J. Am. Chem. Soc. **1983**, *105*, 761–764

Spectra. Infrared spectra (including expanded spectra) were taken with a Perkin-Elmer Model 621 dual-grating spectrophotometer fitted with a Frequency Marker Accessory 221-0348 and flushed with dried air. Raman spectra, normally of the neat solid powders in sealed capillary tubes, were measured with a Japan Spectroscopic Co. Model JASCO R300 spectrometer fitted with a Coherent Radiation Model CR4 argon ion laser; spectral slit widths were in the range 2–3 cm^{-1} and power in the sample compartment 160–320 mW. Frequency precision for reasonably narrow bands is within 1 cm^{-1} in the infrared and within 2 cm^{-1} in the Raman spectra.

Acknowledgment. D. T. Light is thanked for technical assistance, and Dr. J. E. Fildes for microanalyses.

Registry No. $NaH(HCO_2)_2$, 24644-55-1; $NaD(HCO_2)_2$, 84050-15-7; $NaH(DCO_2)_2$, 82941-07-9; $NaD(DCO_2)_2$, 84050-16-8; $NaH(HCO_2)(DCO_2)$, 84050-17-9.

Supplementary Material Available: Frequencies of Raman bands of solid sodium hydrogen bis(formate) below 300 cm^{-1} (Table II); vibrational band frequencies of liquid formic acid (4000–500 cm^{-1}) (Table III) (2 pages). Ordering information is given on any current masthead page.

Correlation between Anisotropic Exchange and Structure of Di-μ-hydroxo Bridged Copper(II) Complexes

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Abstract: The EPR spectra of a series of di-μ-hydroxo bridged copper(II) complexes have been recorded at both X- and Q-band frequency. The zero-field-splitting parameters have been found to be large ($D > 1.1$ cm^{-1}) and to be mainly determined by the exchange interactions between one ion in the ground state and the other one in an excited state. Therefore, the analysis of the EPR triplet spectra provides information on additional exchange pathways as compared to that available through magnetic susceptibility measurements. For the series of complexes the zero-field-splitting parameters are expected to depend mainly on the $J_{x^2-y^2,xy}$ integral. This is found to be ferromagnetic throughout the series, while the integral involving the ground-state orbitals, $J_{x^2-y^2,x^2-y^2}$, changes sign. The implications of this finding are discussed within current models for exchange interactions.

Introduction

Di-μ-hydroxo bridged copper(II) complexes still represent the most elegant case in which a successful correlation between structural parameters and extent of exchange coupling has been established.[2-4] At least 11 examples of such complexes are available and for 9 of them linear relations between J, the isotropic exchange constant, and either the Cu–O–Cu bond angle, ϕ, or the Cu–Cu distance have been found.[2-4] For the few cases which deviate from such a behavior, rationale explanations have been produced.[5,6]

The singlet–triplet splitting is mainly determined by the exchange interaction between the ground magnetic orbitals,[7] $J_{g,g}$. However, it is not the only interaction which is experimentally available, but an analysis of the EPR spectra may in principle yield also information on the anisotropic exchange and consequently on the interaction, $J_{g,n}$, between the ground magnetic orbital, g, and an excited one, n.[8] Although this has long been known, we are not aware of any systematic attempt to obtain $J_{g,n}$ for series of complexes and to relate its values to the geometric and electronic features of the complexes.

It is the purpose of this paper to report the EPR spectra of a series of di-μ-hydroxo bridged copper(II) complexes, for which $J_{g,g}$ has been found to vary linearly on the Cu–O–Cu angle from ferro- to antiferromagnetic, and to check whether a similar relationship is valid for the $J_{g,n}$ integrals.

Experimental Section

The $[Cu(bpy)OH]_2X$ ($X = SO_4{\cdot}5H_2O$, $(ClO_4)_2$, $(NO_3)_2$, bpy = 2,2′-bipyridine), $[Cu(tmpd)OH]_2(ClO_4)_2$ (tmpd = *N,N,N′,N′*-tetramethyl-*o*-phenylenediamine), $[Cu(teen)OH]_2(ClO_4)_2$ (teen = *N,N,N′,N′*-tetraethylenediamine), and $[Cu(tmen)OH]_2(ClO_4)_2$ (tmen = *N,N,N′,N′*-tetramethylethylenediamine) complexes were prepared as previously reported.[3,9-12]

The EPR spectra at X- (9 GHz) and Q-band (35 GHz) frequencies were recorded with a Varian E-9 spectrometer. Q-band spectra, with magnetic fields larger than 1.40 T, were recorded at the Department of Chemical Engineering, Twente University of Technology, Enschede, The Netherlands.

Results and Discussion

EPR Spectra. The polycrystalline powder spectra of $[Cu(bpy)OH]_2X$ ($X = SO_4{\cdot}5H_2O$, $(ClO_4)_2$, $(NO_3)_2$), $[Cu(tmpd)OH]_2(ClO_4)_2$, $[Cu(teen)OH]_2(ClO_4)_2$, $[Cu(tmen)OH]_2(ClO_4)_2$, at both X- and Q-band frequency were recorded. The polycrystalline powder and single-crystal EPR spectra of $[Cu(bpy)OH]_2SO_4{\cdot}5H_2O$ were previously reported,[13] but only to the limit of 1.40 T. Some representative examples of spectra at Q-band frequency are shown in Figure 1. The three bpy complexes show very similar spectra, with a feature at low fields, 0.1–0.3 T, and two additional ones in the range 1.5–1.9 T. Also the tmpd complex

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Table I. Spin-Hamiltonian, Exchange Coupling, and Structural Parameters for Some Di-μ-hydroxo Copper(II) Complexes

complex	g_{xx}[a]	g_{yy}[a]	g_{zz}[a]	$D_{x'x'}$[b]	$D_{y'y'}$[b]	$D_{z'z'}$[b]	$J_{x^2-y^2,x^2-y^2}$[c]	ϕ[d]	r[e]	$J_{x^2-y^2,xy}$[c]
$[Cu(bpy)OH]_2SO_4\cdot 5H_2O$	2.07 (13)	2.06 (13)	2.25 (4)	0.469	0.377	−0.846	−49	97	2.89	−715 ± 220
$[Cu(bpy)OH]_2(ClO_4)_2$	2.18 (13)	2.00 (14)	2.29 (5)	0.426	0.347	−0.773	−93	97	2.87	−441 ± 200
$[Cu(bpy)OH]_2(NO_3)_2$	2.00 (7)	2.09 (7)	2.34 (2)	0.505	0.435	−0.940	−172	96	2.85	−390 ± 50
$[Cu(tmpd)OH]_2(ClO_4)_2$	2.06 (5)	2.06 (5)	2.30 (6)	0.411	0.323	−0.733	−130			−390 ± 220
$[Cu(teen)OH]_2(ClO_4)_2$	2.06 (5)	2.06 (5)	2.30 (6)	0.474	0.273	−0.747	+410	103	2.98	−398 ± 220
$[Cu(tmen)OH]_2(ClO_4)_2$	2.06 (5)	2.06 (5)	2.30 (6)	0.474	0.273	−0.747	+360	102	2.97	−398 ± 220

[a] Estimated error in parentheses. [b] In cm^{-1}. [c] For the spin Hamiltonian in the form $H = JS_1 \cdot S_2$. J is in cm^{-1}. [d] The Cu–O(bridge)–Cu angle. [e] The Cu–Cu distance.

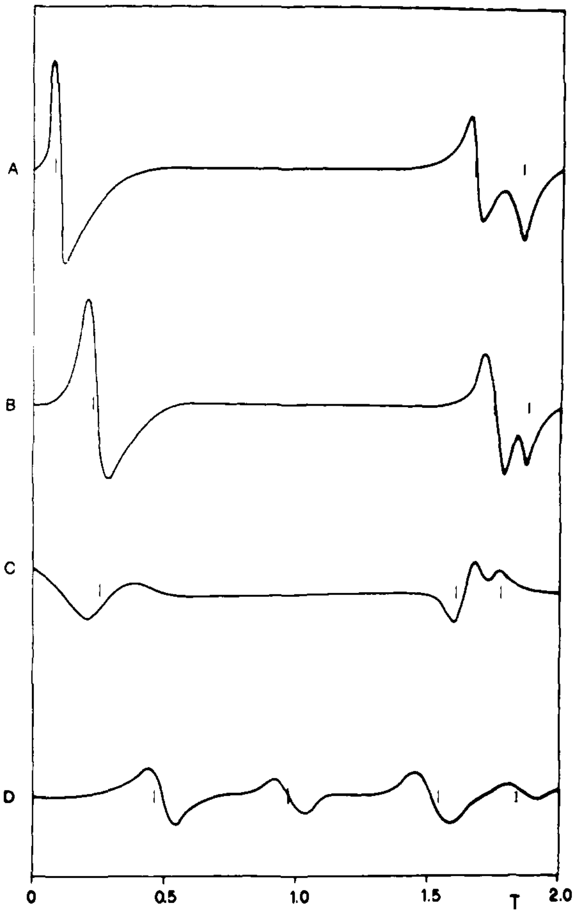

Figure 1. Polycrystalline powder EPR spectra at Q-band frequency of (A) $[Cu(bpy)OH]_2SO_4\cdot 5H_2O$, (B) $[Cu(bpy)OH]_2(NO_3)_2$, (C) [Cu-(bpy)OH]$_2$(ClO$_4$)$_2$, (D) $[Cu(tmen)OH]_2(ClO_4)_2$.

is similar, but at low field a feature very close to zero is observed, and an additional one of lower intensity at 0.35 T.

The similarity of the spectra is preserved also at X-band frequency as shown in Figure 2 with a weak feature at 0.15 T, a more intense one at 0.58–0.68 T, and additional weaker ones up to 0.95 T.

The spectra were recoreded in a range of temperatures, and no substantial variation of the resonating fields was observed. Also no sharpening of the lines was obtained, in agreement with the ferromagnetic coupling operating in these complexes.[3,10,14]

The spectra of the tmen and teen derivatives, which are antiferromagnetically coupled,[3,12,15] are much weaker than those of the bpy and tmpd derivatives. Since the bands are also very broad, it was difficult to obtain good quality spectra. Attempts were made also to record single-crystal spectra, but although crystals as large as 6 × 1 × 0.7 mm have been grown, the signals were disappointingly broad. The spectra of the tmen derivative are shown in Figures 1 and 2.

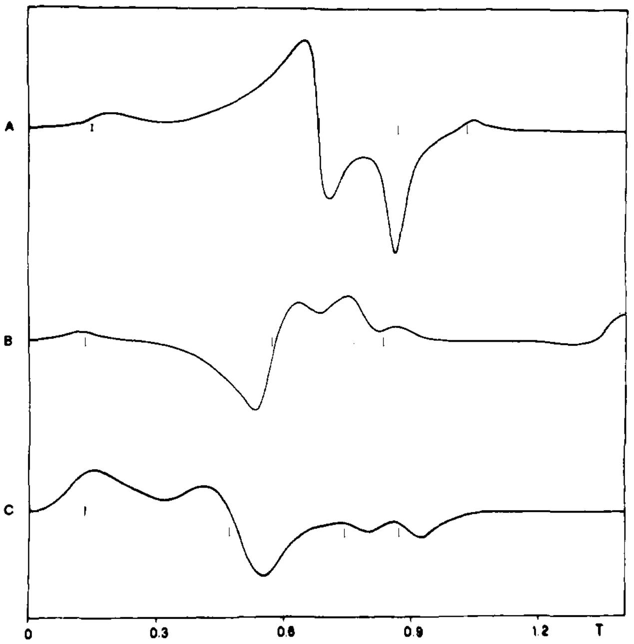

Figure 2. Polycrystalline powder EPR spectra at X-band frequency of (A) $[Cu(bpy)OH]_2(NO)_2$, (B) $[Cu(bpy)OH]_2(ClO_4)_2$, (C) [Cu(tmen)-OH]$_2$(ClO$_4$)$_2$.

The polycrystalline powder spectra of these derivatives, which are essentially identical with each other, show three features at Q-band frequency, at 0.45, 0.95, and 1.58 T, while at X-band frequency a broad feature is seen at 0.15 T, a more intense one at 0.5, and additional weaker ones up to 0.95 T.

For some of these complexes some EPR spectra were previously reported and they compare satisfactorily with our data.[3,10] In no case, however, were the spectra recorded at both frequencies and in such a large field range.

Analysis of the Spectra. As previously found[13] for the spectra of $[Cu(bpy)OH]_2SO_4\cdot 5H_2O$, the polycrystalline powder spectra of all these compounds are not easily referred to standard triplet spectra, in the sense that in no case is it easy either to designate parallel and perpendicular features or to assign transitions to $\Delta M = \pm 1$ and $\Delta M = \pm 2$ transitions. The spectra of the bpy complexes are easily assigned by analogy with the spectra of the sulfate derivative, for which also single crystal data are available.[13]

The data for $[Cu(bpy)OH]_2SO_4\cdot 5H_2O$ have been reexamined using the new data of Q-band frequency at higher magnetic fields. In Figure 3 is shown the calculated angular dependence of the transition fields and the calculated Q-band spectra. It was not attempted to obtain a perfect fit of the spectra owing to the long computer time needed. In any case, the shape of the calculated spectra compares quite nicely with the experimental ones, and the transition fields are in very good agreement. The best fit parameters are shown in Table I. They are identical with those previously reported from the analysis of the single-crystal spectra.

The polycrystalline powder spectra of the other bpy complexes were fit through a nonlinear least-squares procedure which allows for nonparallel **g** and **D** tensors and does not use a perturbative approach to calculate the transition fields. According to the analysis of the spectra of the SO$_4$ derivative, the triplet levels in

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$$\mathbf{D}^{\mathrm{dip}} = \begin{pmatrix} -{}^{1}/_{3}g_x^{\,2} + {}^{1}/_{6}g_y^{\,2} - {}^{1}/_{3}g_z^{\,2} & -{}^{3}/_{2}g_xg_y & 0 \\ -{}^{3}/_{2}g_xg_y & {}^{1}/_{6}g_x^{\,2} - {}^{1}/_{3}g_y^{\,2} - {}^{1}/_{3}g_z^{\,2} & 0 \\ 0 & 0 & {}^{1}/_{6}g_x^{\,2} + {}^{1}/_{6}g_y^{\,2} + {}^{2}/_{3}g_z^{\,2} \end{pmatrix} \mu_{\mathrm{B}}^{\,2} r^{-3} \quad (1)$$

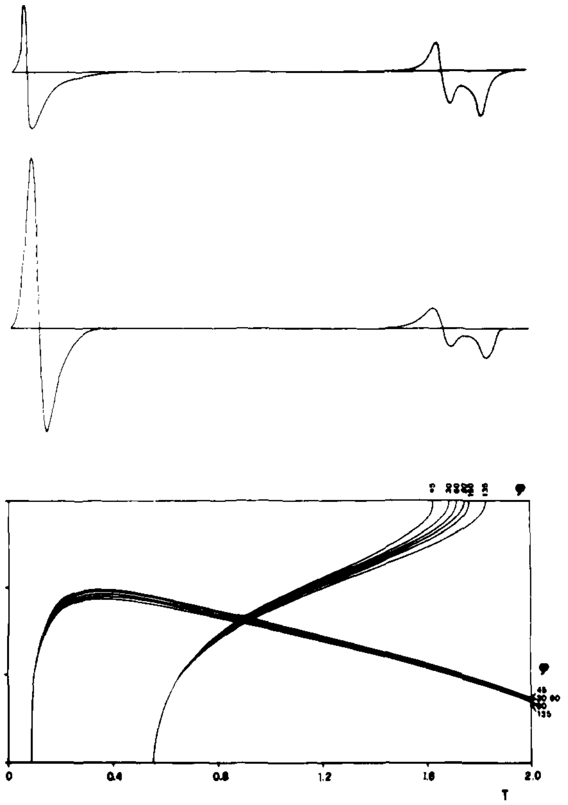

Figure 3. (Bottom) Angular dependence of the calculated transition fields at 35 GHz, (middle) calculated polycrystalline powder EPR spectra, (top) experimental polycrystalline powder EPR spectra.

the magnetic field are labeled as 1, 2, 3, in order of increasing energy, and transitions have been assumed to occur between levels 1–2 and 2–3. The experimental transition fields were used to compute the energy differences between those levels along the principal directions of **D** which were compared with the experimental microwave quantum. The parameters were varied according to the general procedure described elsewhere[13] to minimize the functional

$$\sum_{1}^{N}(\Delta E_i - h\nu)^2$$

where ΔE_i is the energy difference at field i, and $h\nu$ is the microwave energy. In the actual calculation **g** and **D** were considered not to have parallel axes. In particular it was considered that the z axis of **g** is parallel to the z' axis od **D**, while the x' and y' axes are rotated by 45° from x and y as found from the single-crystal spectra of $[\mathrm{Cu(bpy)OH}]_2\mathrm{SO_4}{\cdot}5\mathrm{H_2O}$ and as shown in Figure 4. Attempts to vary the misalignment angle in the xy plane did not improve the quality of the fit; therefore, it was no longer taken into consideration. The best fit parameters are shown in Table I and the computed fields are shown in Figures 1 and 2. The calculated fields are relatively insensitive to the g values; therefore, these are obtained with a large uncertainty.

The spectra of the teen and tmen derivatives are reasonably similar to the previous ones, especially at X-band frequency; therefore, they were assigned in a similar way. The computed fields are shown in Figures 1 and 2 and the best fit parameters are given in Table I. Also alternative assignments, which demanded smaller D values, were attempted, but the agreement between computed and observed fields was lower; therefore, they were discarded.

Analysis of the Spin-Hamiltonian Parameters. According to the above assumption, the z axes of the **g** and **D** tensors are orthogonal to the magnetic plane (the plane of the $x^2 - y^2$ orbitals containing the unpaired electron), while $D_{y'y'}$ is parallel to the metal–metal direction.

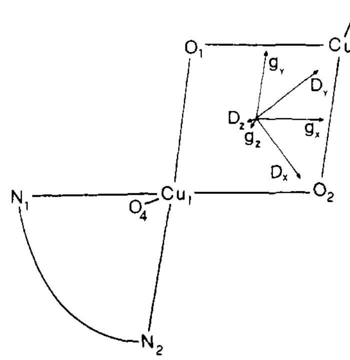

Figure 4. Orientations of the **g** and D tensors in the $[\mathrm{Cu(bpy)OH}]_2\mathrm{SO_4}{\cdot}5\mathrm{H_2O}$.

The expected contributions to the **D** tensor are dipolar and exchange in nature.[7] For the former, in the simplifying assumption of point dipoles centered on the two copper ions, the dipolar tensor can be calculated[16] as shown in eq 1, where r is the metal–metal distance. It is apparent that the tensor is not diagonal, since the D_{xy} component is different from zero. By diagonalizing the matrix, the principal **D** values and directions are obtained. To a good approximation these correspond to the **D** axes defined in Figure 4.

Using the g^{13} an r values[17,18] for $[\mathrm{Cu(bpy)OH}]_2\mathrm{SO_4}.5\mathrm{H_2O}$, one finds $D^{\mathrm{dip}}_{x'x'} = 0.076\ \mathrm{cm^{-1}}$, $D^{\mathrm{dip}}_{y'y'} = -0.167\ \mathrm{cm^{-1}}$, and $D^{\mathrm{dip}}_{z'z'} = 0.091\ \mathrm{cm^{-1}}$.

For the other complexes, the values of $D_{x'x'}$, $D_{y'y'}$, and $D_{z'z'}$ can be calculated if one knows the corresponding **g** components and the relative orientations of **g** and **D** as well as the metal–metal distance.[19-22] The calculated values of $D_{y'y'}$ in any case do not exceed $|0.17|\ \mathrm{cm^{-1}}$, and $D_{y'y'}$ is larger than all the other components, as expected. In any case D_{yy} must be negative. Although a more accurate treatment taking into account either that the charge distribution on the metal ion does not correspond to a point dipole and/or that spin delocalization on the bridge ligands might alter to some extent the calculated values, it does not seem feasible that it might change the calculated values by an order of magnitude, and change the direction of maximum splitting. It may be concluded, therefore, that the observed **D** tensor is mainly determined by the exchange interaction.

The exchange interaction determines also zero-field-splitting effects through spin–orbit coupling. It can be shown[7,8] that the exchange contribution to **D** for two identical $S = {}^{1}/_{2}$ ions with parallel principal **g** axes, $\mathbf{D}^{\mathrm{ex}}$, is given by

$$D^{\mathrm{ex}}_{xx} = {}^{1}/_{2}\alpha_x J_{\mathrm{g},\mathrm{n}_x} \qquad D^{\mathrm{ex}}_{yy} = {}^{1}/_{2}\alpha_y J_{\mathrm{g},\mathrm{n}_y} \qquad D^{\mathrm{ex}}_{zz} = {}^{1}/_{2}\alpha_z J_{\mathrm{g},\mathrm{n}_z} \quad (2)$$

where x, y, and z are parallel to the principal axes of **g**,

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$$\alpha_i = \frac{\Delta g_i^2}{4|\langle n_i|l_i|g\rangle|^2}$$

$|g\rangle$ and $|n_i\rangle$ being the single ion ground and excited states, respectively, which are coupled by the spin–orbit interaction, $\Delta g_i = g_i - 2.0023$ and $J_{g,n_i} = \langle g(1)n_i(2)|H_{ex}|g(1)n_i(2)\rangle$, H_{ex} being the electron exchange operator.

For the present case the single ion ground orbitals can be assumed to be $x^2 - y^2$ to a good approximation, so that the $\mathbf{D}^{ex}$ tensor is diagonal.

Equation 2 becomes, therefore,

$$D_{xx} = {}^1\!/_8 \Delta g_x^{\,2} J_{x^2-y^2,yz} \qquad D_{yy} = {}^1\!/_8 \Delta g_y^{\,2} J_{x^2-y^2,xz}$$
$$D_{zz} = {}^1\!/_{32} \Delta g_z^{\,2} J_{x^2-y^2,xy} \tag{3}$$

Of the three $J_{g,ni}$ integrals which are present in (3) $J_{x^2-y^2,yz}$ and $J_{x^2-y^2,xz}$ are expected to be small since the two orbitals involved are orthogonal to each other and $x^2 - y^2$ is in any case in a nodal plane of the other orbital.[23-26] $J_{x^2-y^2,xy}$, on the other hand, is expected to be ferromagnetic in nature and fairly strong, since in this case the magnetic orbitals, which are orthogonal to each other, have large areas of nonzero overlap density.[27] Indeed, experimentally a moderate ferromagnetic coupling was observed for a copper(II)–oxovanadium(IV) heterodinuclear complex, where the unpaired electrons are in $x^2 - y^2$ and xy orbitals.[28] In these assumptions $\mathbf{D}^{ex}$ is expected to be axial. In order to compare the calculated $\mathbf{D}^{ex}$ tensor with experiment, it is convenient to make it traceless. In this form

$$D_{\parallel}^{\,ex} = {}^1\!/_{48} \Delta g_z^{\,2} J_{x^2-y^2,xy} \qquad D_{\perp}^{\,ex} = -{}^1\!/_{96} \Delta g_z^{\,2} J_{x^2-y^2,xy} \tag{4}$$

It is apparent that the sign of $D_{\parallel}^{\,ex}$ is determined by the sign of $J_{x^2-y^2,xy}$, being negative for a ferromagnetic interaction.

The total zero-field-splitting tensor, $\mathbf{D}$, is given by the sum of $\mathbf{D}^{ex}$ and $\mathbf{D}^{dip}$. Since $\mathbf{D}^{ex}$ is supposed to be axial, the anisotropy in the xy plane is determined only by $\mathbf{D}^{dip}$. Since the dipolar contribution is negative along y' and positive along x', the resulting $\mathbf{D}$ tensor should have $D_{y'y'}$ smaller than $D_{x'x'}$ if $J_{x^2-y^2,xy}$ is ferromagnetic, while the reverse pattern should be observed for an antiferromagnetic coupling. Experimentally it was found in the single-crystal spectra of $[Cu(bpy)OH]_2SO_4 \cdot 5H_2O$ that $|D_{y'y'}| < |D_{x'x'}|$;[28] therefore, the $J_{x^2-y^2,xy}$ interaction may be assumed to be ferromagnetic.

Using the D values obtained from the experiment and the simplified formulas 4, we calculate $J_{x^2-y^2,xy} = -715 \pm 220$ cm^{-1} for $[Cu(bpy)OH]_2SO_4.5H_2O$. This value is larger than the value found for the Cu–VO complex mentioned above,[29] but it may be expected that the exchange mechanism is more efficient for a Cu(II)–Cu(II) complex. Also it must be mentioned that the calculated value is sensitive to the g_z value, which is determined with a moderate uncertainty from experiment.

A confirmation to the above analysis comes from the observed $E = {}^1/_2\,(D_{x'x'} - D_{y'y'})$ value, 0.045 72 cm^{-1}. According to our assumption it is assumed that this value is given by

$$E = {}^1\!/_2 (D_{x'x'}^{dip} - D_{y'y'}^{dip})$$

Using the experimental r distance and the g values obtained from the analysis of the EPR spectra, one calculates $E = 0.045\,55$ cm^{-1}. Although the excellent fit may be fortuitous, it shows that, nevertheless, the analysis we have performed is substantially correct. The similarity of the spectra in the series of complexes suggest that the sign of the E/D ratio does not change. According to the assumption that E is determined by the dipolar coupling, it is expected that E should not vary too much, and also in this case the calculated values seem to agree with the predictions since the E/D ratio tends to increase as D decreases.

The fact that $D_{z'z'}$ varies only slightly throughout the series makes it unlikely that $J_{x^2-y^2,xy}$ changes dramatically, and the most reasonable assumption is that it keeps the same sign for all the studied complexes.

For all the complexes the $L_2CuO_2CuL_2$ moiety remain constant, and, in particular, an approximate symmetry plane passing for the two copper ions is preserved. In these conditions the two orbitals, $x^2 - y^2$ and xy, remain strictly orthogonal, independent of the Cu–O–Cu angle, and the exchange must stay ferromagnetic. The only structural parameter which can influence the extent of the coupling is the metal–metal distance, since in this case the overlap density between the two magnetic orbitals is expected to decrease as the metals are removed further away one from the other.

We do not think it is possible to go further on the quantitative side. If one plots $J_{x^2-y^2,xy}$, against the metal–metal distance, the errors associated with the calculated values are too large to draw any definitive conclusion on the dependence on r. However, it seems safe to conclude that in any case the dependence is not as steep as that observed for $J_{x^2-y^2,x^2-y^2}$.

Acknowledgment. We wish to thank Dr. B. Nieuwenhuijse and Miss N. M. A. Perik, Department of Chemical Engineering, Twente University of Technology, Enschede, The Netherlands, for measuring for us the Q-band spectra up to 2.00 T.

Registry No. $[Cu(bpy)OH]_2SO_4$, 15186-88-6; $[Cu(bpy)OH]_2(ClO_4)_2$, 15186-78-4; $[Cu(bpy)OH]_2(NO_3)_2$, 17685-95-9; $[Cu(tmpd)OH]_2(ClO_4)_2$, 59532-73-9; $[Cu(teen)OH]_2(ClO_4)_2$, 21711-33-1; $[Cu(tmen)OH]_2(ClO_4)_2$, 14266-63-8.

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