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Anisotropic Exchange in Transition-Metal Dinuclear Complexes. 5.[1] Bis(μ-hydroxo)bis[bis(2-methylimidazole)copper(II)] Diperchlorate Dihydrate

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Bis(μ-hydroxo)bis[bis(2-methylimidazole)copper(II)] diperchlorate dihydrate, $Cu_2(Meiz)_4(OH)_2(ClO_4)_2 \cdot 2H_2O$, was prepared according to literature methods, and its crystal structure was solved at room temperature. It crystallizes in the monoclinic system, space group *C*2/*m*, with $Z = 2$. The lattice constants are $a = 14.920$ (6) Å, $b = 13.768$ (7) Å, $c = 7.482$ (4) Å, and $\beta = 103.2$ (3)°. Least-squares refinement of the structure led to a conventional *R* factor of 0.034. The structure consists of centrosymmetric $[Cu_2(Meiz)_4(OH)_2]^{2+}$ cations, perchlorate anions, and water molecules. The bonds connecting the copper ions to the bridging oxygen atoms are longer than usually observed for the series of bis(μ-hydroxo)-bridged complexes; as a consequence the observed singlet-triplet splitting does not fit the previously suggested linear relationship with the Cu-Cu distance or the Cu-O-Cu angle. Single-crystal EPR spectra yielded the zero-field splitting tensor, which was found to have its largest component roughly orthogonal to the equatorial coordination planes of the copper ions, thus showing the presence of a dominant exchange contribution. The observed zero-field splitting is related to the Cu-Cu distance in a series of homologous complexes, showing that D_{zz} decreases as *r* increases.

Introduction

Although several relations between structural parameters and isotropic exchange coupling constants are now available for dinuclear transition-metal complexes,[3-10] no well-established correlation is as yet available for the anisotropic exchange. Recently we reported the EPR spectra of a series of bis(μ-hydroxo)bridged copper(II) complexes[11-13] and found that, while the isotropic exchange parameter, *J*, changes sign as a function of the Cu-O-Cu angle, ϕ, or the Cu-Cu distance, *r*, the zero-field splitting parameter, *D*, which is related to the anisotropic exchange interaction, shows only a less dramatic dependence, remaining always negative throughout the considered series of complexes. Similar conclusions were reached independently also by Russian workers.[14] It must be remembered that the *J* vs. ϕ and the *J* vs. *r* correlations are not independent from each other,[4] but they have been found for complexes containing an almost planar Cu_2O_2 moiety where a biunivocal correspondence exists between ϕ and *r* dependent on the Cu-O distance.

In this article we wish to report the single-crystal EPR spectra of another member of the series, bis(μ-hydroxo)bis[bis(2-methylimidazole)copper(II)] diperchlorate dihydrate, $Cu_2(Meiz)_4(OH)_2(ClO_4)_2 \cdot 2H_2O$, whose synthesis, magnetic susceptibility, and polycrystalline powder EPR spectra were previously reported by Reedijk et al.[15] Since the crystal structure of the complex was not available, we undertook its determination in order to collect the necessary information to relate the anisotropic exchange parameters to the structural parameters of the complex.

Table I. Summary of Crystal Data and Intensity Collection

formula	$C_{16}H_{30}Cl_2Cu_2N_8O_{12}$
fw	724.457
cryst syst, space group	monoclinic, *C*2/*m*
a, Å	14.920 (6)
b, Å	13.768 (7)
c, Å	7.482 (4)
β, deg	103.2 (3)
V, Å^3	1496.3
Z	2
D_{calcd}, g cm^{-3}	1.607
μ(Mo Kα), cm^{-1}	15.9
transmission factor, max-min	0.80-0.72
scan type	ω-2θ
scan speed, deg min^{-1}	3
scan width ($\Delta\omega$), deg	1.10 + 0.30 tan θ
bkgd	stationary counter-stationary cryst symmetric, at each end of scan
collection range	$\pm h,+k,+l$ ($2\theta < 50°$)
no. of data	1234
no. of data, $I > 3\sigma(I)$	1141
no. of variables	99

Table II. Positional Parameters for the Non-Hydrogen Atoms for $Cu_2(Meiz)_4(OH)_2(ClO_4)_2 \cdot 2H_2O$[a, b]

atom	*x*	*y*	*z*
Cu	0	1087	5000
Cl	1686 (1)	0	9001 (2)
O1	−525 (2)	0	6120 (4)
O2	2495 (4)	0	10390 (8)
O3	915 (4)	0	9849 (7)
O4	1586 (3)	841 (2)	7898 (5)
O6*	−2618 (2)	5000	4320 (5)
N11	−776 (2)	2069 (2)	5859 (4)
N12	−1640 (2)	3336 (2)	6008 (5)
C11	−1194 (3)	3133 (3)	3037 (6)
C12	−1195 (2)	2834 (2)	4946 (5)
C13	−972 (3)	2096 (3)	7565 (5)
C14	−1507 (3)	2872 (3)	7663 (6)

[a] Coordinates multiplied by 10^4. [b] Atoms marked with an asterisk belong to water molecules.

Experimental Section

$Cu_2(Meiz)_4(OH)_2(ClO_4)_2 \cdot 2H_2O$ was prepared as previously described.[15] Single crystals were grown by slow evaporation of ethanol solutions of the complex.

EPR spectra were recorded with a Varian E9 spectrometer, equipped with both X- and Q-band frequencies. Variable-temperature spectra

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Table III. Selected Bond Distances (Å) and Angles (deg) for $Cu_2(Meiz)_4(OH)_2(ClO_4)_2 \cdot 2H_2O$

Cu-O1	1.963 (2)	Cu-Cu	2.993 (1)
Cu-N11	1.980 (3)		
O1-Cu-N11	93.6 (1)	N11-Cu-N11′	93.9 (1)
O1-Cu-O1′	80.7 (1)	Cu-O1-Cu′	99.3 (2)
O1-Cu-N11′	168.2 (1)		

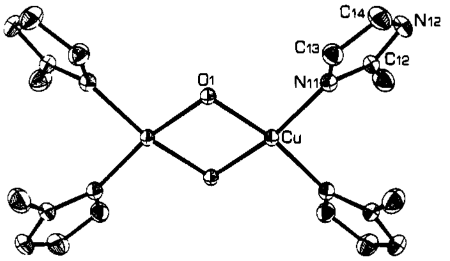

Figure 1. Sketch of the centrosymmetric dinuclear species $[Cu_2(Meiz)_4(OH)_2]^{2+}$ in $Cu_2(Meiz)_4(OH)_2(ClO_4)_2 \cdot 2H_2O$.

were recorded with use of standard Varian apparatus down to liquid-nitrogen temperature and with an Oxford Instruments ESR 9 continuous-flow cryostat below that limit. Single-crystal spectra were obtained by mounting the crystal on a Plexiglas rod. At X-band the rod was rotated with a one-circle goniometer, while at Q-band the static magnetic field was rotated.

X-ray Structure Determination. A crystal of the complex $Cu_2(Meiz)_4(OH)_2(ClO_4)_2 \cdot 2H_2O$, shaped as a monoclinic prism, with approximate dimensions 0.15 × 0.2 × 0.3 mm was used for crystal data and intensity data collection. A Philips PW 1100 automated diffractometer was used for all operations. Lattice constants were determined at 20 °C from the setting angles of 20 reflections with $9° < \theta < 15°$. Details of crystal data and data collection are listed in Table I. Intensities of three standard reflections were measured every 120 min and did not exhibit any significant variations in their intensities during data collection. The data were corrected for Lorentz and polarization effects as well as for absorption. The principal computer programs used in the crystallographic calculations are listed in ref 16.

Systematic absences indicated that the possible space groups are $C2$, Cm, and $C2/m$. The structure was solved in the $C2$ space group by direct methods and refined in the $C2/m$ space group by a full-matrix least-squares method based on minimization of the function $\sum w(|F_o| - |F_c|)^2$ with weights $w = 1/(\sigma^2(F_o) + 0.001F_o^2)$. Anisotropic thermal parameters were used for all the atoms. Hydrogen atoms were introduced in calculated positions (C–H = 0.95 Å) as fixed contributions, each with a temperature factor 20% larger than the isotropic equivalent of the respective carbon atom. Since no extra peak was found near the oxygen atoms, the hydrogens bonded to them were not included in the calculations. The scattering factors for the neutral atoms were taken from ref 17 and the anomalous dispersion correction terms from ref 18. The final R values were $R = 0.034$ and $R_w = 0.036$. The highest peaks in the final difference map were less than 0.5 e Å^{-3}. The final positional parameters for the non-hydrogen atoms are given in Table II. Selected bond lengths and angles are given in Table III. Listings of thermal parameters for the non-hydrogen atoms (Table SI), of hydrogen atom coordinates (Table SII), and of the observed and calculated structure amplitudes are available as supplementary material.[19]

Results

Structure. The structure consists of centrosymmetric $[Cu_2(Meiz)_4(OH)_2]^{2+}$ cations, ClO_4^- anions, and water molecules. The two copper atoms lie on a C_2 site symmetry, and the bridging oxygen atoms have C_s symmetry, so that the overall symmetry of the cation is C_{2h}. Relevant bond distances and angles within the cation are given in Table III. The coordination environment around each copper ion is essentially planar with a small tetrahedral distortion as shown in Figure 1. The angle between the two planes defined by the copper atom and the nitrogen and oxygen donors respectively is 14.3 (2)°. The N–Cu–O angle is 168.2 (1)°, showing that the coordination tetrahedron is severely flattened. In fact, the angle should be 180° for square-planar and 90° for tetrahedral geometry. The imidazole plane makes an angle of 50.3 (4)° with the CuNN′ planes. The $Cu–O_2–Cu'$ bridge is planar by symmetry requirements. The Cu–O bond distances, 1.963 (2) Å, are definitely larger than the average value seen in the complexes thus far used for the J correlation with ϕ or r.[3,4] ϕ is 99.3 (1)°, and the Cu–Cu distance is 2.993 (1) Å.

Table IV. Principal Values and Directions of g and D Tensors[a] for $Cu_2(Meiz)_2(OH)_2(ClO_4)_2 \cdot 2H_2O$

g_{xx}	g_{yy}	g_{zz}
2.011 (9)	2.037 (7)	2.305 (9)
−0.7 (1)	−0.5 (1)	−0.47 (1)
0.3 (2)	−0.83 (8)	0.45 (2)
0.63 (3)	−0.2 (1)	−0.76 (1)
D_{xx}[b]	D_{yy}	D_{zz}
0.281 (3)	0.203 (3)	−0.484 (3)
−0.42 (2)	−0.78 (1)	−0.470 (3)
0.57 (2)	−0.62 (1)	0.526 (2)
0.703 (2)	0.05 (2)	−0.709 (2)

[a] The directions are given by the cosines referred to the crystal axes X, Y, Z. Z is parallel to the c^* crystal axis, and X is orthogonal to the (110) face. [b] All D values in 10^{-4} cm^{-1}.

The perchlorate anion is normal. The chlorine and two oxygen atoms lie on the symmetry plane. A water molecule lies on a symmetry plane, with a distance of 2.85 Å from the N12 nitrogen.

EPR Spectra. Single-crystal EPR spectra were recorded at room temperature by rotating around three orthogonal laboratory axes, X, Y, and Z. Z is parallel to the c^* crystal axis; X is orthogonal to the (110) face. Only one signal for each setting of the crystal in the static magnetic field was observed at X-band frequency, while at Q-band frequency two fine-structure signals were generally observed. These results agree with the structural data, confirming the presence of one site in the crystal. The angular dependence of the transition fields at Q-band frequency is shown in Figure 2. The experimental points were fit with use of a procedure previously described.[12] The curves were calculated by using the g and D tensors given in Table IV. The calculated values compare well with those previously obtained from the analysis of the polycrystalline powder EPR spectra.[15] One of the principal directions of D is within error parallel to the Cu–Cu direction. g_{zz} and D_{zz} are within error parallel to each other, while g_{xx} and g_{yy} are rotated by ~20° from the corresponding D directions. This is surprising since symmetry requires also a g axis parallel to the Cu–Cu direction. However, the g_{xx} and g_{yy} values are rather close to each other (2.011 (9), 2.037 (7)), so that the uncertainty on the principal x and y axes is very large.

EPR spectra were recorded at ~35 K, with the aim of resolving the copper hyperfine splitting, since at that temperature the lattice becomes practically diamagnetic. The attempts, however, were unsuccessful since the signals remain very broad and featureless. It seems now to be a general characteristic of these bis(μ-hydroxo)-bridged complexes to give broad lines,[11,12] probably due to the short electron relaxation time.

Discussion

The reported value for the magnetic susceptibility for $Cu_2(Meiz)_4(OH)_2(ClO_4)_2 \cdot 2H_2O$, 175 (1) cm^{-1}, does not fit in the linear relation suggested for the Cu–O–Cu, ϕ, angle or the Cu–Cu, r, distance.[3,4] In fact, if the ϕ relation is used, a value of 131 cm^{-1} would be anticipated, while if the r relation is employed, J is calculated as 474 cm^{-1}. The origin of the breakdown of the correlation is presumably in the larger metal–oxygen distance observed in the present case as compared to that for the other

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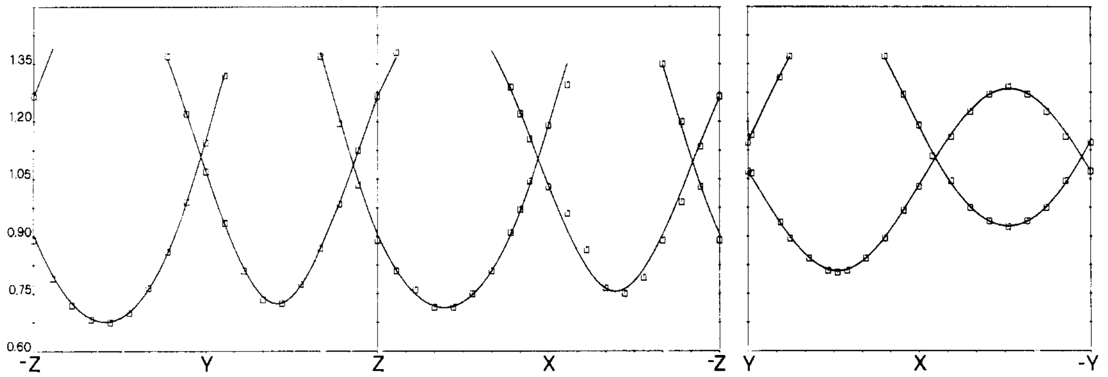

Figure 2. Angular dependence of the transition fields at Q-band frequency for $Cu_2(Meiz)_4(OH)_2(ClO_4)_2 \cdot 2H_2O$.

reported complexes. In fact, the linear relationship of J with either ϕ or r implies a linear relationship between ϕ and r themselves:

$$\phi = 60.49r - 77.12 \qquad (1)$$

(1) requires that the Cu–O distance be 1.91 ± 0.01 Å, which is substantially shorter than 1.963 Å, the value seen in the crystal structure. Therefore, in the present case, for a given angle ϕ the metal–metal distance is longer, and the exchange interaction must be more antiferromagnetic than in the series of well-behaved bis(μ-hydroxo) complexes. Conversely, if we use the r values, the present compound has a smaller angle, therefore the actual J value is less antiferromagnetic than that for the corresponding compound in the series of well-behaved complexes.

An r dependence of the J value was observed for other systems,[4,8-10,20-22] but in those cases the effect was that of decreasing $|J|$. The rationale we can offer is that lengthening the Cu–O distance undoubtedly decreases both the ferro- and the antiferromagnetic contributions to J[23] but the ferromagnetic term decreases more rapidly so that the coupling becomes more antiferromagnetic for a given angle.

Another effect that might be responsible for the deviation of the J value of $Cu_2(Meiz)_4(OH)_2(ClO_4)_2 \cdot 2H_2O$ is the so-called tetrahedral distortion,[24] i.e. the fact that the coordination environment around the copper ion is not planar but distorted tetrahedral. However, this is expected to decrease the antiferromagnetic coupling for a given angle,[24,25] so it does not seem to apply in the present case.

The zero-field splitting tensor of $Cu_2(Meiz)_4(OH)_2(ClO_4)_2 \cdot 2H_2O$ is similar to that previously determined[12] for $Cu_2(bpy)_4(OH)_2SO_4 \cdot 5H_2O$ in the sense that the largest component, D_{zz}, is observed orthogonal to the coordination planes, while the smallest one, D_{xx}, is parallel to the Cu–Cu direction. D_{zz} is markedly smaller than the values previously observed for other bis(μ-hydroxo)-bridged complexes.[11,12,14]

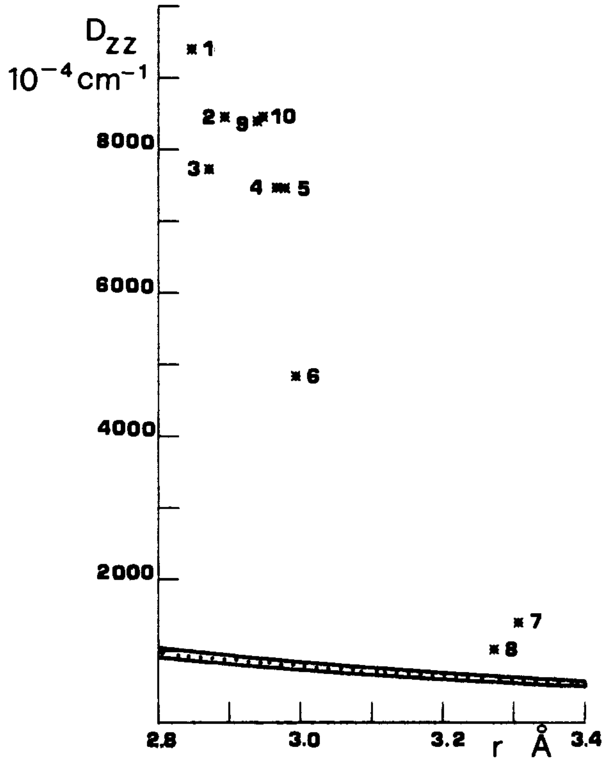

Figure 3. D_{zz} values vs. copper–copper distance in bis(μ-hydroxo)bis[(bipyridyl)copper(II)] dinitrate (**1**), bis(μ-hydroxo)bis[(bipyridyl)copper(II)] sulfate pentahydrate (**2**), bis(μ-hydroxo)bis[(bipyridyl)copper(II)] diperchlorate (**3**), bis(μ-hydroxo)bis[(*N*,*N*,*N'*,*N'*-tetramethylethylenediamine)copper(II)] diperchlorate (**4**), bis(μ-hydroxo)bis[(*N*,*N*,*N'*,*N'*-tetraethylethylenediamine)copper(II)] diperchlorate (**5**), bis(μ-hydroxo)bis[(2-methylimidazole)copper(II)] diperchlorate dihydrate (**6**), bis(μ-pyridine-*N*-oxide)bis[dichloro(pyridine *N*-oxide)copper(II)] (**7**), bis(μ-pyridine *N*-oxide)bis[dichloroaquocopper(II)] (**8**), dipiperidinium {bis[(μ-methoxo)bis(2,4-dinitrophenolato)cuprate(II)]}-2-methanol (**9**), dipiperidinium {bis[(μ-methoxo)bis(2,4-dinitrophenolato)cuprate(II)]} (**10**).

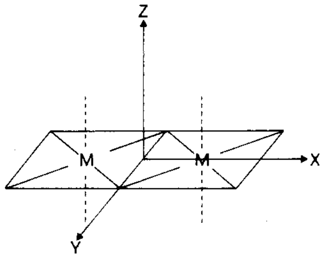

Figure 4. Sketch of a dinuclear species bridged through equatorial ligands.

The experimental **D** tensor is given by the sum of two components[26]

$$\mathbf{D} = \mathbf{D}^{ex} + \mathbf{D}^{dip} \qquad (2)$$

where $\mathbf{D}^{ex}$ is exchange determined, while $\mathbf{D}^{dip}$ depends on the through-space interaction between the two magnetic moments centered on the two metal ions. Both these terms are expected to depend on the geometrical features of the complexes. In Figure 3 the observed D_{zz} values vs. the copper–copper distance, r, for a series of bis(μ-oxo)bridged complexes are reported, in order to verify if a relation can be established between them. The shaded area in Figure 3 corresponds to the values expected for D_{zz}^{dip}. In fact, for complexes that are formed by pairs of tetrahedral units bridged through two equatorial ligands, as shown in Figure 4, the dipolar tensor can be calculated, with use of the simplifying as-

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sumption of axial symmetry around each copper(II) ion and the point dipolar assumption,[27] as

$$\begin{aligned} D_{xx}^{\text{dip}} &= 0.1443(4g_{\perp}^2 - g_{\parallel}^2)/r^3 \\ D_{yy}^{\text{dip}} &= -0.1443(5g_{\perp}^2 + g_{\parallel}^2)/r^3 \\ D_{zz}^{\text{dip}} &= 0.1443(g_{\perp}^2 + 2g_{\parallel}^2)/r^3 \end{aligned} \qquad (3)$$

The shaded area in Figure 3 is limited by the curves calculated by using $g_{\parallel} = 2.40$, $g_{\perp} = 2.10$ and $g_{\parallel} = 2.20$, $g_{\perp} = 2.05$, respectively.

The experimental points correspond to the bis(μ-hydroxo)-bridged complexes (**1**–**6**),[11,12,28–33], bis(μ-pyridine *N*-oxide)-bridged complexes (**7**, **8**), and bis(μ-alkoxo)-bridged complexes (**9**, **10**).[14] Complexes **7** and **8** have been included because accurate single-crystal EPR measurements are available for them,[34,35] showing that the **D** tensor roughly corresponds to the tensors of bis(μ-hydroxo)-bridged complexes, in the sense that D_{zz} is essentially orthogonal to the plane of the magnetic orbitals. Complexes **9** and **10** have been studied only as polycrystalline powders,[14] but the large experimental D value suggests that they are indeed similar to the others.

From Figure 3 it is apparent that for all the reported complexes $|D_{zz}|$ is larger than the D_{zz}^{dip} value and also that $|D_{zz}|$ tends to decrease as the Cu–Cu distance increases. Therefore, a significant exchange contribution must be operative.

In a previous paper we suggested that D_{zz}^{ex} is negative for the bis(μ-hydroxo)-bridged copper complexes,[11,12] and an experiment on a similar bis(μ-alkoxo)bridged complex confirmed this view.[14] The present result seems to reinforce this statement, at least in the sense that it seem reasonable that D_{zz}^{ex} does not change sign on going from the previously reported complexes **1**–**5** to $Cu_2(Meiz)_4(OH)_2(ClO_4)_2{\cdot}2H_2O$, and perhaps also to the bis(μ-pyridine *N*-oxide)-bridged complexes, due to the smooth dependence of D_{zz} on r.

The negative sign of D_{zz}^{ex} was justified on the basis of a dominant ferromagnetic interaction between the ground xy and an excited $x^2 - y^2$ magnetic orbital,[36] similar to those observed between the ground orbitals of heterodinuclear copper(II)–oxovanadium(IV) complexes.[37,38]

The exchange interaction between the $x^2 - y^2$ and xy magnetic orbitals is considered to be ferromagnetic, independent of the ϕ angle, as long as symmetry prevents admixtures of the two orbitals. However, the intensity of the coupling can be expected to depend on the angle, or on the metal–metal distance. In fact, increasing the ϕ angle (increasing r) yields a less efficient overlap of the bridge oxygen p orbital with $x^2 - y^2$ on one ion and xy on the other one, thus reducing the overlap density on the bridge and, consequently, giving a less efficient ferromagnetic interaction. We suggest therefore that the observed decrease of D_{zz}, as the metal–metal distance increases, is essentially determined by the decrease in D_{zz}^{ex}, as shown also by the less dramatic dependence of D_{zz}^{dip} on the distance. Since an increase in r corresponds also to an increase in ϕ, if the metal–bridge oxygen distance is not much varied in the series, a similar relationship is expected to hold also in plotting D_{zz} vs. ϕ. However, we prefer the r plot because in this way it is easy to show the expected D_{zz}^{dip} values.

Conclusions

The analysis of the single-crystal EPR spectra of a series of bis(μ-oxo)-bridged copper(II) complexes has shown that the exchange contribution to the zero-field splitting is dominant. The experimental D_{zz} (D) value is in all the cases found roughly orthogonal to the Cu–Cu direction and parallel to the direction corresponding to the largest g value. The actual D_{zz} value is found to decrease as the metal–metal distance increases. The exchange contributions are still operative for Cu–Cu distances as long as 3.3 Å.

Registry No. $Cu_2(Meiz)_4(OH)_2(ClO_4)_2{\cdot}2H_2O$, 80908-04-9.

Supplementary Material Available: Listings of observed and calculated structure factors, thermal parameters for the non-hydrogen atoms, and positional parameters for the hydrogen atoms of the title compound (9 pages). Ordering information is given on any current masthead page.

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