through the $\delta^1\delta^{*1}$ state, which produces the observed fluorescence.

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Registry No. *cis*-$Mo_2(mhp)_2Cl_2(PEt_3)_2$, 94089-97-1; $Mo_2(mhp)_4$, 67634-80-4; Mo, 7439-98-7.

Supplementary Material Available: Listings of thermal parameters and structure factors (22 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratoire de Spectrochimie des Eléments de Transition, ERA 672, Université de Paris Sud, 91405 Orsay, France, and Department of Chemistry, University of Florence, and ISSECC, CNR, Florence, Italy

Single-Crystal EPR Study of $[Cu_2(t\text{-Bupy})_4(N_3)_2](ClO_4)_2$ (*t*-Bupy = 4-*tert*-Butylpyridine): Anisotropic Exchange in a Ferromagnetically Coupled Copper(II) Binuclear Complex

MARIE-LAURE BOILLOT,[1a] YVES JOURNAUX,[1a] ALESSANDRO BENCINI,[1c] DANTE GATTESCHI,*[1b] and OLIVIER KAHN*[1a]

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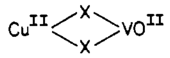
The compound $[Cu_2(t\text{-Bupy})_4(N_3)_2](ClO_4)_2$ is made up of binuclear copper(II) cations and noncoordinated perchlorate anions. Within the binuclear unit, the copper(II) ions are bridged by two azido groups in an end-on fashion. The magnetic behavior had shown that the metal centers were ferromagnetically coupled. This paper presents a single-crystal EPR investigation carried out at X-band frequency at 4.2 K. The principal values and the orientations of the **g** and **D** tensors associated with the triplet ground state were determined. Since two magnetically nonequivalent sites are present in the unit cell, the observed principal directions of **g** and **D** can be oriented in the molecular frame in two different ways. The solution in which one of the principal directions of **D** is as close as possible to the Cu···Cu direction is physically the most likely. **D** is composed of a dipolar contribution $\mathbf{D}^{dip}$ and an anisotropic exchange contribution $\mathbf{D}^{ex}$. This latter contribution is predominant, and its magnitude is related to the value of the two-electron-exchange integral $j^{(x^2-y^2,xy,x^2-y^2,xy)}$ involving the overlap density $\rho^{(x^2-y^2,xy)}$ between the *xy*-type orbital of an ion and the $x^2 - y^2$ type orbital of the other. A rough estimation of 150 cm^{-1} is obtained for $j^{(x^2-y^2,xy,x^2-y^2,xy)}$, leading to around 300 cm^{-1} for the $^3B_{2g}$–$^1B_{3u}$ and $^3B_{3u}$–$^1B_{2g}$ splittings within the states arising from the interaction between the $^2B_1$ (*xy*) ground state of an ion and the $^2A_1$ ($x^2 - y^2$) excited state of the other.

Introduction

The number of copper(II) binuclear complexes in which the ground state is the spin-triplet state is still very limited. Moreover in some cases where the singlet–triplet energy gap is small, the nature of the ground state is questionable. Indeed for these systems, the interpretation of both the magnetic data and the EPR spectra may be ambiguous. This arises from the fact that an intermolecular antiferromagnetic interaction may superimpose on the intramolecular ferromagnetic interaction. The zero-field splitting in the triplet state, when it is not negligible with regard to the isotropic exchange, is also a factor that makes somewhat problematic the univocal interpretation of the magnetic and EPR data. Maybe, it is why some authors recently claimed that the copper(II) binuclear complexes with a triplet ground state did not exist.[2]

In some cases, however, not only is the ground state actually the triplet but this state is largely stabilized with regard to the excited singlet. To our knowledge, up to now, three kinds of compounds exhibit such a situation:[3] (i) the planar bibridged copper(II) dimers with bridging angles close to 90°,[4-6] the ferromagnetic interaction having been interpreted in terms of accidental or quasi-accidental orthogonality of the magnetic orbitals;[7,8] (ii) the complexes with a network,[9] the ferromagnetic interaction then arising from the strict orthogonality of the magnetic orbitals;[7,8] (iii) the end-on azido-bridged copper(II) binuclear complexes where the stabilization of the triplet state has been attributed to a spin polarization effect.[10,11] For these complexes, both the magnetic and EPR data confirm the nature of the ground state: the $\chi_M T$ (molar magnetic susceptibility × temperature) vs. T plot exhibits the characteristic plateau $\chi_M T = 2N\beta^2g^2/3k$ in the temperature range where only the triplet ground state is thermally populated; the EPR spectra at very low temperature exhibit the features characteristic of a triplet state with zero-field splitting and eventually forbidden transitions.



The EPR investigation for these complexes is far from being limited to confirming the nature of the ground state arising from the isotropic exchange. It also provides information on smaller effects such as anisotropic and eventually antisymmetric exchanges.[12-14] If the mechanism of the isotropic exchange appears today rather well understood, the situation is much less advanced for the anisotropic and antisymmetric exchanges,[8,15] and many

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(1) (a) Université de Paris Sud. (b) University of Florence. (c) ISSECC, CNR.

(2) Carlin, R. L.; Burriel, R.; Cornelisse, R. M.; Van Duyneveldt, A. J. *Inorg. Chem.* **1983**, *22*, 831–832.

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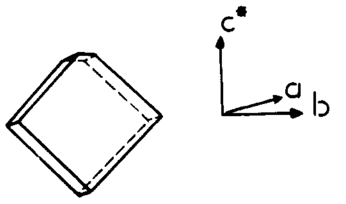

Figure 1. Morphology of the crystal used in the EPR study and orientation of the crystal axes.

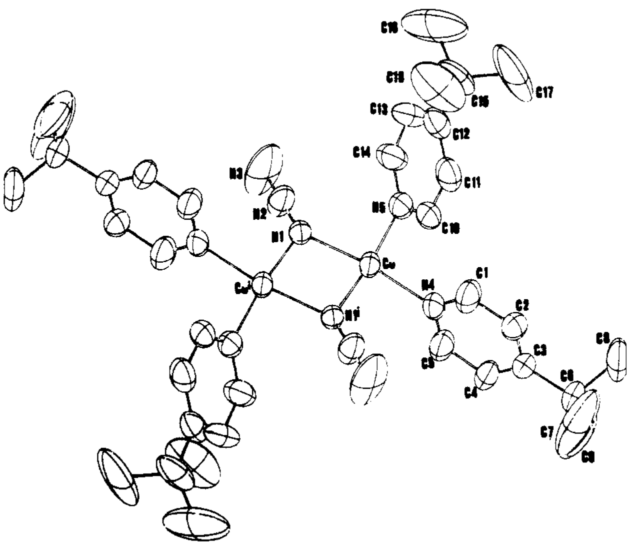

Figure 2. ORTEP view of $[Cu_2(t\text{-}Bupy)_4(N_3)_2]^{2+}$.

investigations will be necessary before being able to predict a priori the sign and the magnitude of the anisotropic exchange in a new complex. However, recently, a trend to a decrease of the zero-field splitting and of the magnitude of the anisotropic exchange on increasing Cu···Cu separation in planar bibridged complexes has been pointed out.[16] This paper represents an investigation of this kind dealing with the complex bis(μ-azido)tetrakis(4-*tert*-butylpyridine)dicopper perchlorate, noted as $[Cu_2(t\text{-}Bupy)_4(N_3)_2](ClO_4)_2$, which has been shown to exhibit a large intramolecular ferromagnetic interaction.[11]

Experimental Section

$[Cu_2(t\text{-}Bupy)_4(N_3)_2](ClO_4)_2$ was synthesized as previously described.[11] Single crystals were obtained by very slow evaporation of an ethanolic solution. The morphology of the crystals used in the EPR study is shown in Figure 1, as well as the orientation of the crystal axes determined with a Weissenberg camera. The compound crystallizes in the monoclinic system, space group $P2_1/c$. The lattice constants are $a = 12.819$ (3) Å, $b = 13.76$ (1) Å, $c = 13.65$ (1) Å, and $\beta = 100.00$ (2)° with $Z = 2$ binuclear units.[11]

The EPR study was carried out at X-band frequency with a Bruker ER 200 D spectrometer equipped with an Oxford Instruments continuous-flow cryostat, a Hall probe, and a Hewlett-Packard frequency meter. The spectra were recorded at 4.2 K in the three orthogonal planes *ab*, *bc**, and *ac**, the crystal being fixed on a vertical Perspex rod that could rotate around its axis. The orientation of the crystal was refined by taking advantage of the symmetry requirements of the monoclinic space group.

The principal values and the orientations of the **g** and **D** tensors were determined by minimizing the function $\sum_i(\Delta E_i - h\nu)^2$ where $h\nu$ is the incident quantum and ΔE_i the energy difference between the levels involved in the transitions. The energies E_i are calculated for each experimental field by diagonalizing the matrix associated with the Hamiltonian (1), given under Results.

Results

The structure of the $[Cu_2(t\text{-}Bupy)_4(N_3)_2]^{2+}$ cation is recalled in Figure 2, and the X-band powder EPR spectrum is recalled in Figure 3. This spectrum, which is typical of a triplet state, has been interpreted by assuming that the **g** and **D** tensor axes were coincident and using Wasserman's equations.[17]

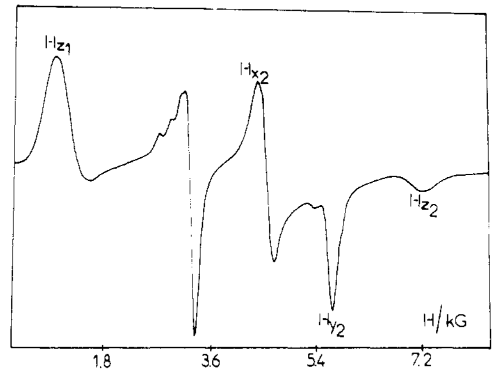

Figure 3. X-Band powder EPR spectrum of the title compound at 4.2 K.

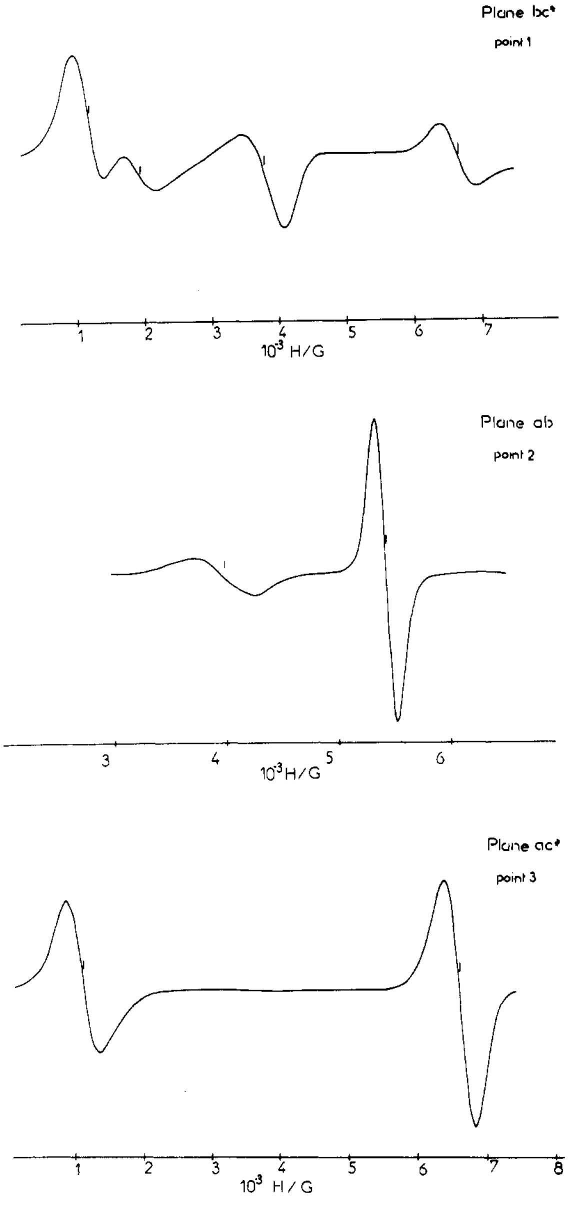

Figure 4. Typical X-band EPR spectra of the title compound at 4.2 K. These spectra refer to the angular settings indicated in Figure 5.

Three typical single-crystal EPR spectra are given in Figure 4. The angular variation of the resonant fields in the three

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(15) Gatteschi, D.; Bencini, A. In ref 3.

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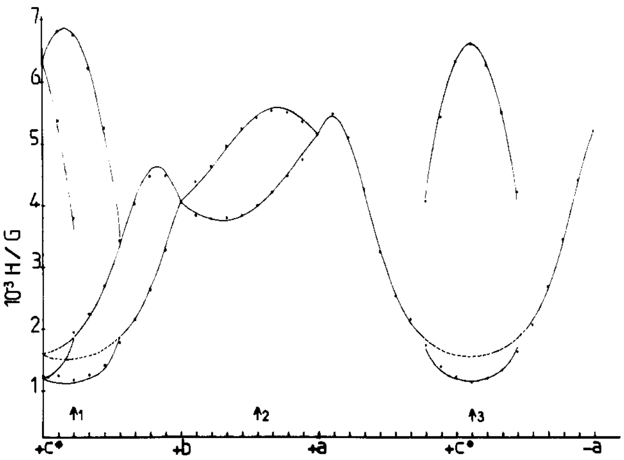


Figure 5. Angular variations of the resonant fields for $[Cu_2(t\text{-}Bupy)_4(N_3)_2](ClO_4)_2$: •, experimental; —, calculated.

Table I. Principal Values and Orientations with Regard to the *abc** Referential of the **g** and **D** Tensors[a]

g	2.07 (2)	−0.1 (6)	0.94 (9)	−0.33 (9)
	2.03 (2)	0.99 (7)	0.1 (6)	0.1 (2)
	2.24 (1)	0.13 (5)	−0.31 (5)	−0.94 (2)
D	−0.119 (3)	−0.35 (5)	0.89 (2)	−0.306 (6)
	−0.170 (3)	0.92 (2)	0.38 (5)	0.06 (2)
	0.288 (3)	0.172 (4)	−0.260 (4)	−0.950 (1)

[a] The uncertainty on the last figure is given in parentheses. The principal values of **D** are given in cm^{-1}.

orthogonal planes is represented in Figure 5. Owing to the symmetry of the crystal, there are two magnetically nonequivalent sites in the *ab* and *bc** planes but only one site in the *ac** plane and along the *a*, *b*, and *c** directions.[18] In the *ac** and *bc** planes, a very strong angular dependence of the resonant fields (several hundreds of gauss per degree) and of the intensity of the signals is observed. The spectra in the *ac** and *bc** planes exhibit either the two signals of the triplet state per magnetic site or only one signal, the vanishing of the second signal occurring within a few degrees. In the *ab* plane, the spectra exhibit only one signal per magnetic site in the whole angular range. The signal associated with the half-field transition cannot be followed in the whole temperature range. However, a weak and broad transition is observed for some angular settings around 1600 G. This transition is often hidden by the allowed transitions.

At 10° of *c** in the *ac** plane and at 15° of *c** in the *bc** plane, a transition around 6800 G is observed, which is close to the highest field transition H_{z_2} of the powder spectrum. In the same way, at 15° of *b* in the *bc** plane and at 10° of *a* in the *ac** plane, one observes transitions close to the H_{x_2} and H_{y_2} transitions, respectively, of the powder spectrum. These results led to a first approximation of **g** and **D**, which, at this stage, were assumed to be coincident. From these orientations and the principal values deduced from the powder spectrum, we performed a first simulation of the spectra in the three orthogonal planes. This allowed us to assign the observed transitions, which is necessary for the fitting procedure we used.[12]

The EPR data are interpreted from the spin Hamiltonian associated with the pair state $S = 1$:

$$\mathcal{H} = \beta H\cdot\mathbf{g}\cdot S + S\cdot\mathbf{D}\cdot S \qquad (1)$$

The principal values and the orientations of the **g** and **D** tensors are given in Table I. Since there are two nonequivalent magnetic sites, two orientations of **g** and **D** with regard to the molecular axes are compatible with the experimental data and it is not possible to choose unambiguously between these two solutions. In the next section, however, we shall propose a choice. It must be noticed that the fitting is not very sensitive to the orientation of the **g** tensor, this being particularly true in the *xy* plane, where the anisotropy of **g** is very weak. This shows up clearly from the calculated uncertainties given in Table I. On the other hand, the orientation of the **D** tensor is determined with better accuracy.

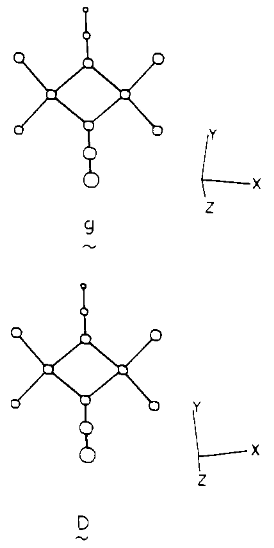


Figure 6. Orientations of **g** and **D** with regard to the binuclear cation (see text).

Table II. Comparison between the Spin Hamiltonian Parameters Obtained in This Work and Those Deduced from the Powder Spectrum[a]

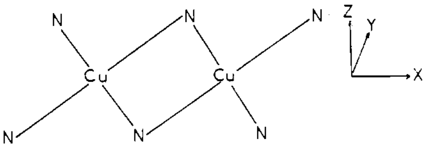
	this work	powder spectrum
g_x	2.07	2.06
g_y	2.03	2.00
g_z	2.24	2.21
$\lvert D\rvert/cm^{-1}$	0.43	0.42 (5)
$\lvert E\rvert/cm^{-1}$	0.026	0.02 (5)

[a] It is recalled that $D = 3D_z/2$ and $E = (D_x - D_y)/2$.

The principal values of the **g** tensor and of the axial *D* and rhombic *E* parameters of the zero-field splitting determined in this single-crystal investigation are compared to the values deduced from the powder spectrum in Table II. The two sets of parameters are close to each other. It must be recalled here that the powder spectrum was interpreted by assuming that **g** and **D** were coincident, which is not rigorously exact.

Discussion

In $[Cu_2(t\text{-}Bupy)_4(N_3)_2](ClO_4)_2$, the two metal ions and their nearest-neighbor nitrogen atoms represented in **1** lie in the same mean plane.[11] We define the molecular axes as shown in **1** with *Z* perpendicular to the mean plane and *X* along the Cu···Cu direction. As already mentioned, the observed principal directions of **g** and **D** can be oriented in the molecular frame in two different ways. According to one choice, g_z makes an angle of 15.8° with the *Z* axis while, for the second choice, one **D** direction is reasonably close to the *X* axis, D_{xx} making an angle of 9.7° with it while, for the latter choice, the closest approach to *X* is 50.7°. Since in all the already reported determinations of **D** in planar bibridged copper(II) binuclear complexes, one principal **D** direction is parallel to the *X* axis,[12-16] we favor the former choice, which is visualized in Figure 6. At first view, the orientation of **g** is surprising. For instance, the g_z direction making an angle of 15.8° with the *Z* axis, g_x and g_y are not rigorously in the *XY* mean plane. Indeed, for a planar binuclear copper(II) complex resulting from



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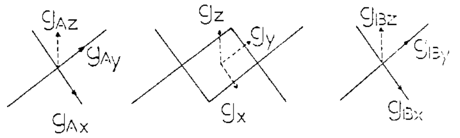
the sharing of an edge between two square-planar monomeric fragments, the orientations of the local $\mathbf{g}_A$ and $\mathbf{g}_B$ tensors and of the molecular **g** tensor are expected to be as shown in **2**, with **g**



2

$= {}^1/_2(\mathbf{g}_A + \mathbf{g}_B)$. Such an orientation for **g** was found in $[Cu_2(bpy)_2(OH)_2](SO_4)\cdot 5H_2O$ (bpy = 2,2′-bipyridyl).[12] In this compound, the terminal ligands bpy are located in the same mean plane as the $Cu(OH)_2Cu$ network. In contrast, in the title compound, the two crystallophically independent *t*-Bupy ligands bound to a same metal ion are tilted with regard to the *XY* mean plane, the tilt angles being 47 and 81°, respectively. It follows that the actual symmetry of each metal ion is far from being D_{4h} or even C_{2v}. The π orbitals of the aromatic rings may interact with the d metal orbitals so that the local ground states are no more pure *XY* states. Therefore, $\mathbf{g}_A$, $\mathbf{g}_B$, and **g** may be significantly desoriented with regard to the ideal situation represented in **2**. This may be due to anisotropic π effects of the *t*-Bupy ligands, similar to those observed by Carlin et al. in their investigations of the EPR and magnetic properties of $[Co(C_5H_5NO)_6](ClO_4)_2$, where C_5H_5NO is pyridine *N*-oxide,[19] and justified subsequently in the frame of the angular-overlap model.[20,21]

The **D** tensor may be expressed as the sum of a dipolar contribution noted as $\mathbf{D}^{dip}$ and an anisotropic exchange contribution noted as $\mathbf{D}^{ex}$.[22] $\mathbf{D}^{dip}$ is usually calculated in the approximation of the magnetic dipoles $\vec{\mu}_1$ and $\vec{\mu}_2$ centered on the metal ions.[23] The interaction energy *W* is then given by

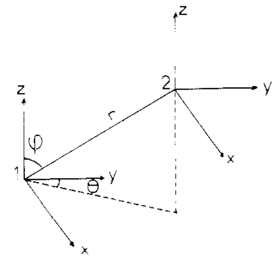
$$W = \frac{1}{r^3}\left|\vec{\mu}_1\cdot\vec{\mu}_2 - \frac{3(\vec{\mu}_1\cdot r)(r\cdot\vec{\mu}_2)}{r^2}\right|$$

where *r* is the metal–metal separation. In the basis set where **g** is diagonal, $\mathbf{D}^{dip}$ may be written as[24]

$$\mathbf{D}^{dip} = \frac{\beta^2}{r^3} \times$$

$$\begin{vmatrix} \begin{matrix} g_x{}^2(1 - 3\sin^2\theta \times \\ \sin^2\varphi) \end{matrix} & \begin{matrix} -3g_xg_y \sin\theta \times \\ \cos\theta \sin^2\varphi \end{matrix} & \begin{matrix} -3g_xg_z \sin\theta \times \\ \sin\varphi\cos\varphi \end{matrix} \\ & \begin{matrix} g_y{}^2(1 - 3\cos^2\theta \times \\ \sin^2\varphi) \end{matrix} & \begin{matrix} -3g_yg_z \cos\theta \times \\ \sin\varphi\cos\varphi \end{matrix} \\ & & g_z{}^2(1 - 3\cos^2\varphi) \end{vmatrix} \qquad (2)$$

where the θ and φ angles are defined as follows:



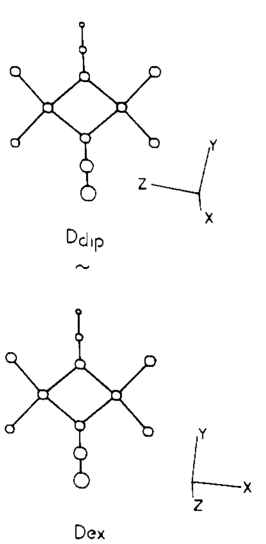


Figure 7. Orientations of $\mathbf{D}^{dip}$ and $\mathbf{D}^{ex}$ with regard to the binuclear cation (see text).

Table III. Principal Values (cm⁻¹) and Orientations with Regard to the *abc** Referential of the $\mathbf{D}^{dip}$ and $\mathbf{D}^{ex}$ Tensors

$\mathbf{D}^{dip}$	0.037	0.134	0.283	−0.949
	0.030	0.991	−0.051	0.125
	−0.067	−0.013	−0.958	−0.288
$\mathbf{D}^{ex}$	−0.055	0.133	0.952	0.277
	−0.196	0.976	−0.175	0.130
	0.251	0.172	0.253	−0.952

$\mathbf{D}^{dip}$ in (2) arises from the Hamiltonian $\hat{S}_A\cdot\mathbf{D}^{dip}\cdot\hat{S}_B$ involving the local spins $\hat{S}_A$ and $\hat{S}_B$. $\mathbf{D}^{dip}$ has then a nonzero trace. To be subtracted from the traceless total **D** tensor defined in (1), the dipolar contribution must be expressed according to $S\cdot\mathbf{D}^{dip}\cdot S$ where $\mathbf{D}^{dip}$ is itself made traceless. For a binuclear copper(II) complex, we have[25]

$$\hat{S}_A\cdot\mathbf{D}\cdot\hat{S}_B = {}^1/_2\hat{S}\cdot\mathbf{D}\cdot\hat{S}$$

From **D** and $\mathbf{D}^{dip}$, it is easy to extract $\mathbf{D}^{ex}$. The principal values and the orientations of the dipolar and anisotropic exchange contributions to **D** for the chosen solution are given in Table III and visualized in Figure 7.

As far as **D** is concerned now, as in the previously studied bibridged copper(II) dimers, the anisotropic exchange contribution is by far predominant. If the zero-field splitting was purely dipolar in nature, the axial and rhombic parameters would be 0.10 cm⁻¹ and 0.002 cm⁻¹ respectively, instead of 0.43 cm⁻¹ and 0.026 cm⁻¹ actually.

The problem at hand is the interpretation of the magnitude of $\mathbf{D}^{ex}$. It is now well established that the anisotropic exchange is due to the combined effect of the local spin–orbit coupling and the interaction within the pair.[8,14,23,26] When the site symmetry of the metal ions is high enough in order for the local ground state $\phi_A{}^{(0)}$ and excited states $\phi_A{}^{(i)}$ to transform as different irreducible representations of the symmetry group, the principal values of $\mathbf{D}^{ex}$ may be written as[8]

$$D_{xx}{}^{ex} = -2A_x + A_y + A_z \qquad D_{yy}{}^{ex} = A_x - 2A_y + A_z$$
$$D_{zz}{}^{ex} = A_x + A_y - 2A_z \qquad (3)$$

with

$$A_x = \frac{1}{3}\,\frac{\lambda^2}{\Delta_1{}^2}L_x{}^{(10)}L_x{}^{(01)}[j^{(1010)} - j^{(1100)}]$$
$$L_x{}^{(i0)} = \langle\phi_A{}^{(i)}|\hat{L}_x|\phi_A{}^{(0)}\rangle \qquad (4)$$
$$j^{(ijkl)} = \langle\phi_A{}^{(i)}(1)\ \phi_B{}^{(j)}(2)|r_{12}{}^{-1}|\phi_A{}^{(k)}(2)\ \phi_B{}^{(l)}(1)\rangle$$

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$\phi_A^{(1)}$ being the excited eigenstate coupling with $\phi_A^{(0)}$ through $\hat{L}_x$ and Δ_1 the energy gap between the two states. λ is the local spin–orbit parameter. A_y and A_z are obtained by circular permutation $x \rightarrow y \rightarrow z$ and $1 \rightarrow 2 \rightarrow 3$. All the terms A_u, $u = x$, y, z, are positive since $j^{(ioio)}$ is much larger than $j^{(iioo)}$ for any i. It has been suggested[13,27] that the integral $j^{(x^2-y^2,xy,x^2-y^2,xy)}$, which involves the overlap density $\rho^{(x^2-y^2,xy)}$ between orthogonal magnetic orbitals localized in the plane of the bridging network, is the largest among the $j^{(ioio)}$ integrals. It follows that we can approximate D_{zz}^{ex} by

$$D_{zz}^{\mathrm{ex}} \simeq -\frac{2}{3}\frac{\lambda^2}{\Delta_z^2}L_z^{(x^2-y^2,0)}L_z^{(0,x^2-y^2)}j^{(x^2-y^2,0,x^2-y^2,0)}$$

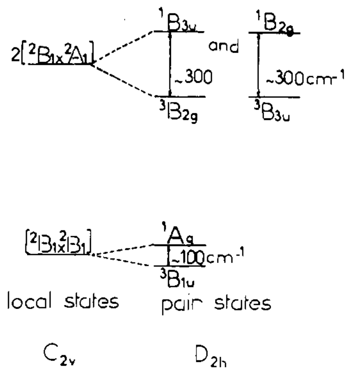
which can be rewritten as

$$D_{zz}^{\mathrm{ex}} \simeq -\frac{1}{24}\Delta g_z^2 k^2 j^{(x^2-y^2,0,x^2-y^2,0)} \qquad (5)$$

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

$$L_z^{(x^2-y^2,0)} = -2ik$$

With $\Delta g_z = 0.2414$ and $k \sim 0.9$, we obtain for $j^{(x^2-y^2,0,x^2-y^2,0)}$ a value of the order of 150 cm^{-1}. Of course, this value should only be considered as a rough approximation. In particular, the equations (3) and (4) are valid only when all the integrals $S^{(oi)} = \langle\phi_A^{(0)}|\phi_B^{(i)}\rangle$ are zero. Otherwise, the A_u's contain additional terms in $\beta^{(oi)}S^{(oi)}$ where $\beta^{(oi)}$ is a one-electron-transfer integral involving the ground state of an ion and an excited state of the other. In the present case, the orientation of **g** suggests that the local ground states are not pure xy states so that some $S^{(oi)}$ may be not rigorously vanishing. Nevertheless, this EPR study completes the magnetic investigation by giving an order of magnitude of $2j^{(x^2-y^2,0,x^2-y^2,0)} \sim 300$ cm^{-1} for the $^3B_{2g}$–$^1B_{3u}$ and $^3B_{3u}$–$^1B_{2g}$ splittings within the states arising from the interaction between the $^2B_1$ (xy) ground state of an ion and the $^2A_1$ ($x^2 - y^2$) excited state of the other in $[Cu_2(t\text{-Bupy})_4(N_3)_2](ClO_4)_2$, as schematized in **3**, where we refer to idealized C_{2v} site symmetries and D_{2h} molecular symmetry.



3

Finally, we can notice that, although the nature of the bridges is different, the title compound closely follows the correlation between D_{zz} and the Cu···Cu separation recently proposed.[16]

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Contribution from the Departments of Chemistry and Physics,
The University of Calgary, Calgary, Alberta, Canada T2N 1N4

Conjugate Base Pathway for Water Exchange on Aqueous Chromium(III): Variable-Pressure and -Temperature Kinetic Study

FAN-CHOU XU,[1a] H. ROY KROUSE,[1b] and THOMAS W. SWADDLE*[1a]

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Oxygen-18 tracer studies at ionic strength 0.7 mol kg^{-1} with [H$^+$] ranging from 0.0031 to 0.12 mol kg^{-1}, temperature from 25 to 55 °C, and pressure from 0.1 to 400 MPa gave the following kinetic parameters for water exchange on aqueous $Cr(H_2O)_6^{3+}$ and $Cr(H_2O)_5OH^{2+}$, respectively: k(298.15 K, 0.1 MPa) = 2.4×10^{-6} and 1.8×10^{-4} s^{-1}; $\Delta H^* = 108.6 \pm 2.7$ and 111.0 ± 2.5 kJ mol^{-1}; $\Delta S^* = +11.6 \pm 8.6$ and $+55.6 \pm 8.1$ J K^{-1} mol^{-1}; $\Delta V^* = -9.6 \pm 0.1$ and $+2.7 \pm 0.5$ cm^3 mol^{-1}. For $Cr(H_2O)_6^{3+}$, ln k is accurately a linear function of pressure to 400 MPa at least, implying no solvational change in the activation process. The mechanistic significance of these results is discussed.

Introduction

Hunt, Plane, and Taube, in their pioneering studies[2-5] of the primary hydration of aqueous metal ions, studied the rate of exchange of $H_2{}^{18}O$ between $Cr(H_2O)_6^{3+}$ and solvent water while varying the reaction conditions including the hydrogen ion concentration. They found no significant dependence of the observed first-order rate coefficient k_{obsd} upon [H$^+$] down to pH ~2. On the other hand, Plumb and Harris[6] found a two-term rate equation of the type

$$k_{\mathrm{obsd}} = k_0 + k_{-1}[H^+]^{-1} \qquad (1)$$

to apply in the exchange of $H_2{}^{18}O$ with Rh^{3+}(aq). More recently it has been shown[7,8] that a similar equation in which the term $k_{-1}[H^+]^{-1}$ is often dominant governs the rate of water exchange on monomeric Fe^{3+}(aq) as given by ^{17}O NMR line broadening with $0.008 \leq [H^+] \leq 6$ mol kg^{-1}.

The reported absence of an exchange pathway for Cr^{3+}(aq) corresponding to the $k_{-1}[H^+]^{-1}$ term, i.e., to exchange on the conjugate base $Cr(H_2O)_5OH^{2+}$

$$Cr(H_2O)_6^{3+} \overset{K_a}{\rightleftharpoons} Cr(H_2O)_5OH^{2+} + H^+ \qquad (2)$$

calls for reinvestigation, since pK_a values for $M(H_2O)_6^{3+}$ (M = Fe, Rh, Cr) do not vary very widely (2.9,[8] 3.3,[6] and 4.1,[9] respectively at 25 °C and ionic strength I = 0.5-1.0 mol L^{-1}). Indeed, preliminary studies by Eagle in our laboratories suggested that $Cr(H_2O)_5OH^{2+}$ is some 60 times more reactive in water exchange than is $Cr(H_2O)_6^{3+}$ at 45 °C, the corresponding ratios for Rh^{3+}(aq) and Fe^{3+}(aq) being ~690 at 64 °C[10] and 750 at

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