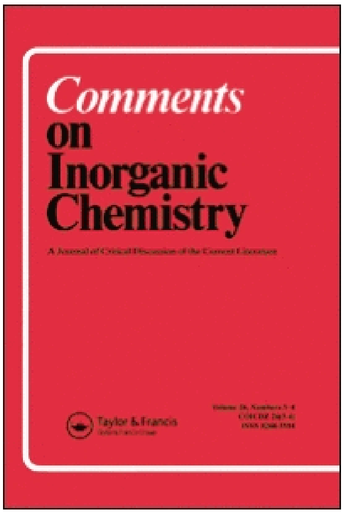

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Effect of Bridge Geometry on Exchange Coupling in Ligand-Bridged Copper(II) Dimers and Chains

William E. Hatfield[a]
[a] Department of Chemistry, University of North Carolina Chapel Hill, North Carolina, USA

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Effect of Bridge Geometry on Exchange Coupling in Ligand-Bridged Copper(II) Dimers and Chains

The singlet triplet splitting resulting from exchange coupling in three series of ligand-bridged copper(II) complexes is primarily controlled by the angle at the bridging ligand atom and by the length of the superexchange pathway. Magnetic and structural data exist for chloro-, bromo-, and sulfur-bridged complexes. The smooth correlation between the exchange coupling constant J and the quotient of structural parameters φ/r_0 (where φ is the angle at the bridging ligand atom and r_0 is the long out-of-plane bond distance) may be explained in terms of extended Hückel molecular-orbital theory, but the theory does not permit an explanation why only complexes which obey the simple correlation exist. It is predicted that a family of such structurally and magnetically related complexes should exist.

Introduction

Systematic studies of the structural and magnetic properties of the series of di-μ-hydroxo-{bis-diamine[copper(II)]} complexes with the general formula shown in Figure 1, and structural and magnetic properties summarized in Table I have established that the single-triplet splitting in this series of compounds is a function of the angle at the bridging oxygen atom only.[1–3] The $N_2CuO_2CuN_2$ units are largely planar with copper oxygen bond distances of 1.92 ± 0.03 Å, copper–nitrogen bond distances of 2.00 ± 0.03 Å, and there are water molecules or counterions coordinated to copper in some, but not all of the compounds.[1,4–25] Consequently, the coordination environments of the single ions are either planar[24] or tetragonal pyramidal. The Cu–O–Cu angle ranges from 95.6(1)° in $[Cu(bpy)OH]_2(NO_3)_2$[4] to 104.1(2)° in $[Cu(tmen)OH]_2Br_2$,[24] and the singlet–triplet splitting varies linearly from $+172\ \mathrm{cm}^{-1}$ (triplet ground state)[5] in the former compound to $-509\ \mathrm{cm}^{-1}$ (singlet ground state)[25] in the latter compound. Since the $Cu–O_2–Cu$ unit is planar, and the copper–oxygen bond distances are equal, the singlet–triplet splitting also varies linearly with the copper–copper separation. As discussed in a subsequent section of this Comment, this observation provides very good

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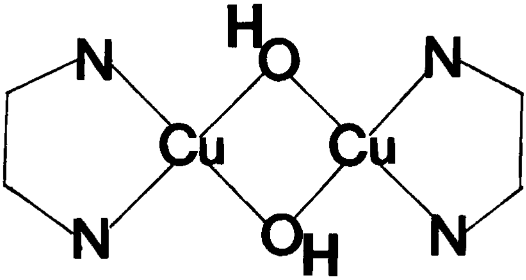

FIGURE 1 General structural formula for the exchange-coupled unit in the di-μ-hydroxo-bridged copper(II) complexes.

evidence for the mechanism of the exchange interaction, since the compound with the greatest singlet state stabilization has the longest copper–copper separation. There is a further extremely interesting trend observed with three di-μ-hydroxo-bridged complexes. These complexes are α–$[Cu(dmaep)OH]_2(ClO_4)_2$,[12,13] $[Cu(bpy)OH]_2(ClO_4)_2$,[1,6] and $[Cu(2\text{-}miz)OH]_2(ClO_4)_2.2h_2O$.[17,18] In addition to the two hydroxo bridges, there are symmetrical perchlorato bridges positioned above and below the N_2Cu–O_2–CuN_2 plane. The singlet–triplet splitting for these three compounds are approximately 50 cm^{-1} more positive than would be predicted by the expression $2J = -74.53(\varphi)+7270\ cm^{-1}$. This problem is not addressed in this Comment.

There has been considerable interest in determining if the singlet–triplet splitting from exchange coupling in other dimeric complexes, small clusters, and low dimensional compounds could be explained in terms of the structural properties of the compounds. The purpose of this Comment is to show that the exchange coupling constants in a number of chloro-, bromo-, and sulfur-bridged copper(II) compounds can be correlated with the structural properties of the compounds.

First, it is instructive to consider what may be expected. The dependence of the singlet–triplet splitting on the angle at the bridging atom for the di-μ-hydroxo-bridged complexes is shown as the solid portion of the line in Figure 2, where the abscissa is the bridge angle and the singlet–triplet splitting is plotted on the ordinate. Although experimental data exist only for a range of bridge angles from 95° to 104°, on the basis of the theoretical calculations by van Kalkeren *et al.*,[26] Hoffmann and coworkers,[27] Kahn and Briat,[28] and Brower and Hatfield,[29] it is anticipated that the singlet–triplet splitting will

TABLE I
Structural and magnetic properties of di-μ-hydroxo-bridged copper compounds

Complex	$R_{Cu\ Cu}$, Å	R_{Cu-O}, Å	$\varphi_{Cu-O-Cu}$, degrees	$2J$, cm^{-1}	g	θ, °K	References
$[Cu(bpy)OH]_2(NO_3)_2$[a]	2.847	1.920–1.923	95.6 (1)	+172	2.10	−0.45	4,5
$[Cu(bpy)OH]_2(ClO_4)_2$	2.870	1.92	96.6 (2)	+93	2.22	−0.5	1,6
$[Cu(bpy)OH]_2SO_4.5H_2O$	2.893	1.92–1.95	97.0 (2)	+49	2.20	0.10	7–11
α-$[Cu(dmaep)OH]_2(ClO_4)_2$[b]	2.938	1.936–1.947	98.35 (9)	−2.4	2.08	—	12,13
$[Cu(eaep)OH]_2(ClO_4)_2$[c]	2.917	1.895–1.930	98.8 99.5 (3)	−130	2.04		14–16
$[Cu(2miz)OH]_2(ClO_4)_2.2H_2O$[d]	—	1.959	99.4 (1)	−175	—	—	17,18
β-$[Cu(dmaep)OH]_2(ClO_4)_2$	2.935	1.900–1.919	100.4 (1)	−200	2.03	—	14,19
$[Cu(tmen)OH]_2(ClO_4)_2$[e]	2.966	1.897–1.931	102.3 (4)	−360	2.09	—	1,20
$[Cu(teen)OH]_2(ClO_4)_2$[f]	2.978	1.899–1.907	103.0 (3)	−410	2.05	—	21,22
$[Cu(tmen)OH]_2Br_2$	3.000	1.902	104.1 (2)	−509	2.0	—	23–25

[a] 2,2′-Bipyridine.
[b] 2-(2-Dimethylaminoethyl)pyridine.
[c] 2-(2-Ethylaminoethyl)pyridine.
[d] 2-Methylimidazole.
[e] *N,N,N′,N′*-Tetramethylethylenediamine.
[f] *N,N,N′,N′*-Tetraethylethylenediamine.

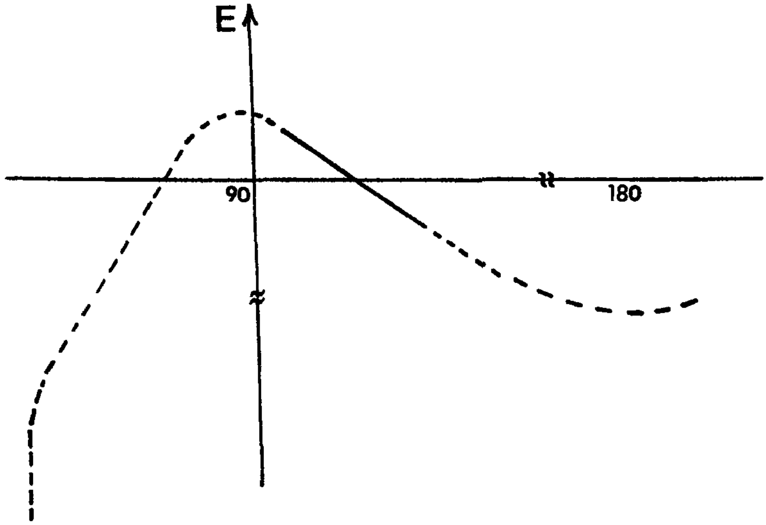

FIGURE 2 Dependence of the singlet–triplet splitting on the angle at the bridging oxygen atom in the exchange-coupled di-μ-hydroxo-bridged copper(II) complexes.

reach a maximum value in the vicinity of 90°, and that the singlet state will be stabilized below that bridge angle.

As indicated in Figure 2, at some smaller bridge angle, a second mechanism of exchange coupling will become important, that being a direct, through-space interaction, and below this angle the singlet state will be stabilized strongly. At larger values for the bridge angle than the current experimental maximum value of 104°, the singlet state will continue to be stabilized with the absolute value of $2J$ reaching some maximum near 180°. In real compounds, it will be necessary for one of the bridging connections to be lost, and that the series of compounds become mono-ligand bridged. Unfortunately, at this time, real bimetallic hydroxo-bridged compounds which exhibit a wide range of angles at the bridging ligand have not been prepared and characterized. However, there are several compounds with either chloro-, bromo-, or sulfur-ligand bridges which do exhibit widely varying bridging angles. A complication exists in the interpretation of the data in that there are changes in structural features other than the bridge angle. It will be shown that these data can be accounted for in terms of a physically meaningful, theoretically based model.

Theoretical Considerations

The Hamiltonian which is appropriate for the description of exchange coupling in copper(II) systems is given in Eq. (1) for the special case of a dimeric cluster.[30]

$$H = -2J_{12}S_1 \cdot S_2 \tag{1}$$

Exchange coupling in copper(II) systems is largely an isotropic phenomenon and, consequently, the Heisenberg exchange theory is appropriate for the clusters and chains which will be discussed in this Comment. As a general rule one can use the g tensor as a gauge for the appropriate theory. If the g tensor is nearly isotropic, as it is for most copper(II) complexes, then an isotropic exchange model is likely to apply. This means that there are no energetic factors which tend to constrain the electron spin to lie along a given preferred direction. In the case of multimetallic complexes with anisotropic g tensors, it is usually necessary to use an anisotropic exchange coupling model with the most commonly used ones being the Ising model or the XY model.

The exchange coupling constant J_{12} is evaluated by fitting the appropriate expression for magnetic susceptibility to experimental data. For a bimetallic complex, the exchange coupling constant thus determined is a measure of the energy separation between the singlet and triplet states, and the J_{12} value is not generally a measure of the *strength* of the exchange interaction. This may be understood in terms of the data which exist for the di-μ-hydroxo-bridged complexes. When a compound with an angle at the bridging oxygen atom somewhere near 97.5° is prepared, the correlation between φ and $2J$ predicts that the singlet–triplet splitting will be zero. The two copper ions in such a complex will be strongly exchange coupled, but the singlet and triplet states will be energetically degenerate. On the other hand, if two copper ions are present in a dimeric complex and are separated by non-bridging, magnetically insulating ligands, say at a distance of approximately 10 Å or greater, the exchange coupling will, for all practical purposes, be nonexistent, each copper ion will exhibit doublet state magnetism, and $2J$ will be zero.

Hoffmann and coworkers[27] have shown that the singlet–triplet splitting is given by

$$E_T - E_S = -2K_{ab} + \frac{(e_1 - e_2)^2}{J_{aa} - J_{ab}} \tag{2}$$

where K_{ab} is the molecular exchange integral, J_{aa} and J_{ab} are the one- and two-center Coulomb repulsion integrals, and e_1 and e_2 are the energies of the orbitals which are involved in the exchange coupling. Hoffmann and coworkers have pointed out that the exchange and Coulomb integrals are relatively insensitive to subtle structural distortion and substituent effects and, as a result, the singlet–triplet splitting is largely determined by the energy difference $(e_1 - e_2)$. When $e_1 = e_2$, the triplet state is the ground state. As will be shown later this occurs when the angle at the bridge is 90°.

It is instructive to examine the nature of the orbitals involved in the

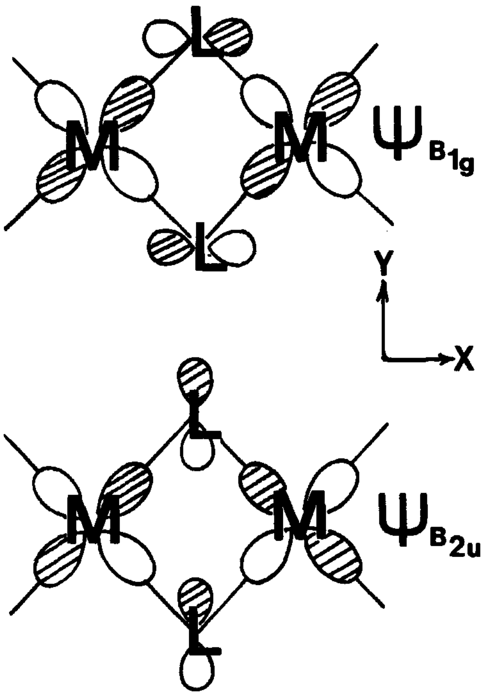

FIGURE 3 The symmetric and antisymmetric combinations of B_{1g} and B_{2u} symmetry in the di-μ-hydroxo-bridged copper(II) complexes.

exchange process. For the di-μ-hydroxo-bridged copper(II) systems these are the largely metal-based, symmetric and antisymmetric combinations of sigma antibonding orbitals of B_{1g} and B_{2u} symmetry which are shown in Figure 3. These symmetric and antisymmetric combinations of largely metal-based orbitals may interact with like combinations of orbitals on the bridging ligands. At 90°, the interactions are equal, the triplet state is the ground state, and the interaction is termed *ferromagnetic*. As the angle deviates from 90°, the overlaps of the two combinations differ and finite values arise for the numerator $(e_S - e_A)$. At some angle the singlet state will become the ground state and the interaction is said to be *antiferromagnetic*. This discussion suggests that a plot of the singlet–triplet splitting as a function of bridge angle would not be symmetric as the angles depart from 90° to larger and smaller values, respectively.

Examination of Experimental Results

Chloro-bridged copper(II) dimers and chains Structural and magnetic data now exist for five examples of chloride-bridged parallel planar copper(II) dimers.[31-38] These five compounds are listed in Table II along with the pertinent structural data[31,32,34,36,37] and the exchange coupling constants which have been determined from magnetic susceptibility measurements.[31,33,35,38] It may be seen by inspecting the data that the angles at the bridging chloride ion range from 86° to over 100°. While the in-plane copper–chloride bond distances are nearly constant at 2.28 ± 0.03 Å, the out-of-plane bond distances vary from 2.7 Å in the dimethylglyoxime compound[37] to 3.37 Å in the 2-methylpyridine compound.[32] It may reasonably be concluded on the basis of the results of the work on the hydroxo-bridged complexes[1] and theoretical calculations[26-29] that the exchange coupling constant will be dependent on the magnitude of the angle at the bridge as well as the bond length in the superexchange pathway. It may be predicted on orbital overlap considerations alone that an increase in the bond distances will be accompanied by a decrease in the magnitude of the exchange coupling constant. These results and considerations suggest that the exchange coupling constants be examined in terms of the quotient φ/r_0, where φ is the angle at the bridging ligand and r_0 is the long, out-of-plane bond distance. Further refinements on the correct structural parameters will probably require that r_0 be raised to some power n, but sufficient data do not exist at this time to justify the refinement.

Magnetic and structural data also exist for a number of mono-μ-chloro-[39-45] and di-μ-chloro-copper(II)[46-54] chain compounds. These data are summarized in Table III. For the sake of completeness data have been listed in Table III for $[Cu(IzH)_2Cl_2]_n$,[41-43] but these data are not considered in the following discussion since the material undergoes long range order below 7 K.[41] The structural and magnetic data for all of the chloro-bridged copper(II) compounds are collected in Figure 4, where it may be seen that the exchange coupling constant increases from approximately $-10\ \mathrm{cm}^{-1}$ at a φ/r_0 value of about 28, reaches a maximum of J equal to about $2.5\ \mathrm{cm}^{-1}$ at φ/r_0 near 37, and then the exchange coupling constant decreases as the angles increase in the series of single chloro-bridged complexes. This observed behavior parallels the expectation outlined in Figure 2. An important question surfaces, and that involves the effect of the number of bridges, and hence the number of superexchange pathways, on the magnitude of the exchange coupling constant.

Although there are large numbers of copper(II) compounds with di-μ-chloro-bridged structures, few have been structurally characterized by single crystal X-ray diffraction studies. Available data[46-54] for these compounds are collected in Table III, where it may be seen that all but one have the general formula $(CuL_2Cl_2)_n$. The structure of these compounds may be visualized as a uniform chain formed by the stacking of parallel planar units. The unique compound in the series is $[(CH_3)_3NH]CuCl_3.2H_2O$,[52-54] which has the basic

TABLE II
Structural and magnetic data for chloride-bridged parallel planar dimers

Compound	Cu–Cu, Å	$\varphi°$(Cu–Cl–Cu)	Out-of-plane Cu–Cl, Å	In plane Cu–Cl, Å	φ/r_0	J, cm^{-1}	Reference
$[Cu(TMSO)_2Cl_2]_2$[a]	3.74	88.5	3.02	2.28	29.30	-8.0	31
$[Cu(\alpha\text{-pic})_2Cl_2]_2$[b]	4.41	100.14	3.37	2.26	29.7	-3.7	32,33
$[Cu(tmen)Cl_2]_2$[c]	4.09	96.8	3.15	2.26	30.7	-2.8	34,35
$[Cu(u\text{-}Me_2en)Cl_2]_2$[d]	3.46	86.13	2.74	2.31	31.4	-1.1	35,36
$[Cu(dmg)Cl_2]_2$[e]	3.44	88.0	2.70	—	32.6	$+3.2$	37,38

[a] Tetramethylene sulfoxide.

[b] 2–Methylpyridine.

[c] *N,N,N′,N′*–Tetramethylethylenediamine.

[d] *N,N*–Dimethylethylenediamine.

[e] Dimethylglyoxime.

TABLE III
Structural and magnetic parameters for chloride-bridged copper(II) chain compounds

Compound	Cu–Cl$_{b,l}$^{h}, Å	Cu–Cl$^i_{b,s}$b,A	Cu–Cu, Å	Cu–Cl$_b$–Cu	φ/r_0	J, cm^{-1}	Reference
Mono-μ-chloro-bridged							
$[Cu(DMSO)_2Cl_2]_n$[a]	2.702(2)	2.290(2)	4.757(2)	144.6(1)	53.5	−6.1	39–41
$[Cu(IzH)_2Cl_2]_n$[b]	2.751(6)	2.365(4)	2.37(?)	117(?)	—	−2.1	41–43
$[Cu(caf)(H_2O)Cl_2]_n$[c]	2.788(2)	2.319(2)	4.597(2)	128.1(?)	46.0	+0.48	41,44
$[Cu(MAEP)Cl_2]_n$[d]	2.785(2)	2.300(2)	4.263(2)	113.58(5)	40.8	+1.58	41,45
Di-μ-chloro-bridged							
$[Cu(py)_2Cl_2]_n$	3.026(2)	2.299(2)	3.87	88.48(5)	29.2	−9.2	46,47
$[Cu(4\text{-v-py})_2Cl_2]_n$[e]	3.10	2.31	3.91	91.5	29.5	−9.1	48,49
$[Cu(4\text{-Et-py})_2Cl_2]_n$[f]	3.21	2.28	4.00	91.9	28.6	−6.7	49,50
$[Cu(tz)_2Cl_2]_n$[g]	2.998(1)	2.322(1)	3.853(4)	91.89(2)	30.7	−3.8	51
$[Me_3NH]CuCl_3.2H_2O$	2.910(6)	2.296(6)	3.739(10)	91.0	—	+0.6	52–54
	2.751(5)	2.286(5)	—	95.8	≃33.0		

[a] Dimethyl sulfoxide.
[b] Imidazole.
[c] Caffeine.
[d] 2-(2-Methylaminoethyl)pyridine.
[e] 4-vinylpyridine.
[f] 4-Ethylpyridine.
[g] Thiazole.
[h] Long bridging bond distance.
[i] Short bridging bond distance.

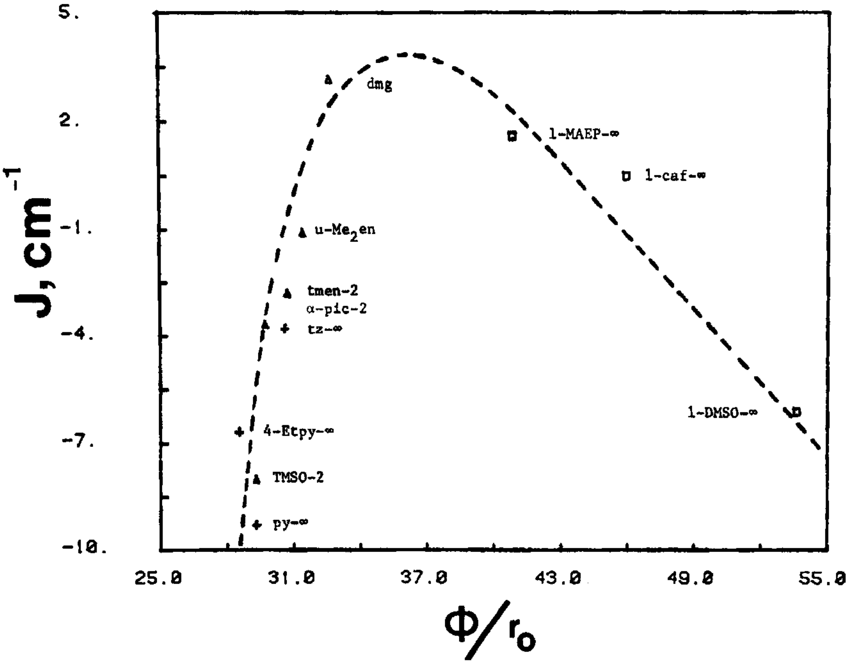

FIGURE 4 The dependence of the exchange coupling constant on the parameter φ/r_0 for the chloro-bridged dimers and chains. Not the antisymmetric nature of the phenomenological curve reflects the number of superexchange pathways. Data points for dimers are designated by △, for mono-μ-chloro-bridged chains by □, and for di-μ-chloro-bridged chains by +.

di-μ-chloro-bridged structure, but in this case the Cu_2Cl_2-bridging unit is antisymmetric[52] with short copper–chloride bond distances of 2.296(6) and 2.268(5) Å, long copper–chloride bond distances of 2.910(6) and 2.751(5) Å, and angles at the bridging chloride ligands of about 91.0° and 95.8°. Although the Cu_2Cl_2 unit is not constrained to be planar, it is nearly planar. An average φ/r_0 values of 33° cm^{-1} is tabulated. The data for these compounds are plotted in Figure 4.

The recent studies by Willett and coworkers[55–57] on the ferromagnetic chains of copper(II) in compounds such as $[(CH_3)_4N]CuCl_3$ have a bearing on the question concerning the effect of the number of superexchange pathways on the exchange coupling. The copper ions in the ferromagnetic compounds studied by Willett and coworkers are bridged by three ligands. Necessarily, one of the bridges spans sigma antibonding orbitals on both copper ions, and the magnetic exchange interactions are much greater than in the chloro-bridged complexes considered here. In these latter complexes, the bridging ligand does not interact with the primary sigma antibonding orbitals on the neighbouring exchange-coupled copper ions. The antisymmetric nature of the phenomenological line in Figure 4 reflects the number of bridges as well as other factors. The significance of the correlation between molecular structural features and magnetic properties are discussed below.

Di-μ-bromo-bridged copper(II) Structural and magnetic data exist for four parallel planar, bromo-bridged copper(II) compounds.[35,36,58–61] These data are summarized in Table IV, where it may be seen that the angle at the bridge ranges from 84° in the complex $[Cu(u\text{-}Me_2en)Br_2]_2$[36] to 100° in the 2-methylpyridine complex.[58] The out-of-plane copper–bromide bond distances range from 2.9 Å in the former compound to 3.9 Å in the latter compound. The dependence of the exchange coupling constant on the quotient of structural parameters φ/r_0 is illustrated in Figure 5, where the four data points are suggestive of the behavior exhibited by the more extensive series of chloro-bridged copper(II) systems, and once again parallels the anticipated behavior of the exchange coupling constant on φ/r_0. Available data[43,47,62–64] for bromide-bridged copper chain compounds present an interesting deviation from the behavior thus far noted for these exchange-coupled systems.

Sulfur-bridged copper(II) complexes The available structural and magnetic data[65–80] for sulfur-bridged copper(II) complexes are collected in Table V, where it may be seen that there are three dimeric complexes, those being the thiocarbonohydrazidium complex,[65] $[Cu(dedtc)_2]_2$,[71] and the α-form of $[Cu(dbtc)_2]_2$,[80] one alternating chain compound, $[Cu(KTS)]_n$,[68] and one uniform chain compound, $[Cu(dmdtc)_2]_n$.[69] For the purpose of this study, the structural features of the more tightly bound unit in $[Cu(KTS)]_n$ are used, since it is anticipated that this unit will dominate the exchange at the low temperatures used by Blumberg and Peisach[67] to estimate the exchange coupling constant by monitoring the intensity of the EPR signal. As shown in Figure 5, the exchange coupling constant once again exhibits the dependence on φ/r_0 seen for the chloro-bridged and the bromo-bridged compounds.

Significance of the Observations

A structural model which is appropriate for the analysis of the experimental results for the parallel planar dimers and the comparable unit in the chains is shown in Figure 6. The symmetry of the idealized model is C_{2h}, and the symmetric and antisymmetric combination of sigma antibonding orbitals transform as A_g and B_u. The appropriate linear combinations of metal orbitals and ligand orbitals may be constructed in the same manner as those given in Figure 3 for the di-μ-hydroxo-bridged complexes. The analysis of the magnetic data for the parallel planar complexes is complicated by an additional

TABLE IV
Structural and magnetic data for bromide-bridged parallel planar dimers

Compound	Cu–Cu, Å	φ^c(Cu–Br–Cu)	Out-of-plane Cu–Br, Å	In plane Cu–Br, Å	φ/r_0	J, cm^{-1}	Reference
$[\mathrm{Cu}(\alpha\text{–pic})_2\mathrm{Br}_2]_2$[a]	4.93	100.4	3.87	2.43	25.9	−2.5	58
$[\mathrm{Cu}(\text{u–Me}_2\text{en})\mathrm{Br}_2]_2$[b]	3.570	83.71	2.868	2.463	29.2	−1.2	35,36
$[\mathrm{Cu}(\text{dmg})\mathrm{Br}_2]_2$[c]	3.599	85.6	2.883	2.387	29.7	−1.8	59,60
$[\mathrm{Cu}(\text{tmen})\mathrm{Br}_2]_2$[d]	4.20	95.6	3.20	2.42	29.9	−2.4	35,61

[a] 2-Methylpyridine.
[b] *NN*,–Dimethylethylenediamine.
[c] Dimethylglyoxime.
[d] *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine.

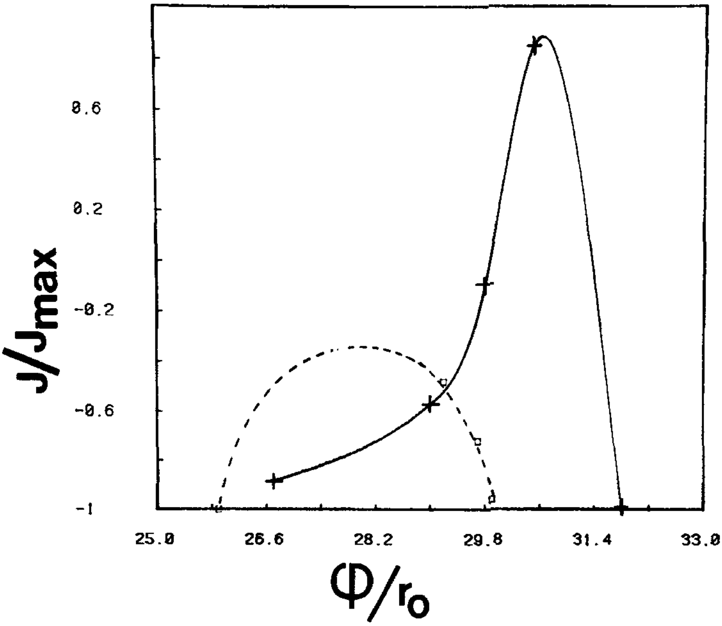

FIGURE 5 The dependence of the normalized exchange coupling constant on the parameter φ/r_0 for the bromo- and sulfur-bridged dimers and chains. The exchange coupling constants have been normalized with the maximum value of J for each set of compounds taken as unity. The solid line is drawn through the data points for the sulfur-bridged compounds, and the broken line is drawn through the data points for the bromide-bridged compounds.

structural feature, that being a wide variation in the out-of-plane bond distance. Furthermore, additional metal orbitals become involved in the exchange mechanism. The A_g and B_u combinations of the d_{z^2} orbitals are not shown in Figure 6 since their inclusion would unnecessarily complicate the drawing. However, it is easy to visualize the appropriate combinations. It is now possible to summarize the metal and ligand orbitals that are primarily involved in the exchange coupling mechanism, these are the sigma antibonding $d_{x^2-y^2}$ orbitals, the d_{z^2} orbitals on the metal, and the ligand p_x and p_y orbitals. The ligand s orbitals are of secondary importance because of the relatively larger difference in energy of these orbitals and the metal orbitals. It must be recognized that the energies of the highest occupied molecular orbitals are influenced by the nature of the ligand which are not primarily involved in the exchange process since the symmetry of the exchange coupled unit is relatively low.

Extended Hückel molecular orbital calculations have been carried out on a number of model systems of chloro-bridged, parallel planar copper(II) complexes[29] and the results are in qualitative agreement with the experimental

TABLE V

Structural and magnetic data for sulfur-bridged copper(II)

Compound	φ°(Cu–S–Cu)	Out-of-plane Cu–S, Å	In plane Cu–S, Å	φ/r_0	J, cm^{-1}	Reference
$[\mathrm{Cu(H^+\text{–}TCH)Cl_2}]_2\mathrm{Cl_2}$[a]	88.4	3.310	2.271	26.7	−12.4	65,66
$[\mathrm{Cu(KTS)}]_n$[b]	89.8 (86.5)	3.101 (3.312)		29.0	−8	67,68
$[\mathrm{Cu(dmdtc)_2}]_n$[c]	94.2	3.159	2.302	29.8	1.22	69,70
$[\mathrm{Cu(dedtc)_2}]_2$[d]	86.9	2.851	2.339	30.5	12	71–79
α–$[\mathrm{Cu(dbdtc)_2}]_2$[e]	92.1	2.899	2.333	31.8	−14.1	80

[a] $1\mathrm{H}^+$–Thiocarbonohydrazidium.

[b] 3–Ethoxy–2–oxobutraldehyde bis(thiosemicarbazonate).

[c] Dimethyldithiocabamate.

[d] Diethyldithiocarbamate.

[e] α–phase; di–n–butyldithiocarbamate.

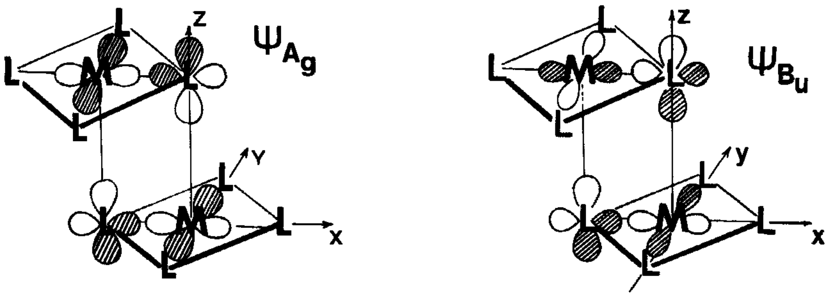

FIGURE 6 The symmetric and antisymmetric combinations of sigma antibonding orbitals for the parallel-planar dimeric units. Note that the combinations of d_{z^2} orbitals are not shown in the drawing.

observations. More importantly, one of the purposes of this Comment is to draw attention to a very interesting and significant question, and that is, why does the simple correlation exist at all. Consider the following: the angle at the bridge is the most important factor in determining the sign of the exchange coupling constant but the bond distances in the superexchange pathway is the primary factor determining the magnitude of J. This leads to the immediate conclusion that there should be a family of J versus φ/r_0 curves, not one universal curve. This conclusion is supported by a limited amount of experimental data which exist for bromide-bridged copper(II) chains. Reedijk and coworkers[63] have summarized the data which exist for $[\mathrm{Cu(pyridine)_2Br_2}]_n$, $[\mathrm{Cu(3,5\text{-}dimethylpyridine)_2Br_2}]_n$, and $[\mathrm{Cu(}M\text{-}\mathrm{methylimidazole)_2Br_2}]_n$. The quotient φ/r_0 for the three compounds is 27.5(2), yet the exchange integral varies from $-5.8\ \mathrm{cm}^{-1}$ for the N-methylimidazole compound[63] to $-21\ \mathrm{cm}^{-1}$ for the 3,5-dimethylpyridine compound.[63] However, it has now been established that $[\mathrm{Cu(}N\text{-}\mathrm{methylimidazole)_2Br_2}]_2$ undergoes a structural phase transformation, probably to an alternating chain structure, and this process presents an additional complication in the interpretation of the magnetic and structural data for the bromide-bridged systems.

Although it is widely known that the energies which result from extended Hückel molecular orbital calculations are subject to question, the results of calculations of minimum energy structural configurations on several model systems yield no information permitting a conclusion concerning the molecular design of appropriate systems. New compounds with structural and magnetic properties which do not fall on the curve in Figure 4 or the normalized curves shown in Figure 5 will emerge from systematic research in this field and will permit an explanation of the diverse array of properties for these compounds as signaled by the results for the bromide-bridged chain systems.

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WILLIAM E. HATFIELD
Department of Chemistry,
University of North Carolina
Chapel Hill, North Carolina 27514, USA

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