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Anisotropic Exchange in Transition-Metal Dinuclear Complexes. 4.[1] (μ-Benzotriazolato-N^1,N^3)bis[[tris(N^1-methylbenzimidazol-2-ylmethyl)amine-N,N^3,$N^{3'}$,$N^{3''}$]copper(II)] Trinitrate

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Single-crystal EPR spectra of the title compound, $[Cu_2(tmbma)_2(bta)](NO_3)_3$, have been recorded at room temperature at both X- and Q-band frequencies. The triplet spectra have been fit with parallel **g** and **D** tensors, whose principal values are $g_{xx} = 2.063$ (1), $g_{yy} = 2.190$ (2), $g_{zz} = 2.130$ (1), $D_{xx} = -45$ (4) $\times 10^{-4}$ cm^{-1}, $D_{yy} = 413$ (3) $\times 10^{-4}$ cm^{-1}, and $D_{zz} = -368$ (5) $\times 10^{-4}$ cm^{-1}. The D values have been compared with those calculated for magnetic dipolar interactions between two $S = {}^1/_2$ spins centered on the two copper ions, which are 5.563 Å apart. The presence of a substantial exchange contribution to the zero-field splitting has thus been recognized, and a possible mechanism for justification is suggested.

Introduction

EPR spectra are widely used for the study of the structure of metalloenzymes and metalloproteins.[3] In particular they have been employed to estimate the metal–metal distance in cases where two metal ions are coupled, by using the magnetic dipolar approximation.[4] Although this is in principle a feasible procedure, it relies on the assumption that the exchange contributions to the zero-field splitting are negligible. Some suggestions have been made[4] that the latter can be neglected if the coupling constant between the two metal ions is smaller than 30 cm^{-1}. However, this approximation has been shown to be invalid in several instances,[1] and the problem therefore must be resolved on a case by case basis.

Since histidine molecules are known, or suspected, to bridge metal ions in natural, or modified, metalloenzymes and metalloproteins,[6] it appeared of interest to us to characterize in detail the EPR spectra of imidazolate-bridged dinuclear copper complexes, in order to study how the anisotropic exchange is transmitted through a polyatomic bridge.[7]

One of us recently reported the X-ray crystal structure of the title compound,[8] $[Cu_2(tmbma)_2(bta)](NO_3)_3$, which is formed by two trigonal-bipyramidal copper(II) moieties bridged by a benzotriazolate ion, as shown in Figure 1. The temperature dependence of the magnetic susceptibility of the compound showed that the coupling in the dinuclear units is antiferromagnetic, the singlet–triplet separation being 24 cm^{-1}. The analysis of the polycrystalline powder EPR spectra showed that the excited triplet is split, the corresponding parameters being $D = 0.10$ cm^{-1} and $E/D = 0.25$. Since the two copper ions are separated by 5.536 Å, the zero-field splitting appeared to be larger than expected for a pure magnetic dipolar interaction between the two spins, and the presence of an exchange contribution was suspected.[7]

In view of the current interest in the characterization of the role of anisotropic exchange in the EPR spectra of dinuclear copper(II) complexes,[1,9-11] we felt it appropriate to obtain single-crystal data on $[Cu_2(tmbma)_2(bta)](NO_3)_3$ in order to find out experimentally the principal directions of the **g** and **D** tensors and to factorize out the exchange and dipolar contributions to the zero-field splitting.

Table I. Principal Values and Directions of the **g** and D Tensors[a] of $[Cu_2(tmbma)_2(bta)](NO_3)_3$

$g_{xx} = 2.063$ (1)	$g_{yy} = 2.190$ (2)	$g_{zz} = 2.130$ (1)
0.51 (1)	0.0000	−0.861 (7)
0.0000	1.0000	0.0000
−0.861 (7)	0.0000	−0.51 (1)
$D_{xx}{}^b = -45$ (4)	$D_{yy}{}^b = 413$ (3)	$D_{zz}{}^b = -368$ (5)
0.507 (9)	0.0000	−0.862 (5)
0.0000	1.0000	0.0000
−0.862 (5)	0.0000	−0.507 (9)

[a] The directions are given by the cosines referred to the crystal axes x, y, z. y is the b axis and z is orthogonal to the $(10\bar{1})$ face. [b] In cm^{-1} $\times 10^{-4}$.

Experimental Section

Single crystals of $[Cu_2(tmbma)_2(bta)](NO_3)_3$ were obtained as previously described.[8] Small crystals with a maximum dimension of 1 mm were found to have a well-developed $(10\bar{1})$ face. They are monoclinic, space group $C2/c$, with $a = 16.880$ Å, $b = 26.011$ Å, $c = 14.686$ Å, $\beta = 100.585°$, and $Z = 4$.

Single-crystal EPR spectra were recorded with a Varian E9 spectrometer, equipped with both X- and Q-band frequencies. Spectra down to 77 K were recorded with a standard liquid-nitrogen apparatus, while those below 77 K were obtained by using an Oxford Instruments ESR 9 cryostat.

Results

The polycrystalline powder EPR spectrum of $[Cu_2(tmbma)_2(bta)](NO_3)_3$ recorded at room temperature is shown in Figure 2.

Single-crystal EPR spectra of $[Cu_2(tmbma)_2(bta)](NO_3)_3$ were recorded with the static magnetic field being in the (010) plane and being parallel to the b crystal axis, respectively. Since the dinuclear cations possess C_2 site symmetry,[8] and consequently only one magnetic site is present in the unit cell, there is no need of three orthogonal rotations. The room-temperature spectra were recorded at both X- (9 GHz) and Q-band (35 GHz) frequencies.

As was observed for the polycrystalline powders, the spectra are typically triplet in nature. The angular dependence of the transition fields in the (010) plane is shown in Figure 3. The signals are fairly broad at room temperature. When the crystal

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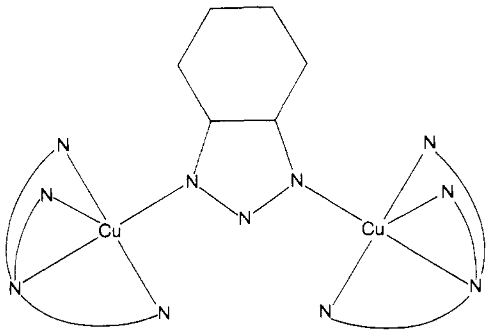

Figure 1. Sketch of the two trigonal-bipyramidal copper(II) moieties bridged by a benzotriazolate anion in $[Cu_2(tmbma)_2(bta)](NO_3)_3$.

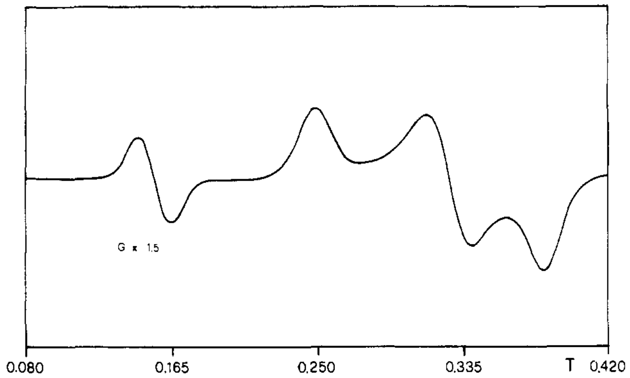

Figure 2. X-Band polycrystalline powder EPR spectrum of $[Cu_2(tmbma)_2(bta)](NO_3)_3$ recorded at room temperature.

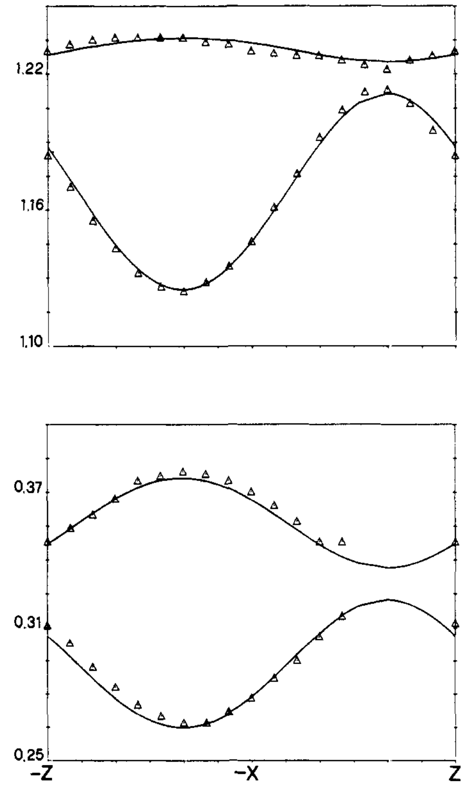

Figure 3. Angular dependence of the transition fields for $[Cu_2(tmbma)_2(bta)](NO_3)_3$ with the static magnetic field in the (010) plane: (upper) Q band (35 GHz); (lower) X band (9 GHz).

is cooled down to 25 K, a substantial sharpening of the bands is observed but no copper hyperfine splitting is resolved. A typical spectrum is shown in Figure 4. On further cooling, the spectra disappear in agreement with the single-triplet separation obtained by the temperature depedence of the magnetic susceptibility.[8] The

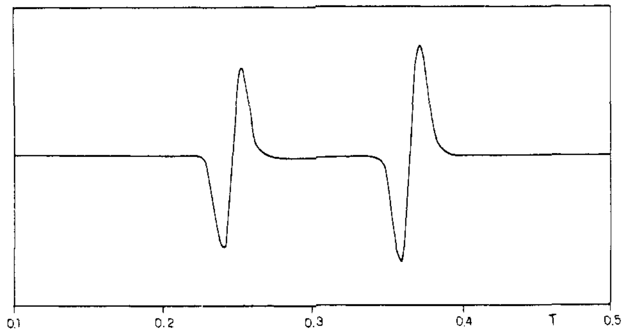

Figure 4. Typical single-crystal EPR spectrum of $[Cu_2(tmbma)_2(bta)](NO_3)_3$ recorded at 25 K at X-band frequency with the static magnetic field in the (010) plane making an angle of 60° with $-z$ (perpendicular to the $10\bar{1}$ crystal face).

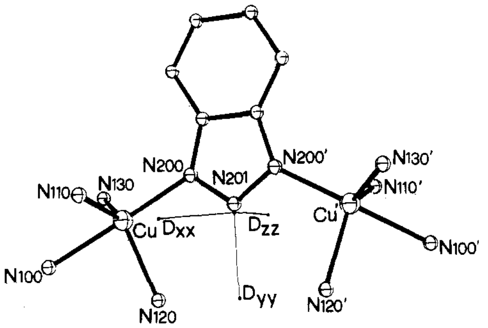

Figure 5. Sketch of the dinuclear cation $[Cu_2(tmbma)_2(bta)]^{3+}$ with **D** tensor principal directions.

transition fields observed at low temperature compare well with those observed at room temperature.

The lack of resolved copper hyperfine splitting is surprising since at low temperature the triplets should be magnetically dilute excluding dipolar broadening of the lines. An intramolecular broadening mechanism is then to be suspected. It must be recalled here that also in several other bis(μ-oxo)-bridged copper(II) complexes[12] only broad lines are resolved, showing no hyperfine splitting. The origin of this behavior is not understood.

The room-temperature spectra were analyzed through a least-squares fitting procedure previously described,[11] using the transition fields observed at two frequencies. Although the program allows for nonparallel **g** and **D** tensors, the best fit yields practically parallel spin-Hamiltonian tensors. The principal g and D values and directions, with estimated errors, are given in Table I. The largest g value, $g_{yy} = 2.190$ (2), is observed parallel to the b crystal axis. The corresponding D_{yy} value is also the largest component of the zero-field splitting (413 (3) $\times 10^{-4}$ cm^{-1}). The smallest D_{xx} component (-45 (4) $\times 10^{-4}$ cm^{-1}) is observed in a direction that makes an angle of ~9° with the copper-copper direction. The corresponding g_{xx} value, 2.063 (1), is also the smallest **g** component. A sketch of the dinuclear cation with the **D** tensor axes is shown in Figure 5.

Discussion

The **g** tensor of the pair is related to the $\mathbf{g}_i$ tensors of the individual ions according to the simple relation[13]

$$\mathbf{g} = \tfrac{1}{2}\mathbf{g}_1 + \tfrac{1}{2}\mathbf{g}_2 \qquad (1)$$

where $\mathbf{g}_1$ and $\mathbf{g}_2$ have nonparallel principal axes. The coordination environment around each copper ion is to a good approximation trigonal bipyramidal, with the direction defined by the metal ion and the binding nitrogen of the benzotriazolato anion defining the z (pseudotrigonal) axis.[8] The copper ion is outside the equatorial plane, toward the bridging benzotriazolate anion, and the in-plane bond angles are different from each other, being 121.9,

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126.6, and 103.8°. The individual **g** tensors can be reasonably assumed to have a principal direction parallel to z, while no safe prediction can be made for the other two principal directions. In the hypothesis of a molecular g direction parallel to z, we calculated the principal molecular g values from the experimental g values for several different orientations of the x and y axes, employing eq 1. We found that acceptable solutions (i.e. with all the g values larger or about equal to 2) yield $g_z \simeq 2.00$, $g_x = 2.25$ (2), and $g_y = 2.13$ (2), with y roughly parallel to the Cu–N110 bond direction. These calculated molecular g values agree with a trigonal-bipyramidal description of the complex,[14] showing that the ground state of the individual copper ions is essentially d_{z^2} in nature with a small admixture of $d_{x^2-y^2}$ in it.

The zero-field splitting tensor, as previously observed,[8] is much larger than expected for a purely magnetic dipolar interaction between the two spins. In fact, using the above estimated $\mathbf{g}_i$ tensors and the experimental metal–metal distance, one calculates[15] $D_{xx}{}^{\text{dip}} = -111 \times 10^{-4}$ cm^{-1}, $D_{yy}{}^{\text{dip}} = 57 \times 10^{-4}$ cm^{-1}, and $D_{zz}{}^{\text{dip}} = 54 \times 10^{-4}$ cm^{-1}, the largest value as expected being parallel to the Cu–Cu direction. Since the experimental **D** tensor has its smallest value parallel to this direction, it is evident that exchange contributions must be taken into account.

In order to evaluate the exchange contribution to **D**, integrals of the type $\langle n|L_i|g\rangle$ are required,[16,17] where $|g\rangle$ and $|n\rangle$ are the ground and one excited metal orbital, respectively, and L_i is the ith component of the orbital angular momentum. If, for the sake of simplicity, we assume a d_{z^2} ground-state orbital, we find that the exchange contributions to **D** along the principal directions are given by

$$\begin{aligned} D_{zz}{}^{\text{ex}} &= (9/4)(\lambda^2/\Delta_{yz}{}^2)J_{z^2,yz} \\ D_{xx}{}^{\text{ex}} &= (3/4)(\lambda^2/\Delta_{yz}{}^2)J_{z^2,yz} \\ D_{yy}{}^{\text{ex}} &= (3\lambda^2/\Delta_{xz}{}^2)J_{z^2,xz} \end{aligned} \tag{2}$$

where λ is the spin–orbit coupling constant, Δ_{yz} and Δ_{xz} are the energy separations between the ground-state d_{z^2} orbital and the indicated orbital, respectively, and the J parameters are the corresponding exchange interactions between the indicated orbitals.

$[Cu_2(tmbma)_2(bta)](NO_3)_3$ has strict C_2 symmetry,[8] but the overall symmetry is not far from C_{2v}, as shown by the principal directions of the spin-Hamiltonian tensors. One plane is defined by the benzotriazolate anion and the Cu–N200 vectors, which are coplanar within 3°. In C_{2v} symmetry the d_{z^2}, $d_{x^2-y^2}$, and d_{xz} orbitals on the individual copper ions yield molecular orbitals of symmetry $a_1 + b_1$, while the xy and yz orbitals yield $a_2 + b_2$. The reference frames are defined in Figure 5. Since the MO's obtained from d_{z^2} and d_{xz} have the same symmetry, $a_1 + b_1$, while that of the MO's obtained from d_{yz} is different, $a_2 + b_2$, J_{z^2yz} must be ferromagnetic, while $J_{z^2,xz}$ must be antiferromagnetic. As a consequence from (2) we learn that $D_{zz}{}^{\text{ex}}$ and $D_{xx}{}^{\text{ex}}$ are negative, with $D_{xx}{}^{\text{ex}} = {}^1/{}_3D_{zz}{}^{\text{ex}}$, and $D_{yy}{}^{\text{ex}}$ is positive. If $\mathbf{D}^{\text{ex}}$ is made traceless, to yield a new tensor $\mathbf{D}^{\text{exc}}$, (2) becomes

$$\begin{aligned} D_{xx}{}^{\text{exc}} &= -{}^1/{}_9D_{zz}{}^{\text{ex}} - {}^1/{}_3D_{yy}{}^{\text{ex}} \\ D_{yy}{}^{\text{exc}} &= -{}^4/{}_9D_{zz}{}^{\text{ex}} + {}^2/{}_3D_{yy}{}^{\text{ex}} \\ D_{zz}{}^{\text{exc}} &= {}^5/{}_9D_{zz}{}^{\text{ex}} - {}^1/{}_3D_{yy}{}^{\text{ex}} \end{aligned} \tag{3}$$

From (3) and the above considerations we learn that $D_{yy}{}^{\text{exc}}$ and $D_{zz}{}^{\text{exc}}$ are positive and negative, respectively, while $D_{xx}{}^{\text{exc}}$ is undetermined, depending on the relative value of $D_{zz}{}^{\text{ex}}$, and $D_{yy}{}^{\text{ex}}$.

The exchange contribution to **D** can be estimated by using the relation[16]

$$\mathbf{D} = \mathbf{D}^{\text{exc}} + \mathbf{D}^{\text{dip}} \tag{4}$$

If from the experimental **D** tensor, whose sign is not known, we subtract the dipolar contribution estimated through the point-dipolar approximation, we find two different sets of components of $\mathbf{D}^{\text{exc}}$, corresponding to the two different choices of sign for **D**. In either case we find that $D_{xx}{}^{\text{exc}}$ is calculated to be positive and smaller than the other two components, which in turn have opposite signs. In fact for one choice we calculate $D_{xx}{}^{\text{exc}} = 73 \times 10^{-4}$ cm^{-1}, $D_{yy}{}^{\text{exc}} = 353 \times 10^{-4}$ cm^{-1}, and $D_{zz}{}^{\text{exc}} = -426 \times 10^{-4}$ cm^{-1}, while for the other $D_{xx}{}^{\text{exc}} = 163 \times 10^{-4}$ cm^{-1}, $D_{yy}{}^{\text{exc}} = -473 \times 10^{-4}$ cm^{-1}, and $D_{zz}{}^{\text{exc}} = 310 \times 10^{-4}$ cm^{-1}.

According to (3) a positive $D_{xx}{}^{\text{exc}}$ can be obtained only if the $D_{zz}{}^{\text{ex}}$ contribution outweighs $D_{yy}{}^{\text{ex}}$. If we try to estimate the value of $D_{zz}{}^{\text{ex}}$, we may set $D_{yy}{}^{\text{ex}} = 0$. In this hypothesis $D_{yy}{}^{\text{exc}}$ and $D_{zz}{}^{\text{exc}}$ are predicted to be positive and negative, respectively; therefore, the first sign choice appears to be more appropriate. Again, using eq 3, we predict $D_{xx}{}^{\text{exc}}:D_{yy}{}^{\text{exc}}:D_{zz}{}^{\text{exc}} = 1:4:-5$, which is not too far from the calculated values 1:4.8:–5.8. The corresponding value of the exchange integral J_{z^2yz} can be calculated to be of the order of some wave numbers. This conclusion does not seem to be unreasonable, since although the metal centers are separated by a long distance, the ground-state d_{z^2} and the excited d_{yz} can interact through the π orbitals of the benzotriazolate anion.

Concluding Remarks

In view of the current interest in the possibility of obtaining structural information from the EPR spectra, it is apparent that the present information is an important result. In fact we have shown that even if the metal–metal distance is 5.536 Å, an exchange contribution to the zero-field splitting is operative. If one would attribute the experimental **D** tensor to the dipolar interaction only, the complex might have been described as having two copper ions at 3.5 Å, which is much shorter than the experimental value. The other important result is that ferromagnetic exchange interactions can also be propagated through imidazolate bridges connecting ions that are more than 5.5 Å apart.

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Registry No. $[Cu_2(tmbma)_2(bta)](NO_3)_3$, 82373-17-9.

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