

The experimental evidence leads to the conclusion that a one-electron redox step is involved in the oxidation of methyl ethyl ketone and cyclohexanone with Cu(III) and that in the rate-limiting step Cu(III) is reduced to Cu(II) only.

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Registry No. $K_3[Cu(H_2TeO_6)_2]$, 74606-82-9; methyl ethyl ketone, 78-93-3; cyclohexanone, 108-94-1.

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Anisotropic Exchange in Transition-Metal Dinuclear Complexes. 3. Bis(μ -1,3-azido)bis(1,1,4,7,7-pentamethyldiethylenetriamine)dicopper(II) Bis(tetraphenylborate)

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The single-crystal EPR spectra of bis(μ -1,3-azido)bis(1,1,4,7,7-pentamethyldiethylenetriamine)dicopper(II) bis(tetraphenylborate), $Cu_2(Me_5dien)_2(N_3)_2(BPh_4)_2$, have been recorded in the range 5–140 K at both X- and Q-band frequencies. The g and D tensors have been found to be temperature dependent and not parallel to each other. The spectra at 5 K yield $g_{xx} = 2.056$, $g_{yy} = 2.038$, $g_{zz} = 2.211$, $D_{xx} = -136 \times 10^{-4} \text{ cm}^{-1}$, $D_{yy} = -432 \times 10^{-4} \text{ cm}^{-1}$, and $D_{zz} = 569 \times 10^{-4} \text{ cm}^{-1}$. The x and x' axes are practically parallel, while y and y' and z and z' make an angle of $\sim 20^\circ$. The experimental zero-field splitting has been found to exceed the value expected for point dipoles centered on the metal ions. The deviation is attributed to a substantial exchange contribution, which is discussed in terms of the interaction between the ground state of one ion with an excited state of the other ion.

Introduction

The study of the terms of the exchange spin Hamiltonian

$$H = JS_1 \cdot S_2 + S_1 \cdot D \cdot S_2 + d \cdot S_1 \times S_2 \quad (1)$$

has been mainly limited to the isotropic term,¹⁻⁶ for which now many useful correlations exist with the structural parameters of the complexes.⁷ Much less information is available on the parameters of the anisotropic exchange, D , and of the anti-symmetric exchange interactions, d , although in principle they can yield precious information on the interaction between the ground and excited states of the dinuclear units.^{8,9} Recently we have reported that a very large zero-field splitting is operative in the triplet state of bis(μ -hydroxo)copper(II) complexes, much larger than would be expected on the basis of magnetic dipolar interactions between the two copper ions.¹⁰ We interpreted the experimental data to show that a ferromagnetic coupling is operative between $x^2 - y^2$ and xy magnetic orbitals centered on the two metal ions.

Recently, Hendrickson¹¹ reported the magnetic susceptibility data and the crystal structure of bis(μ -1,3-azido)bis(1,1,4,7,7-pentamethyldiethylenetriamine)dicopper(II) bis(tetraphenylborate), $Cu_2(Me_5dien)_2(N_3)_2(BPh_4)_2$. The temperature dependence of the magnetic susceptibility yielded $J = 13 \text{ cm}^{-1}$, and the zero-field splitting of the triplet state was found to be fairly large. On the basis of polycrystalline powder spectra, and of an analysis according to which the g and D tensors were considered as parallel to each other, the spin Hamiltonian parameters were assumed as $D = 870 \times 10^{-4} \text{ cm}^{-1}$, $E = 162 \times 10^{-4} \text{ cm}^{-1}$. These data clearly show that exchange contributions are operative in the anisotropic term, since the reported parameters largely exceed the values expected for a dominant dipolar mechanism,¹¹ but single-crystal data are required in order to obtain information on the relative orientation of g and D within the dinuclear units. We wish to report here the results of such a study with the aim of

understanding the mechanism of exchange involving the ground and excited orbitals.

Experimental Section

The compound was prepared as previously described.¹¹ Single crystals were grown by slow evaporation of acetone solutions and found to conform to the reported crystal structure¹¹ with use of a Philips PW1100 automatic diffractometer. The unit cell is monoclinic, space group $P2_1/n$, with $a = 12.798 \text{ \AA}$, $b = 19.538 \text{ \AA}$, $c = 13.072 \text{ \AA}$, $\beta = 93.64^\circ$, and $Z = 4$.

Single-crystal EPR spectra were recorded with a Varian E-9 spectrometer equipped with both X- and Q-band frequency (9 and 35 GHz). Spectra at liquid-helium temperature were measured with use of Oxford Instrument ESR 9 and ESR 35 continuous-flow cryostats.

Results

Single-crystal EPR spectra of $Cu_2(Me_5dien)_2(N_3)_2(BPh_4)_2$ were recorded at X-band frequency in the range of temperature 5–140 K. The static magnetic field was rotated around the three orthogonal directions a , b , c^* . The spectra are temperature dependent as shown in Figure 1. At low temperature the spectra comprise four septets of lines, for a general orientation in the static magnetic field, in agreement with the presence of two magnetically nonequivalent pairs of copper(II) ions. The spectra in Figure 1 are recorded in the bc^* plane with the static magnetic field parallel to c^* . When the temperature is increased, the signals broaden until eventually the hyperfine splitting at 77 K is completely washed out. Also, the resonance fields are found to be affected by the temperature. Complete rotation data were collected at 5 and 140 K, respectively. The angular dependences of the transition

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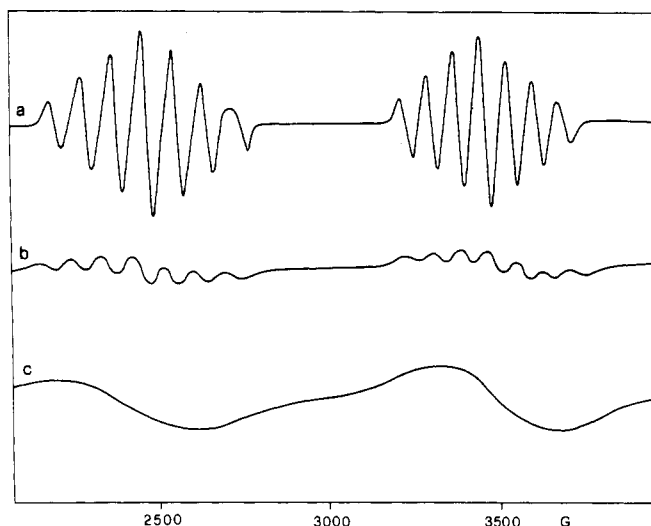


Figure 1. Single-crystal EPR spectra of $\text{Cu}_2(\text{Me}_5\text{dien})_2(\text{N}_3)_2(\text{BPh}_4)_2$ recorded with the static magnetic field parallel to the c^* direction at different temperatures: (a) 5 K; (b) 35 K; (c) 77 K.

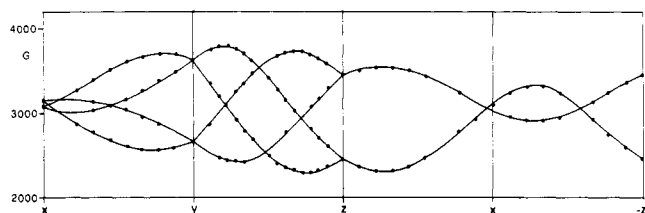


Figure 2. Angular dependence of the transition fields at X-band frequency at 5 K. The curves were calculated as described in the text. The x , y , z axes are defined in Table I.

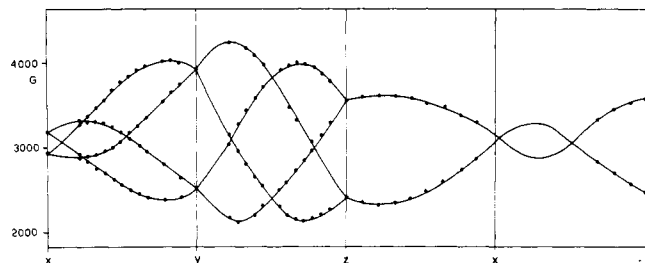


Figure 3. Angular dependence of the transition fields at X-band frequency at 140 K. See caption to Figure 2.

fields at the two temperatures are shown in Figures 2 and 3. In all the orientations the half-field transition was observed as well, which, as expected, showed small angular variation but a more consistent variation of the intensity. The spectra were fit to a triplet spin Hamiltonian by diagonalization of the Hamiltonian matrix, using the procedure previously described¹² in which \mathbf{g} and \mathbf{D} are allowed to be not parallel. The principal \mathbf{g} and \mathbf{D} values and directions at the two temperatures are given in Table I. The principal directions of the two tensors are practically unaffected by temperature, but the principal values do show some changes. In particular the g values increase on lowering the temperature, while D_{yy} and D_{zz} decrease and D_{xx} increases. Our calculated values of D at low temperature are practically identical with the values previously reported for the powder spectra. The g values are slightly different from those previously reported, as must be expected, since the powder spectra were analyzed on the assumption of parallel \mathbf{g} and \mathbf{D} tensors. The x and x' axes are

Table I. Principal Values and Directions of the \mathbf{g} and \mathbf{D}^d Tensors at 5 and 140 K^{b,c}

Direction Cosines (5 K)					
$g_{xx} =$	$g_{yy} =$	$g_{zz} =$	$D_{x'x'} =$	$D_{y'y'} =$	$D_{z'z'} =$
2.056 (2)	2.038 (2)	2.211 (3)	-136 (2)	-432 (2)	569 (3)
0.8990	0.0114	-0.4371	0.9198	-0.1096	-0.3769
0.0000	-0.9997	-0.0262	0.0409	-0.9282	0.3699
-0.4373	0.0235	-0.8990	-0.3903	-0.3556	-0.8492
Direction Cosines (140 K)					
$g_{xx} =$	$g_{yy} =$	$g_{zz} =$	$D_{x'x'} =$	$D_{y'y'} =$	$D_{z'z'} =$
2.046 (3)	2.015 (2)	2.178 (3)	-1 (2)	-683 (2)	682 (3)
0.9270	-0.0869	-0.3648	0.9230	0.1627	0.3486
-0.1077	-0.9935	-0.0370	-0.0024	0.9086	-0.4176
-0.3592	0.0730	-0.9304	-0.3847	0.3846	0.8391

^a The values are in 10^4 cm^{-1} . ^b The x , y , and z axes are defined as follows: x parallel to a , y parallel to b , and z in the ac plane. ^c The errors were estimated according to ref 13.

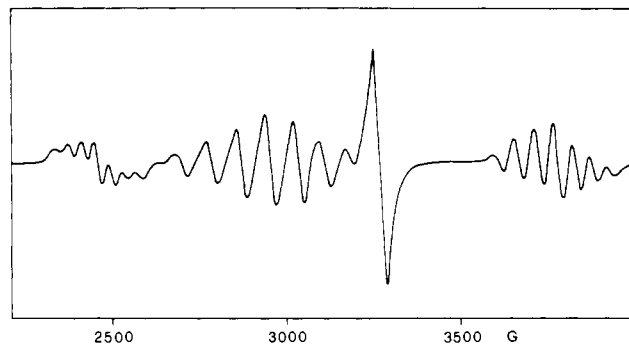


Figure 4. Single-crystal EPR spectrum of $\text{Cu}_2(\text{Me}_5\text{dien})_2(\text{N}_3)_2(\text{BPh}_4)_2$ with the static magnetic field in the (100) plane, making an angle of 65° with the z direction.

roughly parallel to each other (they make an angle of 4°) while the zz' and yy' axes are rotated by $\sim 20^\circ$.

Another feature of the spectra at low temperature is the uneven spacing of the hyperfine splitting of the two fine-structure transitions. A particularly striking example of such a behavior is shown in Figure 4. The sets of lines at lowest and highest field respectively correspond to one pair of fine-structure transitions, and the other pair corresponds to the intermediate-field lines. For the former pair of separation between successive hyperfine lines averages 37 G in the low-field and 53 G in the high-field transition. For the second pair the low-field transition shows an average splitting of 85 G, while for the high-field transition the upper limit for the hyperfine splitting is 15 G. It must also be noticed that the spacings of successive lines within a septet are not identical, but differences up to 10 G are observed.

Since this behavior presumably has to be attributed to relevant mixing of the $M = \pm 1$ levels within the $M = 0$ level, due to second-order zero-field splitting effects,^{14,15} a rotation with the static magnetic field in the (010) plane was performed also at Q-band frequency (35 GHz) at 10 K in order to reduce the importance of such effects. The (010) plane was chosen because it corresponds to a well-developed face of the crystals and also because \mathbf{g} and \mathbf{D} show to a good approximation two principal directions in this plane, namely x and z (or x' and z'). In fact in this rotation the differences in hyperfine spacings between the low- and the high-field components of a pair of fine-structure transitions reduce to a maximum of 5 G, while differences of up to 45 G were observed in the same rotation at X-band frequency. Therefore, a first-order analysis of the

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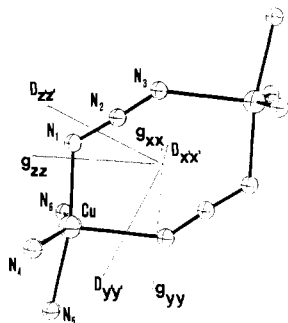


Figure 5. Orientation of the g and D tensors in the molecular frame.

hyperfine structure of the Q-band rotation is possible, showing that g and A are parallel to each other within error in this plane. The principal values of A are $A_{zz} = 93 \times 10^{-4} \text{ cm}^{-1}$ and $A_{xx} = 23 \times 10^{-4} \text{ cm}^{-1}$ in the (010) plane.

Discussion

The copper coordination environment seen in the crystal structure¹¹ determination is intermediate between that of a trigonal bipyramid and that of a square pyramid, closer to the latter limit as shown in Figure 5. The tetragonal axis of the pyramid is parallel to the Cu–N₃ bond, while the unique axis of the trigonal bipyramid is individuated by the Cu–N₁ and Cu–N₅ bonds. Deciding about the description of the coordination environment is important in determining the nature of the ground magnetic orbital, since an $x^2 - y^2$ ground state is expected for a square pyramid and a z^2 orbital for a trigonal bipyramid.¹⁶ The g and A values are extremely useful to discriminate between these two limit stereochemistries and also to determine the degree of distortion, as was shown for simple mononuclear copper(II) complexes.^{17,18}

The temperature dependence of g and D suggests that some rearrangement of the coordination polyhedron is occurring in the range 5–300 K. The principal g values are completely anisotropic at both 5 and 140 K, in agreement with the distorted five-coordinate geometry of the complex. The highest g value is found almost parallel to the Cu–N₃ bond (Figure 5), and the lowest g value is found very close to the Cu–N₁ direction.

The anisotropy of the g values is larger at higher temperature, with the smallest g value close to the free-electron value. On lowering temperature this value increases and so does the highest g value. The observed variation of the g values at the two temperatures is at least 10 times larger than the estimated errors, thus giving significance to the above observations. Since the g values of a pair correspond to a good approximation to those of the individual ions,^{19–21} it can be concluded that when the temperature is lowered the coordination environment of the copper ion goes closer to the square-pyramidal limit and that the unpaired electrons are in magnetic orbitals that are linear combinations of $x^2 - y^2$ and z^2 orbitals, $x^2 - y^2$ having a coefficient not too far from 1 at low temperature.

A confirmation to this interpretation comes from the hyperfine splitting, which has principal axes parallel within error to the g tensor, as expected. The highest A value, which is observed parallel to the highest g value, is in agreement with an essentially $x^2 - y^2$ ground state.²² The actual value, which

is expected to be half the single-ion value,^{19–21} is slightly higher than expected for a true square-pyramidal environment and seems to indicate weak axial interaction.

The D tensor has the y' and z' axes in the yz plane of g , with the z' axis making an angle of $\sim 20^\circ$ with the z axis. It must be noticed that the principal directions of D are rotated also from the Cu–Cu direction, which would give the maximum zero-field splitting if the magnetic dipolar interaction were dominating.^{9,10} This contribution can be evaluated with use of the experimental g values and the copper–copper distance on the basis of a point dipole approximation.²³ In order to use a unique coordinate frame, it is useful to refer to the g tensor axes in any case. The calculated dipolar zero-field splitting tensor (all D values in cm^{-1}), for the $\hat{S} \cdot \hat{D} \cdot \hat{S}$ Hamiltonian, is $D_{xx}^{\text{dip}} = -0.0071$, $D_{xy}^{\text{dip}} = -0.0205$, $D_{xz}^{\text{dip}} = 0$, $D_{yy}^{\text{dip}} = -0.0060$, $D_{yz}^{\text{dip}} = 0$, and $D_{zz}^{\text{dip}} = 0.0131$. This gives the largest zero-field splitting parallel to the Cu–Cu direction, with $D_{\text{max}}^{\text{dip}} = 0.0270$. The D^{dip} tensor must be compared to the experimental D tensor, which expressed in the diagonal g frame is $D_{xx} = \pm 0.0136$, $D_{xy} = \pm 0.0022$, $D_{xz} = \pm 0.0020$, $D_{yy} = \pm 0.0311$, $D_{yz} = \pm 0.0326$, and $D_{zz} = \pm 0.0447$. By assuming that $D = D^{\text{ex}} + D^{\text{dip}}$,⁸ the exchange contribution to D can be evaluated as $D_{xx}^{\text{ex}} = -0.0065$, $D_{xy}^{\text{ex}} = 0.0183$, $D_{xz}^{\text{ex}} = 0.0020$, $D_{yy}^{\text{ex}} = -0.0251$, $D_{yz}^{\text{ex}} = -0.0326$, and $D_{zz}^{\text{ex}} = 0.0316$ for one choice of sign and $D_{xx}^{\text{ex}} = 0.0207$, $D_{xy}^{\text{ex}} = 0.0225$, $D_{xz}^{\text{ex}} = -0.0020$, $D_{yy}^{\text{ex}} = 0.0372$, $D_{yz}^{\text{ex}} = 0.0326$, and $D_{zz}^{\text{ex}} = -0.0578$ for the other. It is apparent that the exchange contribution is not diagonal for either choice of signs. Also the diagonal values of the experimental D largely exceed the dipolar contributions. One might question about the validity of the point dipolar approximation for the evaluation of D^{dip} . Although this is a matter yet to be discussed in depth, it seems reasonable that the point dipolar approximation should hold for the unpaired spin densities centered on the two metal ions, which are largely separated.^{24,25} Some additional contribution might come from the unpaired spin densities transferred on the ligand atoms,²⁶ but in the few cases where calculations of these contributions were attempted,^{26–29} they were found to differ from the values estimated with the point dipolar model by only 20–30%. It seems therefore that the exchange contribution to the experimental D tensor in this case is fairly substantial.

In order to attempt a rationalization of these data, it is useful to recall the underlying theory for evaluating the exchange contribution to the zero-field splitting tensor. The expressions for D^{ex} were given by Moriya,^{30,31} using a third-order perturbation treatment:

$$D_{ij}^{\text{ex}} = \sum_{e_1 e_1'} \lambda_1^2 \frac{\langle g_1 | L_{1i} | e_1 \rangle \langle e_1' | L_{1j} | g_1 \rangle}{\Delta_1 \Delta_1'} J_{e_1 g_2 e_1' g_2} + \sum_{e_2 e_2'} \lambda_2^2 \frac{\langle g_2 | L_{2i} | e_2 \rangle \langle e_2' | L_{2j} | g_2 \rangle}{\Delta_2 \Delta_2'} J_{e_2 g_1 e_2' g_1} \quad (2)$$

where $J_{e_1 g_2 e_1' g_2} = \langle e_1 g_2 | H_{\text{ex}} | e_1' g_2 \rangle$, Δ_i is the energy separation between g_i and e_i , and the other symbols are defined accordingly. H_{ex} is the proper exchange Hamiltonian.

A comparison with the analogous expressions for the g tensor

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$$g_{ij} = g_e \delta_{ij} + \lambda_1 \sum_{e_1} \frac{\langle g_1 | L_{1i} | e_1 \rangle \langle e_1 | L_{1j} | g_1 \rangle}{\Delta_1} + \lambda_2 \sum_{e_2} \frac{\langle g_2 | L_{2i} | e_2 \rangle \langle e_2 | L_{2j} | g_2 \rangle}{\Delta_2} \quad (3)$$

where $g_e = 2.0023$ and the other symbols have the same meaning as in (2), immediately shows that \mathbf{g} and \mathbf{D} have nonparallel axes if the symmetry is lower than orthorhombic, i.e. if ij components ($i \neq j$) are different from zero. The origin of the difference is twofold: first, in the zero-field splitting tensor each term in the summation contains matrix elements involving different excited states $|e\rangle$ and $|e'\rangle$, while only one excited state is present in each summation term for the \mathbf{g} tensor. This difference is determined by the fact calculated while \mathbf{D} is obtained through a third-order perturbation treatment, \mathbf{g} is obtained at second order. The other difference is that even if the integrals of the type $J_{e_1 g_2 e_1' g_2}$ were zero unless $|e_1\rangle = |e_1'\rangle$ nevertheless the $g_{ij}/(g_{ii} - g_{jj})$ and $D_{ij}/(D_{ii} - D_{jj})$ ratios, which determine the principal values and directions of \mathbf{g} and \mathbf{D} , respectively, would be different since the latter include exchange integrals that are not present in the former. The two tensors might again have parallel principal axes only if the $J_{e_1 g_2 e_1' g_2}$ and $J_{e_2 g_1 e_2' g_1}$ integrals were assumed to be all identical and equal to the ground-state $J_{g_1 g_2 g_1 g_2}$ integral. This assumption does not seem to be tenable theoretically,³² and experimental results also showed its inapplicability.³³⁻³⁶ In the use of expression 2 for the analysis of the \mathbf{D}^{ex} tensor, the off-diagonal elements are certainly most difficult to estimate, since they are expected to depend heavily on low-symmetry components. Therefore, we plan to tackle globally the problem using a series of complexes, where useful comparisons can be made. The diagonal elements, if an $x^2 - y^2$ ground magnetic orbital is assumed, can be expressed as¹⁰

$$D_{xx}^{\text{ex}} = \frac{\Delta g_{xx}^2}{8} J_{x^2-y^2, yz} \quad D_{yy}^{\text{ex}} = \frac{\Delta g_{yy}^2}{8} J_{x^2-y^2, xz} \quad (4)$$

$$D_{zz}^{\text{ex}} = \frac{\Delta g_{zz}^2}{32} J_{x^2-y^2, xy}$$

where $J_{x^2-y^2, n}$ is a shorthand notation for $J_{x^2-y^2, n_1 x^2-y^2, n_2}$.

In order to compare the \mathbf{D}^{ex} tensor with the experiment, the former must be made traceless; then with use of the observed Δg_{ii} values the three $J_{x^2-y^2, n}$ unknowns can be calculated. For the first choice of sign the calculated values are $J_{x^2-y^2, yz} = 51.0 \text{ cm}^{-1}$, $J_{x^2-y^2, xz} = 0.0 \text{ cm}^{-1}$, and $J_{x^2-y^2, xy} = 41.5 \text{ cm}^{-1}$, while for the second they are $J_{x^2-y^2, yz} = 45.0 \text{ cm}^{-1}$, $J_{x^2-y^2, xz} = 0.0 \text{ cm}^{-1}$, and $J_{x^2-y^2, xy} = -69.5 \text{ cm}^{-1}$. In either case the $J_{x^2-y^2, xz}$ integral is calculated as zero, while moderate couplings are expected for both $x^2 - y^2 - yz$ and $x^2 - y^2 - xy$ pathways, antiferromagnetic in one case and ferromagnetic in the other.

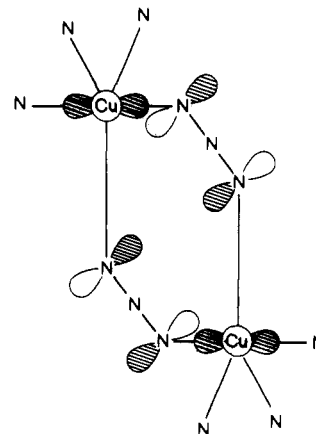


Figure 6. Sketch of the dinuclear unit, assuming a C_{2h} symmetry. The orbitals indicated are $x^2 - y^2$ of copper and π_{g_1} of N_3^- (see text).

In order to discuss the mechanism of the exchange interactions, it is useful to assume a C_{2h} symmetry for the complex, as schematized in Figure 6. In this symmetry the molecular orbitals that have metal $x^2 - y^2$, z^2 , and xz character are labeled as a_g and b_u , while yz and xy are bases for a_u and b_g . Therefore, in the limit of this symmetry, pathways involving the ground $x^2 - y^2$ orbital and yz and xy excited orbitals lead to ferromagnetic coupling, while pathways involving xz are antiferromagnetic in nature. On this assumption therefore the choice of sign that leads to negative values for both $J_{x^2-y^2, yz}$ and $J_{x^2-y^2, xy}$ seems more appropriate. In a recent discussion on the mechanism of exchange interaction of bridging azido groups it was suggested that the N_3^- orbitals that are responsible for the interaction are π_g in nature,²⁵ as shown in Figure 6.

In the present case the π_g orbitals in the xz plane, π_{g_1} , span the $a_g + b_u$ irreducible representations of C_{2h} , while those out of the plane, π_{g_2} , are $b_g + a_u$. The effective pathway then might be $x^2 - y^2 \parallel \pi_{g_1} \perp \pi_{g_2} \parallel yz$ or xy .

A moderate ferromagnetic coupling similar to that claimed to be responsible for the zero-field splitting of the present compound has already been observed for $Ni_2(NCS)_2$ ³⁸ moieties, where the two metal centers are 578 pm apart. The quantitative results we have obtained are rather surprising, since the calculated exchange integrals are much larger than the J value that involves the ground magnetic orbitals, obtained from the temperature-dependent magnetic susceptibility.¹¹ Although the orbitals that are involved in the exchange pathways are different, it is surprising that excited-state interactions are so effective in overcoming the long Cu-N distance that substantially quenches the interaction between the ground $x^2 - y^2$ orbitals. On the other hand, also in the case of bis(μ -hydroxo)-bridged copper(II) complexes^{10,12} we calculated very strong ferromagnetic interactions (300–700 cm^{-1}). Whether these large values are real or reflect some inadequacy of the theory thus far developed is difficult to say now. We are planning to collect more experimental data in related series of compounds to test the assumptions we have made.

Registry No. $Cu_2(\text{Me}_3\text{dien})_2(\text{N}_3)_2(\text{BPh}_4)_2$, 61651-90-9.

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