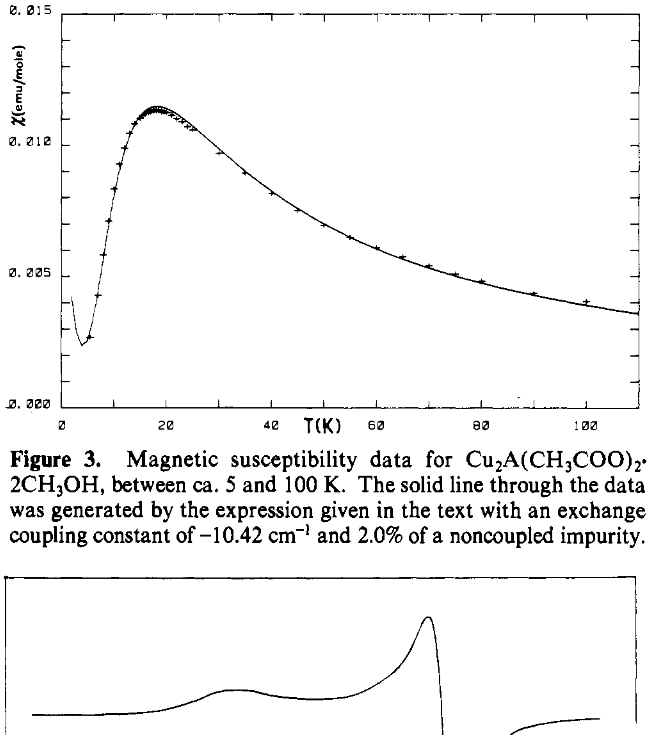

Figure 3. Magnetic susceptibility data for $Cu_2A(CH_3COO)_2 \cdot 2CH_3OH$, between ca. 5 and 100 K. The solid line through the data was generated by the expression given in the text with an exchange coupling constant of -10.42 cm^{-1} and 2.0% of a noncoupled impurity.

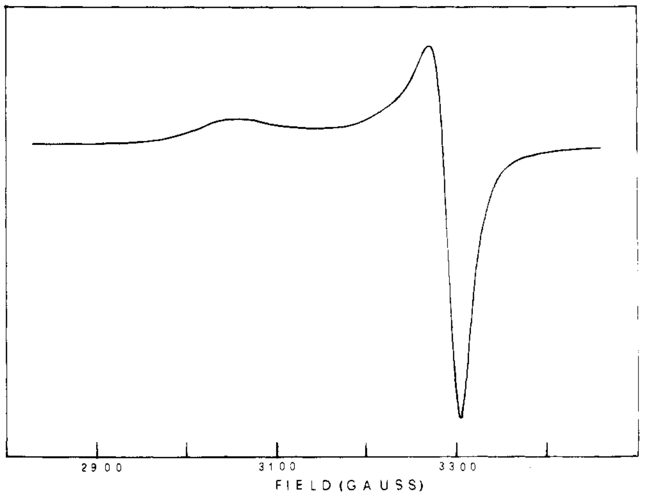

Figure 4. Room-temperature powder X-band ESR spectrum for $Cu_2A(CH_3COO)_2 \cdot 2CH_3OH$.

Magnetic Properties. Variable-temperature susceptibility data for $Cu_2A(CH_3COO)_2 \cdot 2CH_3OH$ are given in Figure 3. The presence of an antiferromagnetic interaction is clearly indicated by the maximum at ca. 18 K in the χ_M vs. T curve.

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

The μ_{eff}/Cu value ranges from 1.80 μ_B at 100 K to 0.34 μ_B at 5.5 K.

The X-band ESR spectra of powdered samples of the compound (Figure 4) are axial with $g_{\parallel} = 2.219$ and $g_{\perp} = 2.051$ ($g_{av} = 2.107$). The spectra were taken at ca. 300 and ca. 77 K. There were no additional features (Cu hyperfine, zero-field splitting, or half-field $\Delta M_S = 2$ transition) from one temperature to the other.

The usual dipolar coupling approach of Van Vleck, with a perturbing Hamiltonian $-2J(\hat{S}_A \cdot \hat{S}_B)$ and $S_A = S_B = {}^1/_2$, was used to fit the experimental susceptibility data. The magnetic susceptibility expression was

$$\chi_M(\text{per Cu}) = \frac{Ng^2\beta^2}{3kT}\left(1 + \frac{1}{3}X^2\right)^{-1}(1-p) + \left(\frac{Ng^2\beta^2}{4kT}\right)p + N\alpha \quad (1)$$

where $X = \exp(-J/kT)$. The parameter p gauges the amount of a possible magnetically dilute copper(II) impurity. Other symbols have their usual meaning. The function that was minimized in curve fitting, with use of a nonlinear fitting routine written in our laboratory, was $F = \sum(\chi_i^{obsd} - \chi_i^{calcd})(\chi_i^{obsd})^{-1}$. The experimentally determined ESR g value of 2.107 and the temperature-independent paramagnetism, $N\alpha$, assigned as previously indicated were held constant during all the fitting calculations. The average g value for the monomeric impurity was assumed to be the value found for the binuclear compound. The best fit to the data yielded $J = -10.42$ cm^{-1} and $p = 0.020$. The agreement factor F was 1.4×10^{-4} for 38 observations. The fit is illustrated in Figure 3.

Discussion

A main purpose of the present work was to study a multiatom-bridged dinuclear system for which the M–M σ pathway of superexchange could be specified in detail and to determine the strength (and sign) of magnetic exchange associated with it.

The novel $Cu_2A(CH_3COO)_2 \cdot 2CH_3OH$ affords this opportunity.

The X-ray analysis of the compound does not reveal any close contacts between dinuclear units that may be regarded as bonding interactions. This, by itself, is strongly indicative that individual dinuclear units interact weakly in the solid. This view is in line with the results of several detailed ESR studies[30] performed on undiluted, monomeric paramagnetic compounds involving intermolecular distances comparable with those observed in the present case. These results uniformly indicate that the intermolecular exchange interactions are on the order of 10^{-2} cm^{-1}. The same order of magnitude is suggested by an analysis[31] of the line width (ca. 35 G, at room temperature) of the $g_{\perp}$ signal in the ESR spectra of powdered samples of our compound. Therefore, although (as a reviewer has correctly noted) the absence of copper hyperfine splitting in the spectrum of $Cu_2A(CH_3COO)_2 \cdot 2CH_3OH$ could result from intermolecular exchange interactions (an electron exchanging between dinuclear units will experience an average of copper nuclear hyperfine states), it is most likely that these interactions are very small.

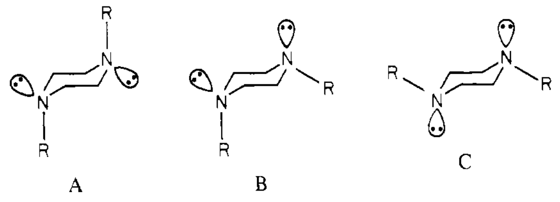
An even stronger indication of the essentially intramolecular nature of the antiferromagnetic interaction present in $Cu_2A(CH_3COO)_2 \cdot 2CH_3OH$ is given by the magnetic susceptibility data. Figure 3 shows that the dimer model rather nicely reproduces the susceptibility data for the compound in the temperature region where the maximum susceptibility is observed. It is well-known, on both experimental and theoretical grounds, that the principal effect of the presence of significant extended interactions between dimers throughout the solid is to broaden the susceptibility peak calculated from the dimer model, to shift it to a lower temperature, and to reduce its height.[21,32] None of these features are observed here. In addition, no significant improvement of the fit shown in Figure 3 was achieved by substituting the term $T - \theta$ for T in eq 1, a common procedure, although not strictly correct theoretically, for obtaining information about interdimer interactions and other complicating factors.[33]

To conclude, there seems to be little doubt that the observed antiferromagnetic exchange interaction occurs is an essentially intramolecular fashion.

It may be noted at this point that an extended M–O···M arrangement somewhat similar to that found along [101] for our compound has been very recently observed in the structure of monomeric $Cp_2TiO_2CC_6H_5$.[34] Since, apparently, a linear-chain model better fits the magnetic susceptibility data ($J = -3.3$ cm^{-1}) for this compound than a previously proposed dimer model, it has been suggested that the extended M–O···M arrangement could be responsible for the unexpected antiferromagnetic exchange that is observed (perhaps through some change in the molecular packing at low temperatures). The use of a linear-chain model gives an unreasonable fit to our susceptibility data.

In the present dinuclear units the Cu···Cu separation of 6.881 Å is large enough to effectively preclude significant "direct" overlap of metal ion orbitals. The observed antiferromagnetic coupling between the copper atoms must be propagated by the piperazine bridge, and, since the piperazine framework lacks a π system, only a σ type of exchange pathway can be present.

There are considered to be two mechanisms that underlie the viability of piperazine to mediate exchange interaction between the copper ions, namely direct N···N delocalization (through space) or via the two intervening C–C bonds (through bond).[35] The amount of through-bond (or through-space) mixing has a strong conformational dependence. For example, for the three chair conformations A, B, and C that are conceivable as possibilities for unsubstituted or *N*,*N*′-substituted piperazines, one expects a dominant through-bond interaction for A, in which the C–C bonds are aligned with the N lone-pair axes, much smaller through-bond interactions for B and C, and the largest through-space interaction for B. The interaction energies, for R = H, have been estimated to be 1.654, 0.476, and 0.168 eV for A, B, and C, respectively.[36] These figures are consistent with the absence of any splitting in the photoelectron spectrum of C (with R = CH_3),[36] for which a reliable assignment of the diequatorial *N*-methyl conformation



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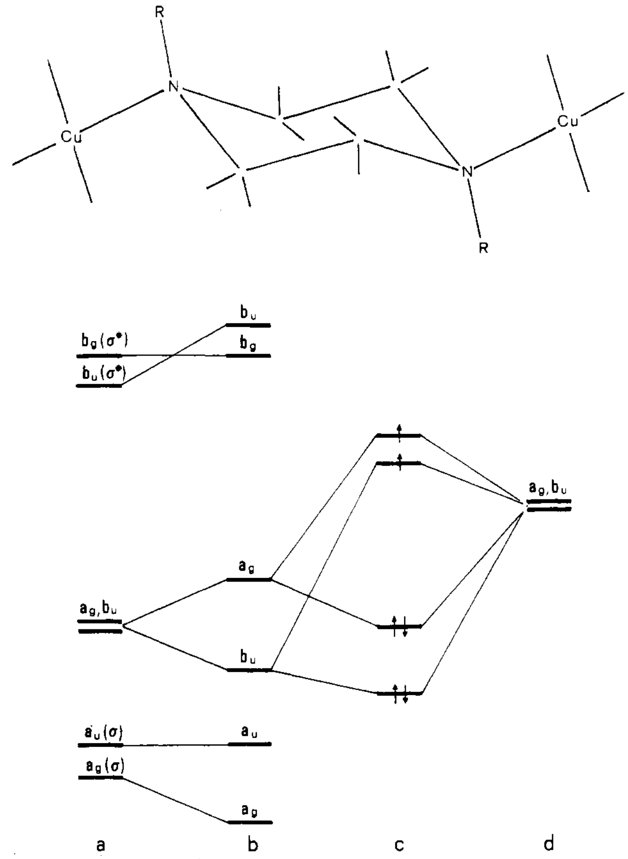

Figure 5. Schematic picture of the Cu_2(piperazine) bridging unit and a qualitative interaction diagram (assuming local C_{2h} symmetry) showing the splitting of the two highest occupied, metal-based MO's: (a, :) "before–after" picture of the interaction of the $a_g(n_1 + n_2)$ and $b_u(n_1 - n_2)$ combinations of the piperazine N lone pairs with the C–C σ bond orbitals of the same symmetry; (c) splitting of the metal-based orbitals as a consequence of their interaction with the nitrogen orbitals; (d) symmetric and antisymmetric combinations of the metal-based $d_{x^2-y^2}$ orbitals. According to current theoretical models the square of the energy separation between the a_g and b_u antibonding MO's is a measure of the difference in energy between the triplet (shown) and singlet molecular states.

was made on the basis of its solution NMR spectrum[37] and microwave spectrum.[38]

The combined ESR and X-ray crystallographic data for $Cu_2A(CH_3COO)_2 \cdot 2CH_3OH$ show that the Cu_2(piperazine) bridging unit has an almost ideal symmetry for propagating magnetic exchange between the copper atoms through a dominant through-bond mechanism.

The X-band ESR spectrum of the compound, notwithstanding the observed tetrahedral distortion of the environment around the metal, show a predominantly σ-type $d_{x^2-y^2}$ ground state, and the angle formed by the Cu–N(piperazine) directions with the crucial coupling C(16)–C(17)′ or C(16)′–C(17) bonds are, when viewed along an N–C bond, only 1.9°.

A schematic view of the Cu_2(piperazine) fragment and a qualitative interaction diagram (assuming local C_{2h} symmetry) showing the splitting of the highest occupied, metal-based MO's are given in Figure 5. According to current theoretical models[3,39] for magnetic exchange interaction, it is this splitting that determines the antiferromagnetic coupling.

As mentioned above, the Cu···Cu separation in the Cu_2(piperazine) bridging unit is 6.881 (5) Å, and a consideration of the σ-bonded pathway of superexchange increases the path distance between the copper ions to ca. 8.65 Å. The present structural and magnetic results, therefore, represent direct evidence supporting the view[3,21] that through-bond coupling can provide a mechanism for propagating magnetic exchange over long distances.

A final point for discussion is the magnitude of the J value, $-10.42\ cm^{-1}$, observed for $Cu_2A(CH_3COO)_2 \cdot 2CH_3OH$. An adequate interpretation of the magnitude of the exchange coupling, particularly as it relates to the splitting in energy between symmetric and antisymmetric combinations of the nitrogen lone pairs in the bridge (~1.7 eV), clearly requires a detailed theoretical calculation.

Meanwhile, the magnitude of the exchange interaction in the title compound may be judged, in a statistical way, upon consideration of presently existing structural data and superexchange data for long-range antiferromagnetic exchange in insulating solids. Coffman and Buettner[6] have proposed, on the basis of these data, a limit function that gives a limiting magnitude for the J parameter for a given internuclear distance R. Assuming an $H = -2J(\hat{S}_A \cdot S_B)$ Hamiltonian, the form of this function is

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

For the Cu···Cu distance observed in our compound, 6.881 (5) Å, the calculated limiting J value is $-28.2\ cm^{-1}$. The fact that the experimental data point ($-10.42\ cm^{-1}$) is among those that are closest to the limiting curve defined by eq 2 seems to provide statistical evidence for the efficiency of the σ pathway of superexchange described for $Cu_2A(CH_3COO)_2 \cdot 2CH_3OH$.

Registry No. $Cu_2A(CH_3COO)_2 \cdot 2CH_3OH$, 90605-86-0; AH_2, 90605-87-1; 1,4-piperazinediylbis(ethanenitrile), 5623-99-4; *o*-hydroxybenzophenone, 117-99-7.

Supplementary Material Available: Listings of the hydrogen atom coordinates, anisotropic temperature factors, and observed and calculated structure factor amplitudes for $Cu_2A(CH_3COO)_2 \cdot 2CH_3OH$ (8 pages). Ordering information is given on any current masthead page.

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