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# Magneto-Structural Correlations and ESR Spectra of Dinuclear Copper(II) Complexes of Thiophenophane Ligands Containing Thioether Donor Atoms

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Magnetic susceptibility data on powdered samples of the dinuclear complexes $(CuCl_2\cdot L1)_2$ and $(CuCl_2\cdot L2)_2$ (L1 = 2,5,8-trithia[9](2,5)thiophenophane; L2 = 2,5,9,12-tetrathia[13](2,5)thiophenophane) have been collected in the temperature range 5-297 K. The data have been fitted to the Friedberg magnetization expression containing a molecular field correction, and from the fit, values for intradimer exchange, $-2J$ [7.4 (3) $cm^{-1}$, $(CuCl_2\cdot L1)_2$; 20.8 (1) $cm^{-1}$, $(CuCl_2\cdot L2)_2$], interdimer exchange, $J'$ [-0.9 (1) $cm^{-1}$, $(CuCl_2\cdot L1)_2$; -0.3 (3) $cm^{-1}$, $(CuCl_2\cdot L2)_2$], and $g$ [2.066 (9), $(CuCl_2\cdot L1)_2$; 2.08 (1), $(CuCl_2\cdot L2)_2$] have been obtained. ESR spectra yield values for $g_\parallel$ and $g_\perp$ that give average $g$ values for $(CuCl_2\cdot L1)_2$ and $(CuCl_2\cdot L2)_2$ of 2.077 and 2.084, respectively. The experimental results are correlated with structural details of the complexes.

## Introduction

Recent developments in the field of superconductors have kindled considerable interest in the electronic structures of substances that by conventional criteria should be composed of noninteracting molecules or ions and yet show signs of long-range internal communication of electronic or magnetic information.[1] The mechanisms of these interactions may be studied by a variety of techniques, but measurements of magnetic susceptibility and ESR spectra seem particularly sensitive probes.[2-5] Both types of measurement are strongly influenced by sometimes subtle structural changes, and magneto-structural correlations are therefore an important route to the understanding of long-range atomic interactions.[6,7]

The simplest model system for such a study would involve just two interacting atoms and one electron. A reasonable approximation that has some practical relevance is a binuclear copper(II) system having two interacting nuclei each bearing a single electron. Such a system is relevant in the sense that chemists are keenly interested in the role, properties, and interactions of copper atoms in biomolecules like laccase and the oxyhemocyanins where magnetic interactions have been detected and in some cases are large enough to render copper(II) ESR silent.[8,9]

A dinuclear copper(II) molecule is a simple system because there is only one unpaired electron per copper atom, and in principle it should be possible to prepare species that have reasonably isolated dimers in the solid state.[10-12] Under these conditions, the magnetic interactions of greatest importance are likely to be those within a dimer rather than those between dimers, and the intradimer interaction can be relatively easily described mathematically.[3,13-15] Magneto-structural correlations involving systems of this type have shown clearly that magnetic interactions between pairs of copper(II) sites that are linked by one or more bridging atoms are to be expected and may produce splittings between the singlet ground state and triplet excited state of 1000 $cm^{-1}$ or more.[16] Even at Cu-Cu separations of 11-12 Å, which is far greater than the separation of 2.56 Å found in copper metal,[17] an exchange interaction of $J = -70$ $cm^{-1}$ has been reported.[18]

When interacting coppers are joined by one or more bridges, the interaction (or exchange) occurs through both the $\sigma$ and $\pi$ orbitals of those ligands bridging the magnetically active copper orbitals. The efficiency of this superexchange mechanism is affected by the coordination geometry at the metal centers, the nature of the bridging ligand, the bridgehead angle, and the fold angle between the planes defined by a pair of copper and a pair of bridge atoms, as well as a number of other factors. Discussion of these is available in the literature.[3,16]

Perhaps as a result of the desire to develop models for the ESR-silent type III copper(II) enzymes, recent interest has devolved mainly onto synthetic compounds containing pairs of strongly coupled copper(II) centers where the singlet-triplet splitting, $-2J$, is >200 $cm^{-1}$. In contrast, we have synthesized a pair of binuclear copper(II) species (Figure 1 and 2), the structural characteristics of which we have reported previously,[19] that have rather limited exchange ($-2J < 21$ $cm^{-1}$). For these compounds, where intradimer exchange is only moderate and not large enough to swamp smaller effects, it has been possible to detect the much smaller interdimer exchange ($-J' < 1$ $cm^{-1}$) and to observe the effects upon both $-2J$ and $-J'$ of small structural alterations.

## Experimental Section

The preparations and structural details of both $(CuCl_2\cdot L1)_2$ and $(CuCl_2\cdot L2)_2$ have been previously described.[19]

Variable-temperature magnetic susceptibility data on powder samples were obtained in the range 5-300 K by using an Oxford Instruments superconducting Faraday magnetic susceptibility system with a Sartorius 4432 microbalance. Main solenoid fields of 1.5 and 2.0 T and a gradient field of 10 $T\cdot m^{-1}$ were employed, and the susceptibility data were corrected for diamagnetism by using Pascal constants. A value of $60 \times 10^{-6}$ cgsu/mol of copper *atoms* was used as a correction for temperature-independent paramagnetism (TIP) where such a term appears in our calculations.[20] The calibrant was $HgCo(NCS)_4$. Curve fittings were carried out by using a locally modified program for nonlinear weighted least squares as proposed by Wentworth[21] on the basis of work by Deming.[22]

ESR spectra of polycrystalline samples and of dichloromethane solutions were recorded at room temperature and 77 K on a Bruker ESP-300 X-band spectrometer at ~9.5 GHz.

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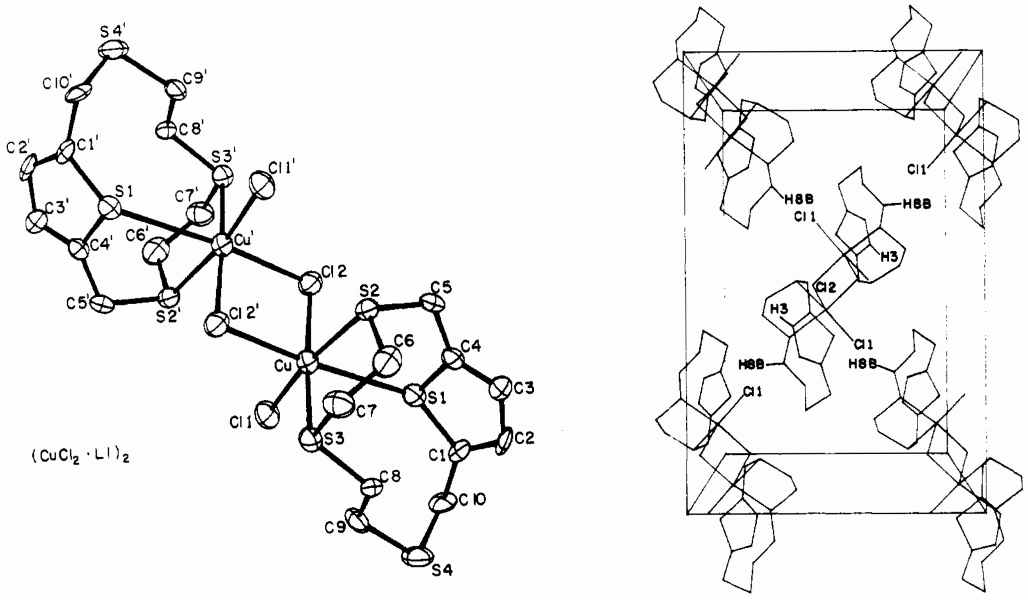

**Figure 1.** Atom-numbering scheme and molecular packing in crystals of $(CuCl_2{\cdot}L1)_2$.

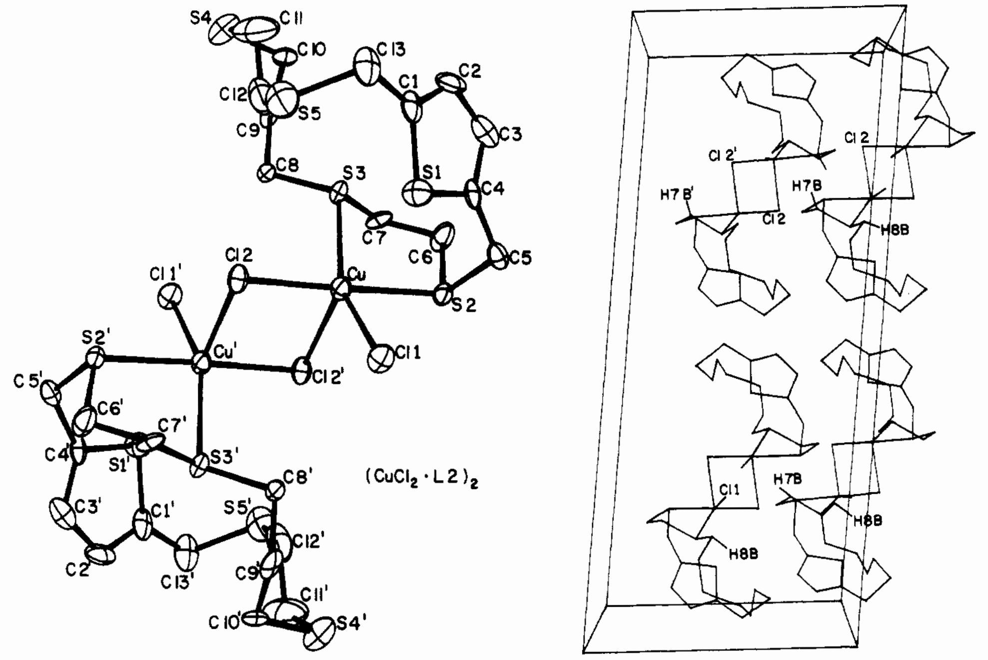

**Figure 2.** Atom-numbering scheme and molecular packing in crystals of $(CuCl_2{\cdot}L2)_2$.

## Results and Discussion

Plots of either $\chi_M T$ versus $T$ or $\chi_M$ versus $T$ (Figures 3 and 4) clearly indicate the presence of antiferromagnetic interactions that become apparent only at low temperatures.

From eq 1, a value of $-2J$, the exchange interaction, may be estimated[23] from the temperature ($T_M$) at which the susceptibility is a maximum.

$$\frac{-2J}{kT_M} \sim \frac{8}{5} \tag{1}$$

In both compounds, the exchange or singlet–triplet splitting in the dimers is not large (5–25 cm$^{-1}$). It is reasonable therefore to expect small magnetic interactions between dimers to be relatively more significant in these compounds and therefore more readily detectable than in those where the major interaction is a much stronger ($>10^2$ cm$^{-1}$) intradimer exchange.

The mathematical model often employed to describe magnetic interactions between copper atoms in isolated dimers is that developed by Bleaney and Bowers[24] using the isotropic (Heisenberg) exchange Hamiltonian (eq 2) to solve the Van Vleck equation.[3]

$$\hat{H} = -2JS_1{\cdot}S_2 \tag{2}$$

The Bleaney–Bowers equation, (3), and its variations[25] in which $\chi_M$ is expressed per mole of metal atoms and $N\alpha$ is a correction for temperature-independent paramagnetism are based on several assumptions.

$$\chi_M = \frac{Ng^2\beta^2}{kT}\left[\frac{1}{3 + \exp(-2J/kT)}\right] + N\alpha \tag{3}$$

It is assumed that inversion symmetry exists so that $S_1 = S_2$ and $g_1 = g_2$ and that intradimer interactions are much stronger than interdimer ones. Furthermore, the Bleaney–Bowers model requires that the lowest energy Zeeman triplet level lie significantly above the singlet level (or that $|J| > g\beta H$). Although our compounds do have inversion symmetry, neither of the remaining

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**Table I**

| | Friedberg model with molecular field correction | | | | ESR | | |
|---|---|---|---|---|---|---|---|
| compd | $-2J$, cm$^{-1}$ | $-J'$, cm$^{-1}$ | $g$ | $(\sigma_{\rm fit}{}^2)_{\rm ext}$ | $g_\perp$ | $g_\parallel$ | $g_{\rm av}$ |
| $(CuCl_2{\cdot}L1)_2$ | 7.4 (3) | 0.9 (1)<br>($z$ = 6) | 2.066 (9) | $5.79 \times 10^{-10}$ | 2.04 | 2.14 | 2.08 |
| $(CuCl_2{\cdot}L2)_2$ | 20.8 (1) | 0.3 (3)<br>($z$ = 4) | 2.08 (1) | $1.33 \times 10^{-8}$ | 2.04 | 2.18 | 2.08 |

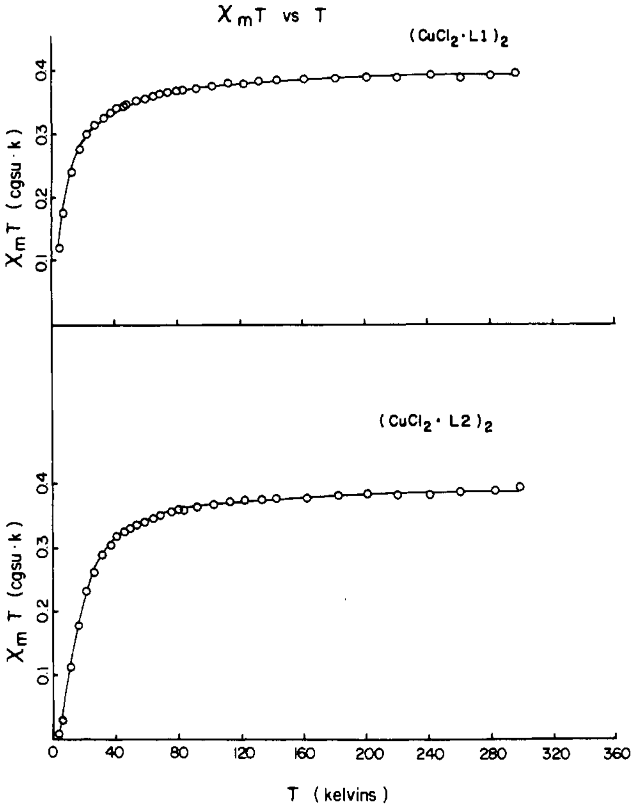

Figure 3. Molar susceptibility (powder) multiplied by absolute temperature as a function of temperature.

conditions is met with certainty a priori. Not surprisingly, therefore, the best fits of the data to the Bleaney–Bowers model give $g$ values for both compounds that do not compare well with those found by ESR spectroscopy (Table I). Furthermore, the fits were poorest near the maxima in the curves, suggesting the presence of interdimer exchange.

The data were then fitted to the magnetization expression (eq 4) developed by Friedberg[26] utilizing the exchange Hamiltonian in eq 2.

$$M = \frac{Ng\beta \sinh (g\beta H/kT)}{\exp(|-2J|/kT) + 2 \cosh (g\beta H/kT) + 1} \qquad (4)$$

In (4), $M$ is the magnetization of 1 mol of cupric ions and $\chi_M - N\alpha = M/H$. This expression is based upon a model involving interactions of pairs of adjacent copper atoms and includes the Zeeman terms of an energetically nearby triplet level. The results obtained by fitting the data to (4) were a marked improvement over those obtained from the Bleaney–Bowers model, and the $g$ values were closer to those obtained by ESR spectroscopy. The fit remained poor near $T_M$, however, again suggesting weak interdimer exchange. Such an interaction between nearby dimers in a crystal can be accomodated in the Friedberg expression by incorporating[26] a molecular field correction, $\gamma$ (eq 5).

$$H = H_0 + \gamma M \qquad (5)$$

In this case, $H$ is the effective field, $H_0$ is the applied field, and as usual $\chi_M - N\alpha = M/H$. The value of $\gamma$ is related to $J'$, the interdimer exchange, by (6) in which $z$ is the number of nearest-neighbor dimers and has the value of 6 for $(CuCl_2{\cdot}L1)_2$ and 4 for $(CuCl_2{\cdot}L2)_2$ as determined by X-ray methods.[19]

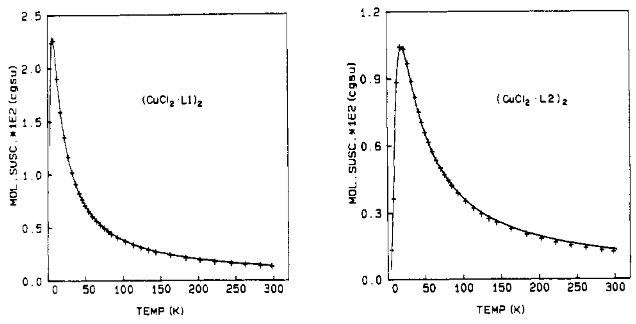

Figure 4. Molar susceptibility (powder) as a function of absolute temperature.

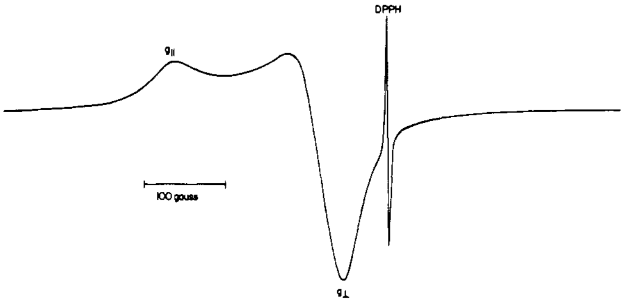

Figure 5. X-Band ESR spectrum of $(CuCl_2{\cdot}L1)_2$.

$$J' = \frac{\gamma N g^2 \beta^2}{2z} \qquad (6)$$

The data were fitted to the self-consistent equation produced by combination of (4) and (5), with the results shown in Table I and Figure 4.

ESR spectra of polycrystalline samples of both compounds were obtained at 298 and 77 K. None of the spectra show resolvable metal hyperfine coupling or any detectable half-field absorption associated with a $\Delta M_s = \pm 2$ transition. The absence of ESR evidence for nonnegligible zero field splitting confirms that those effects ascribed earlier in this paper to interdimer exchange are correctly explained and are not due to zero-field splitting instead.[12] The spectra, an example of which is shown in Figure 5, are all similar and can be interpreted in terms of an axial spin Hamiltonian. Values of $g_\parallel$, $g_\perp$, and $g_{\rm av}$ are given in Table I.

The interdimer exchange, $J'$, obtained from the curve fitting discussed earlier is rather large, at least for $(CuCl_2{\cdot}L1)_2$, and so is the difference between its values in $(CuCl_2{\cdot}L1)_2$ and $(CuCl_2{\cdot}L2)_2$ (Table I). Although the margin of error in both values of $J'$ is substantial, the values are nonetheless significant, and therefore pathways along which the exchange is propagated should be apparent in the solid-state structures of these compounds. Furthermore, some differences in the pathways used by the two compounds that would offer an explanation for the larger value of $J'$ in $(CuCl_2{\cdot}L1)_2$ should also be apparent.

In Table II are listed some interdimer distances and the sum of the van der Waals radii for the atoms involved. As may be seen from these data and the packing diagrams (Figures 1 and 2), the shortest distances between a copper atom in one dimer and any atom of another dimer are too long to provide a pathway for exchange. There are, however, some other interdimer distances that are shorter than the sum of the van der Waals radii of the

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**Table II**

| | minimum interdimer distances[a] | | | | |
|---|---|---|---|---|---|
| | $(CuCl_2{\cdot}L1)_2$ | | $(CuCl_2{\cdot}L2)_2$ | | |
| vector | dist, Å | atoms | dist, Å | atoms | $\Sigma$radii (vdW), Å[b] |
| Cu–Cu | 8.205 | Cu–Cu | 7.183 | Cu–Cu | 2.80 |
| Cu–Cl | 6.202 | Cu–Cl1 | 5.973 | Cu–Cl2 | 3.30 |
| Cu–S | 5.580 | Cu–S4 | 4.936 | Cu–S2 | 3.20 |
| Cu–C | 4.526 | Cu–C3 | 4.572 | Cu–C7 | 3.10 |
| Cu–H | 3.582 | Cu–H3 | 3.787 | Cu–H5A | 2.60 |
| Cl–H | 2.654 | Cl1–H8B | 2.635 | Cl1–H8B | 3.10 |
| | 2.523[c] | Cl2–H3 | 2.959 | Cl2–H7B | |
| Cl–C | | | 3.514 | Cl2–C5 | 3.60 |
| H–H | | | 2.399 | H7A–H8A | 2.40 |
| | | | 2.325[c] | H11B–H11B | |

[a] Based on data from ref 19. [b] From ref 27. [c] Shortest intermolecular contact.

**Table III**

| compd | $2J$, cm$^{-1}$ | $\theta$, deg | $r$, Å | $\theta/r$, deg/Å | ref |
|---|---|---|---|---|---|
| $(CuCl_2{\cdot}L1)_2$ | −7.4 | 86.87[d] | 2.702[d] | 32.15 | |
| $(CuCl_2{\cdot}L2)_2$ | −20.8 | 90.94[d] | 2.661[d] | 34.18 | |
| $[Cu(dmgH)Cl_2]_2$[a] | 6.3 | 88.0 | 2.698 | 32.6 | 10 |
| $[Cu(Et_3en)Cl_2]_2$[b] | 0.1 | 94.84 | 2.728 | 34.75 | 10 |
| $[Cu(4\text{-}metz)(DMF)Cl_2]_2$[c] | −3.6 | 95.3 | 2.724 | 34.99 | 10 |

[a] dmgH = dimethylglyoxime. [b] $Et_3en$ = *N,N,N′*-triethylenediamine. [c] 4-metz = 4-methylthiazole; DMF = *N,N*-dimethylformamide. [d] Reference 19.

atoms involved. In particular, both a bridging and a terminal chlorine in each compound are close to ligand hydrogen atoms of nearby dimers. In the case of $(CuCl_2{\cdot}L1)_2$, there are two such routes through which significant interdimer interaction is likely. These lie between Cl1 of one dimer and H8B of another (see Figures 1 and 2 for numbering) and between Cl2 of one and H3 of another. For $(CuCl_2{\cdot}L2)_2$ there are also two obvious routes for interdimer interaction. These are Cl1 to H8B of one neighbor and Cl2 to H7B of another neighbor. There are, in addition, three other short interdimer distances (Table II), but these are so close to the sum of the van der Waals radii of the atoms concerned that, compared to the other routes, these probably contribute little to the total interdimer exchange. In the solid, each $(CuCl_2{\cdot}L1)_2$ interacts with six others in a three-dimensional manner whereas each $(CuCl_2{\cdot}L2)_2$ interacts with four others in a two-dimensional fashion using the two routes previously identified for each. One of the routes (Cl1 to H8B) is virtually identical in both compounds except for a slight (0.7%) difference in interdimer separation, but the other route is quite different in each compound.

In $(CuCl_2{\cdot}L1)_2$ the two routes are 14.4% and 18.6% shorter than the sum of the van der Waals radii of the atoms concerned, while for $(CuCl_2{\cdot}L2)_2$ they are 15.0% and 4.5% shorter. Assuming that the only differences in transmission of magnetic information between dimers is due to the size of the interdimer gap, the significantly shorter distance between Cl2 and H3 in $(CuCl_2{\cdot}L1)_2$ compared to the Cl2–H7B gap in $(CuCl_2{\cdot}L2)_2$ may be the source of the differences between $J'$ for these two compounds.

Unlike electronic effects, which require a delocalized $\pi$-system for long-range transmission, magnetic effects seem to be transmitted effectively through $\sigma$-networks alone. Therefore the presence of a $\pi$-system in a portion of one route for $(CuCl_2{\cdot}L1)_2$ but not in the corresponding route for $(CuCl_2{\cdot}L2)_2$ is probably not particularly important.

The coordination geometry about the copper atoms in each mononuclear unit that comprises the dimers is best viewed as slightly distorted square pyramidal rather than severely distorted trigonal bipyramidal.[19] However, since the dimers are formed from monomers linked apex-to-base and apex-to-base, the distinction between these structural types is unimportant to the discussion of intramolecular magnetic properties because in both cases, $d_{x^2-y^2}$ orbitals are the partially occupied or magnetically active orbitals, in contrast to the situation when monomers are linked apex-to-apex and base-to-base.[10] The small intramolecular coupling between monomer units that is found in the dimers is not unexpected since the $d_{x^2-y^2}$ orbitals lie in the basal plane of each monomer, and it is clear that the magnetic orbital of a copper that is involved in one half of a bridge is orthogonal to the $d_{z^2}$ orbital that is involved in the other half of the bridge. Therefore, according to this simple bonding description, there should be very little antiferromagnetic coupling between the copper atoms. That there is weak coupling, however, is quite apparent and further studies are underway to clarify its mechanism.

Regardless of the coupling mechanism, $J$ will be composed of antiferromagnetic and ferromagnetic components that are of opposite signs. The ferromagnetic term should be relatively constant for a series of similar complexes, and the antiferromagnetic term is related to the square of the splitting in energy between the members of a pair of dimeric molecular orbitals derived from mainly a magnetically active metal d orbital plus some bridging ligand orbital in each case.[16] This squared term will always be positive, and as it varies through a minimum, the values of $J$ must pass through a maximum. At least one observation of such a variation in $J$ has been reported recently.[10] Theory predicts[16] and experiment confirms[10,15] that $J$ varies directly with $\theta$, the angle at the bridging ligand, and inversely with $r$, the longer bond distance between metal and bridgehead. In contrast to a set of similar compounds[10] involving N-donors instead of S-donors, our compounds have significantly more negative values of $2J$ for similar values of $\theta/r$ (Table III). This illustrates the fact that the nature of the nonbridging ligands can also be important in determining the net magnetic properties of a complex, with our results suggesting that use of "softer" donors enhances intradimer antiferromagnetic exchange.

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