

(113°)b - 102°. The value calculated for this structure, based on a bite of 1.292, is 55.4°.

The bond length alternation in the C-C distances of catechol rings seen in other complexes also occurs here (Table III); each ring also exhibits a slight bending along the O-O vector. The dihedral angles between the O-As-O plane and the catechol planes are 14.7 and 11.2° for the ligands involved in H-bonding, while the third ligand shows an angle of only 4.3°. The bending along the O-O vector is not due simply to steric effects or hydrogen bonding; ligand O1...O2, which is hydrogen bonded on both oxygens, has the largest dihedral angle, but the hydrogen bonds are on opposite sides of the plane.¹⁸⁻²¹

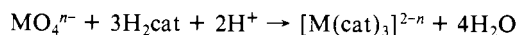
H₇O₃⁺ Cation. There are many structural reports on oxonium (H_{2n+1}O_n⁺) cations.²²⁻²⁸ The most common is the H₅O₂⁺ aggregate,²⁴ which has been characterized by neutron diffraction. However, H₇O₃⁺²⁷⁻²⁹ and H₉O₄⁺²⁴ structures have also been reported. The structure and environment of the cation in this compound are shown in Figure 2 and show a distinct H₇O₃⁺ unit. The proton positions have not been well determined, but presumably the structure is the same as that found for H₇O₃⁺ cations characterized by neutron diffraction. The O-O bond lengths and O-O-O angles in this H₇O₃⁺ salt are consistent with earlier reports. A recent tabulation of data from neutron diffraction studies of hydrogen bonding in crystalline hydrates sets the average OH-O distance at 2.8 (1) Å.³⁰

The asymmetric unit also contains two unique half *p*-dioxane molecules. These are centered at two inversion centers (0, 0, 1/2 and 1/2, 0, 1/2). The first dioxane (O1D...C2D) fits in the packing arrangement very nicely. The bond distances and angles are nominal, and the torsion angles average 56.8°. It is hydrogen bonded to O2W. The second dioxane molecule exhibits very large thermal motion. It appears that this is coupled with the disorder of O3WA/B, to which it is hydrogen bonded. The bond distances are consequently poor, and the torsion angles are anomalously low (25.6°). Models assuming disorder, with alternate chair

conformations, were not successful in improving the fit to the data; the structure does not allow sufficient room for a well-ordered, hydrogen-bonded arrangement for this conformer.

Conclusion

This structure exemplifies the stability of the [M(cat)₃]ⁿ⁻ coordination complex, particularly for a formal +5 ion. Structures have been reported containing cations ranging from amines to simple alkali metals to the oxonium ion (the present case). Conditions for the crystallizations are equally varied. For trivalent metal ions such as Fe³⁺, full complexation by the weakly acidic catechol ligand occurs only at high pH (0.1 M KOH has been a typical host solution¹⁸) while for the oxoanions of metals (or metalloids) in very high oxidation states the complexation reaction occurs in acid as



Examples of the latter are As(V), Mo(VI), P(V), Si(IV), V(IV), and Ti(IV). The structural features of the resultant [M(cat)₃]ⁿ⁻ complexes are remarkably consistent and predictable (e.g. the twist angle from assumed M-O and O-O distances). The present structure, though originally formulated as a protonated complex with an alternate mode of coordination, is no exception. Even under extremely acidic conditions, the complex retains a fully coordinated tris(catecholato) structure with essentially D₃ symmetry.

Acknowledgment. This research is supported by NIH Grant AI-11744. The CHEXRAY structural facility was established with a grant from the NSF.

Registry No. [H₇O₃][As(C₆H₄O₂)₃]-*p*-dioxane, 100447-63-0.

Supplementary Material Available: Hydrogen atom parameters for [H₇O₃][As(cat)₃]-C₄H₈O₂ (Table IV), temperature factor expressions (*B*'s) (Table V), least-squares planes (Table VI), and structure factors for [H₇O₃][As(cat)₃]-*p*-C₄H₈O₂ (Table VII) (27 pages). Ordering information is given on any current masthead page.

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(18) It appears that this bend is a consequence of (1) the tetrahedral (sp³) hybridization of the oxygen atoms (stabilized by hydrogen bonding), (2) the rigid As-O bonds, and (3) the constraints imposed by the octahedral packing of the oxygen atoms around the As. In fact, the M-O-C bond angle tends to be about 110° for all metal catecholates, while the O-C1-C2 angle is always compressed with respect to the ideal 120° angle (112° in [P(cat)₃]³⁻ to 118° in [Fe(cat)₃]³⁻).^{19,20} In free catechol the O-O distance is 2.72 Å compared to the shorter distances found in most of the metal complexes, and the O-C1-C2 angle is about 120°. The bend arises from rotation of the oxygen-metal vector out of the plane of the catechol ligand in order to accommodate the constraints described above. For example, consider the O-M-O geometry if the whole metal-chelate moiety is assumed to be planar and the ligand geometry is assumed to be the same as the free ligand. Such a hypothetical structure results in a calculated M-O distance of 2.15 Å and an O-M-O angle of 81.1°. In order to fit metals of smaller size the ligand distorts and a rotation of the O-M vector out of the ligand plane occurs, resulting in a dihedral angle between the O-M-O and ligand planes.

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Anisotropic Exchange in Bibridged Copper(II) Dimers: A Topological Approach

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The magnetostructural correlations represented quite an important step in the history of molecular magnetism.² They allowed one to specify the main factors governing the sign and the magnitude of the isotropic interaction between two metal ions. They are at the origin of several concepts that have been utilized to design polymetallic systems exhibiting predictable magnetic properties.³ The best established correlation concerns bibridged copper(II) dimers, particularly the bis(μ-hydroxo) complexes.⁴

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Table I. Structural Data and Isotropic and Anisotropic Exchange Parameters for Oxygen-Bridged Copper(II) Dimers

compd	$r(\text{Cu}-\text{Cu})$, Å	$\text{Cu}-\text{O}-\text{Cu}$, deg	J , cm^{-1}	D , cm^{-1}	ref
bis(μ -hydroxo)bis[bipyridylcopper(II)] dinitrate	2.847	96	+172	1.41	<i>a</i>
bis(μ -hydroxo)bis[bipyridylcopper(II)] sulfate pentahydrate	2.893	97	+49	1.269	<i>b-d</i>
bis(μ -hydroxo)bis[bipyridylcopper(II)] diperchlorate	2.871	97	+93	1.16	<i>e</i>
bis(μ -hydroxo)bis[<i>N,N,N',N'</i> -tetramethylethylenediamine]copper(II) diperchlorate	2.966	102	-360	1.121	<i>f</i>
bis(μ -hydroxo)bis[<i>N,N,N',N'</i> -tetraethylethylenediamine]copper(II) diperchlorate	2.978	103	-410	1.1205	<i>g</i>
bis(μ -hydroxo)bis[bis(2-methylimidazole)copper(II)] diperchlorate dihydrate	2.993	99.3	-175	0.726	<i>h</i>
bis(μ -pyridine <i>N</i> -oxide)bis[(pyridine <i>N</i> -oxide)dichlorocopper(II)]	3.306	110	-550	0.21	<i>i,j</i>
bis(μ -pyridine <i>N</i> -oxide)bis[dichloroaquocopper(II)]	3.272	109.4	-885	0.1545	<i>j-l</i>
bis(μ -pyridine <i>N</i> -oxide)bis[dichloro(dimethyl sulfoxide)copper(II)]	3.342	109.4		0.1906	<i>m</i>
bis(piperidinium) bis[(μ -methoxo)bis(2,4-dinitrophenolato)cuprate(II)]-methanol (1/2)	2.947	99.0	0	1.27	<i>n</i>
bis(piperidinium) bis[(μ -methoxo)bis(2,4-dinitrophenolato)cuprate(II)]	2.939	98.3	-130	1.26	<i>n</i>
bis[μ -2-(diethylamino)ethanolato]dibromodicopper(II)	3.033	105	-817	0.5578	<i>o</i>

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In this case, Hatfield and Hodgson have shown that the singlet triplet (S-T) energy gap J varied steadily versus the CuOCu (θ) bridging angle, with a singlet ground state for $\theta > 97.5^\circ$ and a triplet ground state for $\theta < 97.5^\circ$.

In addition to the S-T splitting, the interaction between copper(II) ions in a binuclear entity leads to a zero field splitting within the triplet state, quantitatively characterized by the axial D and rhombic E zero field splitting parameters.⁵ These parameters can be deduced from the EPR spectra. This effect has two origins, namely the magnetic dipolar interaction and the anisotropic exchange interaction.⁶ The former contribution can be calculated, at least approximately, by assuming that the magnetic dipoles are centered on the metal ions, so that an estimation of the contribution to the zero field splitting parameters due to the anisotropic interaction can be obtained. The Florence group has systematically investigated the EPR spectra of bis(μ -hydroxo)copper(II) dimers and reached the following conclusions:^{7,8} (i) In any case, the zero field splitting within the triplet state is much larger than it would be if only the dipolar interaction was operative. (ii) D is always negative, which means that the $|0\rangle$ component of the triplet state is the highest in energy. In other words, D does not present the change of sign exhibited by the S-T gap J when the bridging angle varies. (iii) Finally, a trend to a decrease of $|D|$ on increasing the Cu...Cu separation has been observed. More precisely, $|D|$ varies from 1.41 cm^{-1} in [Cu(bpy)(OH)]₂(NO₃)₂ (bpy = 2,2'-bipyridyl, where $\theta = 95.6^\circ$ and Cu...Cu = 2.847 Å) to 0.73 cm^{-1} in [Cu(2-MeIm)₂(OH)]₂(ClO₄)₂·2H₂O (2-MeIm = 2-methylimidazole, where $\theta = 99.2^\circ$ and Cu...Cu = 2.993(1) Å) as shown in Table I, where we gathered the reported structural, magnetic, and EPR data dealing with oxygen bridged copper(II) dimers. This decrease of $|D|$ is more pronounced than variation of the dipolar interaction alone would suggest. If not only hydroxo bridges but also alkoxo and *N*-oxo bridges are taken into consideration, the range of available Cu...Cu separations increases and a more marked tendency to a decrease in $|D|$ with Cu...Cu separation emerges.⁹

As far as the dependence of J vs. θ is concerned, two semi-quantitative interpretations have been proposed so far. The former

is based on an orthogonalized magnetic orbital approach of the interaction.¹⁰ J is expressed as a sum of an antiferromagnetic J_{AF} and a ferromagnetic J_F components. J_F is assumed to be weakly sensitive to small structural changes while J_{AF} is found to vary as $-\Delta^2$, Δ being the energy gap between the two singly occupied molecular orbitals in the low-lying triplet state. The latter interpretation is based on natural (nonorthogonalized) magnetic orbitals and on the overlap density between them.¹¹ If we define the two natural magnetic orbitals in a copper(II) dimers as $\phi_A^{(0)}$ and $\phi_B^{(0)}$, then the overlap density is expressed as

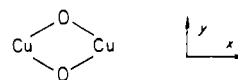
$$\rho(i) = \phi_A^{(0)}(i) \phi_B^{(0)}(i)$$

The overlap integral S and the two-electron-exchange integral j are given by

$$S = \int_{\text{space}} \rho(i) dV(i)$$

$$j = \int_{\text{space}} \rho(i) \rho(j) \frac{dV(i) dV(j)}{r_{ij}}$$

Again, J appears as the sum of J_{AF} and J_F , with J_{AF} varying as $-S^2$ and J_F as j . Since the magnetic orbitals in the bridging network



are of the d_{xy} type, the overlap density, noted as $\rho^{(xy,xy)}$, presents two positive lobes along the x axis and two negative lobes along the y axis around each bridge. For a θ value close to 90° around each bridge, positive and negative lobes compensate themselves, so that the integral S of the overlap density is zero as is J_{AF} . The magnetic orbitals are said to be accidentally orthogonal, and J reduces itself to its ferromagnetic component. When θ increases, the magnitude of the positive lobes along the x axis increases and that of the negatives lobes along the y axis decreases. The result is that S^2 increases as well as $|J_{AF}|$. This interpretation is schematized in Figure 1, where we represented the overlap density for $\theta = 92.5^\circ$, a value for which S is found to be equal to zero¹¹ and $\theta = 110^\circ$.

The problem at hand is this: Is it possible to propose the same kind of topological approach to understand the variation of D ? The purpose of this work is to answer this question.

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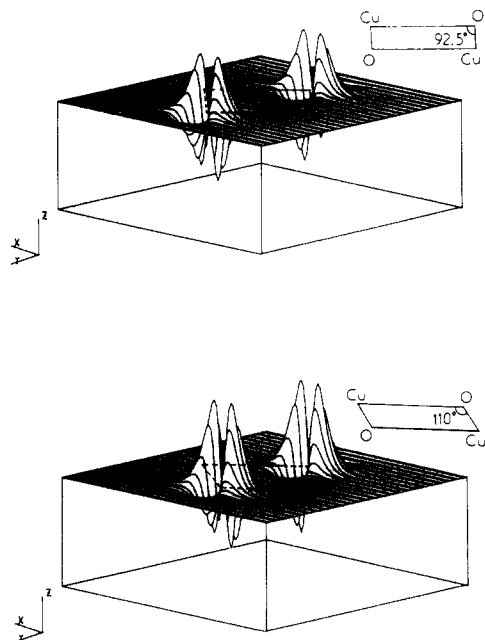


Figure 1. Overlap density $\rho^{(xy,xy)}$ for two values of the bridging angle. $\rho^{(xy,xy)}$ exhibits two positive and two negative lobes around each of the bridges. For $\theta = 92.5^\circ$, the magnitude of the positive lobes and that of the negative lobes compensate themselves, so that $S = 0$; and the magnetic orbitals are accidentally orthogonal. For $\theta = 110^\circ$, the magnitude of the positive lobes prevails over that of the negative lobes, so that S is positive.

It is now well-understood that the anisotropic interaction in a copper(II) dimer is due to the synergic effect of the single-ion second-order spin-orbit coupling and the interaction between the ground state of an ion and the excited states of the other.^{3,5,7} The planar bibridged copper(II) dimers represent a relatively simple case since the site symmetry of the metal ions is high enough in order for the single-ion ground state $\phi_A^{(xy)}$ and the excited states $\phi_A^{(i)}$ to transform as different irreducible representations (b_1 and $2a_1 + a_2 + b_2$, respectively) of the symmetry group C_{2v} . In this favorable case, the contribution D^{ex} to D due to the anisotropic interaction may be expressed as^{3,12}

$$D^{ex} = \frac{3}{2}(A_x + A_y - 2A_z)$$

with

$$A_x = \frac{1}{3} \frac{\lambda^2}{\Delta_1^2} L_x^{(1,xy)} L_x^{(xy,1)} [j^{(xy,1,xy,1)} - j^{(1,1,xy,xy)}]$$

$$L_x^{(1,xy)} = \langle \phi_A^{(1)} | L_x | \phi_A^{(xy)} \rangle$$

$$j^{(i,j,k,l)} = \langle \phi_A^{(i)}(1) \phi_B^{(j)}(2) | r_{12}^{-1} | \phi_A^{(k)}(2) \phi_B^{(l)}(1) \rangle$$

$\phi_A^{(1)}$ being the excited eigenstate coupling with $\phi_A^{(xy)}$ through L_x and Δ_1 the energy gap between the two states. λ is the single-ion spin-orbit coupling parameter. A_y and A_z are obtained by circular permutation $x \rightarrow y \rightarrow z$ and $1 \rightarrow 2 \rightarrow 3$. The terms A_u , $u = x, y, z$, are all positive since $j^{(xy,i,xy,i)}$ is much larger than $j^{(i,i,xy,xy)}$ for any i . Among the four $j^{(xy,i,xy,i)}$ integrals involved in the full expression of D^{ex} , one clearly plays a preponderant role, namely that with $i = x^2 - y^2$. Indeed, the xy and $x^2 - y^2$ type orbitals are localized in the plane of the bridging network and are favorably oriented to give zones of strong overlap density (see below). In contrast, the xy molecular plane is a nodal plane for the overlap densities involving the xy type orbital on one hand and the yz and xz type orbitals on the other hand so that the corresponding $j^{(xy,i,xy,i)}$ integrals are expected to be extremely small, if not negligible. As for the $j^{(xy,x^2-y^2,xy,x^2-y^2)}$ integral, it could be rather large since the z^2 type orbital may overlap the xy type orbital in the molecular plane but

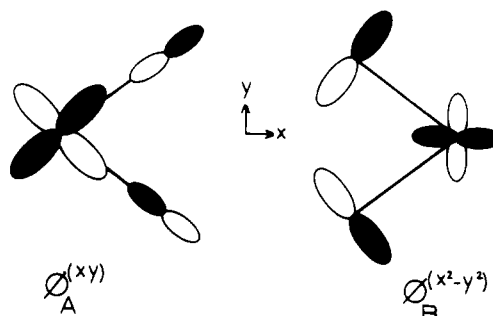


Figure 2. $\phi_A^{(xy)}$ and $\phi_B^{(x^2-y^2)}$ orbitals involved in the anisotropic interaction.

these two orbitals do not couple through spin-orbit interaction. It follows that D^{ex} can be approximated by

$$D^{ex} \simeq -\frac{\lambda^2}{\Delta_3^2} L_z^{(x^2-y^2,xy)} L_z^{(xy,x^2-y^2)} j^{(xy,x^2-y^2,xy,x^2-y^2)}$$

which can be rewritten as

$$D^{ex} \simeq \frac{1}{16} (\Delta g_z)^2 k^2 j^{(xy,x^2-y^2,xy,x^2-y^2)}$$

where $\Delta g_z = 2 - g_{A_z}$ refers to the single-ion ground state. k is a covalent factor defined as

$$L_z^{(xy,x^2-y^2)} = 2ik$$

Since Δg_z and k are local parameters, they are not expected to depend significantly on θ or on the Cu...Cu separation. Therefore, D^{ex} should vary as $j^{(xy,x^2-y^2,xy,x^2-y^2)}$. The xy and $x^2 - y^2$ type orbitals are schematized in Figure 2. In the former the metal orbital interacts in an antibonding σ fashion and in the latter in an antibonding π fashion with the 2p ligand orbitals. When θ is close to 90° , the 2p ligand orbitals involved in $\phi_A^{(xy)}$ and $\phi_B^{(x^2-y^2)}$ have the same orientation, so that the overlap density exhibits two strongly positive lobes along a Cu-O direction and two strongly negative lobes along the other Cu-O direction. When θ increases beyond 90° , the directions of the 2p ligand orbitals made an angle of $\theta = 90^\circ$ and the extremum of the overlap density is roughly multiplied by $\sin \theta$; i.e., it decreases. Since the magnitude of $j^{(xy,x^2-y^2,xy,x^2-y^2)}$ is governed by the extrema of the overlap density¹¹ $\rho^{(xy,x^2-y^2)}$, D^{ex} is expected to decrease in absolute value but not to change sign, confirming the experimental data.⁷⁻⁹

It is interesting to notice here that the variation of the extremum $\rho_E^{(xy,xy)}$ of the overlap density between xy type orbitals is greater than that of the extremum $\rho_E^{(xy,x^2-y^2)}$ of the overlap density between xy and $x^2 - y^2$ type orbitals. Indeed, from trivial trigonometric considerations, it is easy to check that $\rho_E^{(xy,xy)}$ varies as $(\cos^2 \theta)/2$, so that we have

$$d\rho_E^{(xy,xy)} / \rho_E^{(xy,xy)} = -\tan(\theta/2) d\theta$$

$$d\rho_E^{(xy,x^2-y^2)} / \rho_E^{(xy,x^2-y^2)} = -\cot \theta d\theta$$

In Figure 3 we represented $\rho^{(xy,x^2-y^2)}$ for two θ values, namely 95 and 110° . The former value corresponds to the case where the extremum of the overlap density is the most marked. This value is different from 90° owing to the admixture of 2s ligand orbitals in the expression of $\phi_A^{(xy)}$ and $\phi_B^{(x^2-y^2)}$. In the same way, the extremum of $\rho^{(xy,xy)}$ was obtained for 92.5° instead of 90° . When Figures 1 and 3 are compared, it clearly appears that $\rho^{(xy,x^2-y^2)}$ is much less sensitive to the θ value than $\rho^{(xy,xy)}$. In other words, J is more influenced by a small change of the bridging angle than D^{ex} ; i.e., $d\rho_E / \rho_E$ is more slowly varying in the former than in the latter. Since Figures 1 and 3 are drawn at the same scale, it is also visible that $\rho_E^{(xy,x^2-y^2)}$ is about twice larger than $\rho_E^{(xy,xy)}$. The magnitude of $\rho_E^{(xy,x^2-y^2)}$ explains why the ferromagnetic interaction in $\text{Cu}^{II}\text{VO}^{II}$ species was so pronounced.^{13,14} We already

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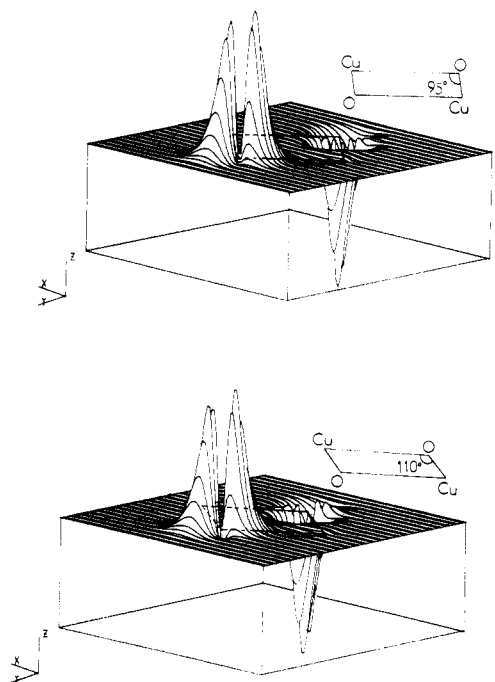


Figure 3. Overlap density $\rho^{(xy, x^2-y^2)}$ for two values of the bridging angle. $\rho^{(xy, x^2-y^2)}$ exhibits two positive lobes around one of the bridges and two negative lobes around the other bridge, of which the extrema are weakly sensitive to the variations of θ .

pointed out that D^{ex} in a bibringed copper(II) dimer was related to J , in the $Cu^{II}VO^{II}$ complex with the same bridging ligands.⁷⁻¹⁵

To approach in a more quantitative way the influence of θ on the magnitude of the zero field splitting within the triplet state, we explicitly calculated $j^{(xy, x^2-y^2, xy, x^2-y^2)}$ from $\phi_A^{(xy)}$ and $\phi_B^{(x^2-y^2)}$ as obtained from the EH method.¹⁶ The result is shown in Figure 4. $j^{(xy, x^2-y^2, xy, x^2-y^2)}$ has a maximum for θ close to 95°. On the same Figure 4 we plotted the variation of $j^{(xy, xy, xy, xy)}$ which is proportional to the ferromagnetic component of the S-T splitting. Since D^{ex} is expected to depend only on $j^{(xy, x^2-y^2, xy, x^2-y^2)}$, its angular behavior should be parallel to that of the latter. In fact, the experimental data⁷⁻⁹ available so far show that the D^{ex} dependence vs. the Cu...Cu separation d is not so dramatic for small values of d but becomes more marked as d increases. Since the variation of d is parallel to that of θ , it seems that the present results are in fairly good agreement with the experimental data.

To conclude this work, we want again to emphasize that the topological approach we propose cannot replace an ab initio calculation with large basis set and extended CI of the type of those that recently appeared in the field of the coupled systems.¹⁷⁻¹⁹ However, these calculations only dealt with the isotropic interaction

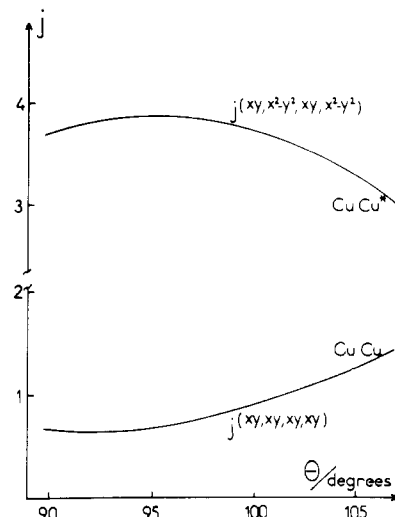


Figure 4. Variations of $j^{(xy, x^2-y^2, xy, x^2-y^2)}$ and $j^{(xy, xy, xy, xy)}$ vs. the bridging angle. The EH method exaggerates the delocalization of the metal orbitals toward the nearest neighbors, so that the unit of j should be considered as arbitrary.

characterized by J . This work is to our knowledge one of the first attempts to interpret the variation of the anisotropic interaction in a series of related compounds. Moreover, a sophisticated calculation, even when it reproduces the experimental data in a satisfying way, has the form of a black box. We think that our approach owing to its conceptual simplicity may be more appealing for the experimentalists looking to understand the EPR spectra of coupled complexes.

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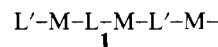
Contribution from the Department of Chemistry, University of Florence, and ISSECC, CNR, Florence, Italy, and Department of Chemistry, University of Modena, Modena, Italy

Magnetic Properties and Crystal Structure of a Linear-Chain Copper(II) Compound with Bridging Acetate and Oxamidate Ligands

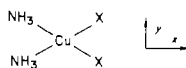
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The magnetic properties of linear-chain compounds have been actively investigated,²⁻⁴ particular attention being devoted to alternating chains. In order to synthesize complexes that have these structural (and hopefully magnetic) properties, several strategies are possible. One is that of reacting metal ions with two different potentially bridging ligands to yield structures of type **1**.



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 (16) For each θ value, the $\phi_A^{(xy)}$ and $\phi_B^{(x^2-y^2)}$ orbitals were determined as in ref 11 on the model monomeric fragment



The calculations were performed according to the Forticon 8 version of the EH method with charge iteration on all atoms. The parametrization is the same as in ref 11, and the Cu-X distance was taken equal to 1.92 Å. From the magnetic orbitals, the two-electron-exchange integrals were explicitly calculated from: "Table of Molecular Integrals"; Kotani, M., Amemiya, A., Ishiguro, E., Eds; Mazuren: Tokyo, 1963.

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