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Anisotropic Exchange in Transition-Metal Dinuclear Complexes. 2.[1] Crystal and Molecular Structure and EPR Spectra of a Dinuclear Copper Oxamidato Complex

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The compound (μ-*N*,*N*′-bis(6-ethyl-3,6-diazaoctyl)oxamidato(2−)-N^1,N^3,N^6,*O*:$N^{1'}$,$N^{3'}$,$N^{6'}$,*O*′)dicopper(II) bis(tetraphenylborate)–2-acetone, $Cu_2L(BPh_4)_2 \cdot 2(CH_3)_2CO$, was synthesized and its crystal structure solved at room temperature. It crystallizes in the monoclinic system, space group $P2_1/n$, with $Z = 2$. The lattice constants are $a = 16.639$ (7) Å, $b = 18.305$ (9) Å, $c = 11.089$ (9) Å, and $\beta = 103.2$ (2)°. Least-squares refinement of the structure led to a conventional *R* factor of 0.055. The structure consists of centrosymmetric dinuclear species Cu_2L^+, tetraphenylborate anions, and acetone solvent molecules. The single-crystal EPR spectra reveal that the zero-field splitting tensor is dominated by the magnetic dipolar contribution, although substantial magnetic exchange is operative between the two $x^2 - y^2$ ground magnetic orbitals. The small exchange contribution to the zero-field splitting is related to the exchange pathway between a ground $x^2 - y^2$ and an excited *xy* magnetic orbital, which is rather ineffective in the present case.

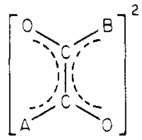
Introduction

Dinuclear copper(II) complexes have been much studied in the last few years,[3-9] and it can be safely stated that their magnetic behavior is reasonably well-understood, in the sense that the extent of magnetic coupling is satisfactorily rationalized on the basis of the overlap of magnetic orbitals. In contrast, the EPR spectra of copper(II) pairs are much less understood and as yet the full information that is contained in them has hardly been used. As a matter of fact, the zero-field splitting tensor of the triplet state of a centrosymmetric couple is determined by the sum of two terms, the magnetic dipole and the exchange contribution.[1,6,10,11] Knowledge of the latter could in principle give useful information on the coupling between the ground magnetic orbital on one ion and an excited magnetic orbital on another ion. This point has sometimes been overlooked, and the exchange contribution to the zero-field splitting tensor has been estimated through the value of the coupling constant *J*, relative to the interaction between the two ground magnetic orbitals. Generally this approximation can yield at least the order of magnitude of *D*, as was the case for copper(II) acetate hydrate,[12] but there are reported cases where very weakly coupled pairs yield large zero-field splittings,[13-15] much larger than would be expected on the basis of the magnetic dipole interaction between the two unpaired spins.

Table I. Summary of Crystal Data, Intensity Collection, and Structure Refinement

formula	$C_{66}H_{78}Cu_2N_6O_2B_2 \cdot 2C_3H_6O$
fw	1252.3
space group	$P2_1/n$
a, Å	16.639 (7)
b, Å	18.305 (9)
c, Å	11.089 (9)
β, deg	103.2 (2)
V, Å^3	3288.2
Z	2
D_{calcd}, g cm^{-3}	1.26
cryst size, mm	0.22 × 0.12 × 0.10
μ(Cu Kα), cm^{-1}	10.84
transmission factors	0.80–0.86
scan type	ω–2θ
scan width ($\Delta(2\theta)$), deg	1.00 + 0.30 θ
scan speed, deg min^{-1}	5.4
2θ limits, deg	5–110
data collection range	$\pm h,+k,+l$
no. of data	2839
no. of data $F_o^2 > 3.5\sigma(F_o^2)$	2021
no. of variables	263
R	0.055
R_w	0.055

During the course of a study of a series of copper(II) complexes bridged by extended ligands[16] such as



where A, B = NH, O; we found that although the exchange in the ground state is fairly substantial, with *J* values, defined by the Hamiltonian $H = J(\mathbf{S}_1 \cdot \mathbf{S}_2)$, ranging from 300 to 500 cm^{-1}, the polycrystalline powder EPR spectra did not show any other evidence of a triplet but a very weak half-field transition. With the aim of understanding the origin of this behavior, we determined the X-ray structure of one of these derivatives and recorded single-crystal EPR spectra.

Experimental Section

Synthesis. *N*,*N*′-Bis(6-ethyl-3,6-diazaoctyl)oxamide was obtained in solution by reacting 100 mmol of diethyloxalate in 2 mL of absolute ethanol with 200 mmol of *N*,*N*-diethyldiethylenetriamine in 4 mL of ethanol. The mixture was kept under reflux for 4 h and the volume

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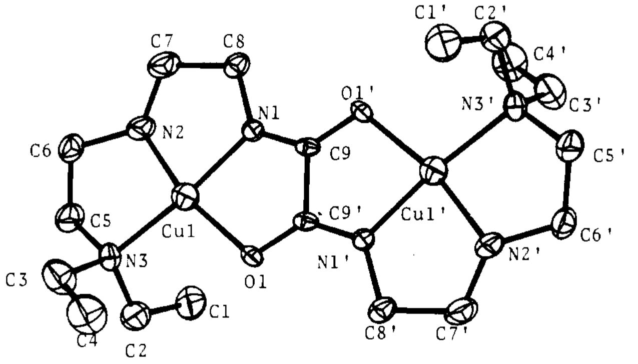

Figure 1. Perspective view of the centrosymmetric dinuclear species Cu_2L^{2+}.

brought to 25 mL with ethanol. One millimole of ligand and 2 mmol of $Cu(NO_3)_2 \cdot 3H_2O$ in 10 mL of water were treated with 2 mmol of LiOH in 4 mL of water. Two millimoles of sodium tetraphenylborate in 2.5 mL of ethanol was slowly added under stirring to the cold solution. A violet precipitate was formed, which was filtered and washed with water/ethanol. By recrystallization from acetone well-formed crystals were obtained, which gave a satisfactory analysis for $Cu_2L(BPh_4)_2 \cdot 2(CH_3)_2CO$. Anal. Calcd for $Cu_2C_{72}H_{90}N_6O_4B_2$: C, 69.06; H, 7.24; N, 6.71. Found: C, 69.02; H, 7.34; N, 6.90.

EPR Measurements. EPR spectra were recorded with a Varian E9 spectrometer.

X-ray Structural Determination. Diffraction data for (μ-*N*,*N*′-bis(6-ethyl-3,6-diazaoctyl)oxamidato(2−)-N^1,N^3,N^6,*O*:N^{1},$N^{3\prime}$,$N^{6\prime}$,-*O*′)dicopper(II) bis(tetraphenylborate)−2-acetone, $Cu_2L(BPh_4)_2 \cdot 2\text{-}(CH_3)_2CO$, were collected at room temperature on a Philips PW1100 automated diffractometer using graphite-monochromated Cu Kα radiation ($\lambda = 1.5418$ Å). Details on crystal data, intensity collection, and refinement are reported in Table I. Lattice constans were obtained by a least-squares fit of 19 reflections in the range $30\,° < 2\theta < 50°$. Stationary background counts were taken at each end of the scan for a time equal to half the scan time. The intensities of three standard reflections measured every 90 min showed a smooth decrease indicative of decomposition. The overall change in intensities was ca. 32%. A correction for such effects, based on the linear decay in standard intensities, was applied in the subsequent data correction procedure. The *R* factor for averaging equivalent measurements was 0.03. The principal computer programs used in the crystallographic calculations are listed in ref 17. Data were processed with use of a *p* value of 0.03 in the calculation of $\sigma(I)$'s.[18] Corrections for the Lorentz and polarization effects[17a] as well as for absorption[17b] were applied. The space group $P2_1/n$ was identified by the systematic absences $0k0$ ($k = 2n + 1$) and $h0l$ ($h + l = 2n + 1$). Standard Patterson and Fourier techniques were used to solve the structure. A total of 2021 reflections having $F_o > 7\sigma(F_o)$ were retained during the refinement.

The function minimized was $\sum w[|F_o| - |F_c|]^2$ with weights $w = 1/(\sigma^2(F_o) + 10^{-3}F_o^2)$. The scattering factors for the neutral atoms were taken from ref 19, and anomalous dispersion terms for the metal atom were included in F_c.[20] All the non-hydrogen atoms in the cation were assigned anisotropic temperature factors, whereas B and C atoms in the anion were assigned isotropic thermal parameters. The non-hydrogen atoms in the solvate acetone molecule were refined anisotropically. Hydrogen atoms were introduced in calculated positions (C–H = 1.00 Å, N–H = 1.00 Å), and their contributions were included in F_c. Each hydrogen atom was assigned an isotropic temperature factor ca. 20% higher than the isotropic factor (or the isotropic equivalent) of the corresponding C or N atom. In the final least-squares cicle no shift/error ratio was higher than 0.15. The final values of the discrepancy indices, defined by $R = \sum[|F_o| - |F_c|]/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$, were $R = 0.055$ and $R_w = 0.055$. The highest peaks in a different Fourier map calculated at the end of the refinement were less than 0.2 e Å^{-3}. The final atomic positional parameters for the non-hydrogen atoms are listed in Table II. Thermal parameters and positional parameters of the hydrogen atoms are listed in Tables SI and SII, respectively.[21] A listing of the observed and calculated structure amplitudes is available.[21]

Table II. Positional Parameters for the Non-Hydrogen Atoms for $Cu_2L(BPh_4)_2 \cdot 2C_3H_6O^{a,b}$

atom	*x*	*y*	*z*
Cu1	3545 (1)	4601 (1)	5223 (1)
N1	4497 (4)	5060 (3)	6199 (5)
N2	3149 (4)	4676 (4)	6800 (6)
N3	2503 (4)	4069 (4)	4481 (6)
O1	4203 (3)	4534 (3)	3939 (4)
C1	3387 (5)	2947 (5)	4808 (10)
C2	2675 (5)	3340 (5)	4022 (9)
C3	1900 (5)	4468 (6)	3508 (9)
C4	2189 (6)	4698 (6)	2427 (9)
C5	2065 (5)	3985 (5)	5518 (8)
C6	2253 (5)	4600 (5)	6398 (8)
C7	3561 (5)	5264 (5)	7486 (8)
C8	4456 (4)	5310 (4)	7435 (7)
C9	4893 (5)	4839 (4)	4340 (7)
C10*	3107 (6)	6511 (6)	4362 (9)
C11*	3918 (6)	6845 (5)	4853 (10)
C12*	2474 (7)	6933 (6)	3486 (10)
O2*	2952 (4)	5908 (4)	4654 (7)
B	−429 (5)	2610 (5)	4197 (8)
C13	−313 (4)	3113 (4)	5475 (7)
C14	−140 (4)	3857 (4)	5510 (7)
C15	−3 (5)	4262 (5)	6588 (7)
C16	−43 (5)	3942 (5)	7696 (8)
C17	−210 (5)	3210 (5)	7715 (8)
C18	−340 (5)	2806 (5)	6620 (7)
C19	−539 (4)	3137 (4)	2995 (6)
C20	−1156 (4)	3680 (4)	2702 (7)
C21	−1238 (5)	4140 (4)	1693 (7)
C22	−693 (5)	4109 (5)	950 (8)
C23	−57 (5)	3619 (4)	1183 (8)
C24	17 (5)	3144 (4)	2220 (7)
C25	−1246 (4)	2076 (4)	4137 (7)
C26	−1166 (5)	1429 (4)	4816 (7)
C27	−1843 (5)	1001 (5)	4921 (8)
C28	−2621 (5)	1195 (5)	4312 (7)
C29	−2738 (5)	1803 (4)	3596 (8)
C30	−2052 (4)	2243 (4)	3509 (7)
C31	368 (4)	2082 (4)	4303 (6)
C32	1096 (4)	2120 (4)	5231 (7)
C33	1774 (4)	1680 (4)	5275 (7)
C34	1764 (5)	1165 (4)	4363 (7)
C35	1069 (4)	1098 (4)	3421 (7)
C36	392 (4)	1546 (4)	3414 (7)

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

Table III. Selected Bond Distances (Å) and Angles (deg)[a]

Cu1–N1	1.899 (6)	Cu1–N2	2.008 (7)
Cu1–N3	1.994 (6)	Cu1–O1	1.988 (5)
Cu1–Cu1′	5.189 (2)	Cu1–O2	2.609 (8)
N2–Cu1–N1	82.6 (3)	N3–Cu1–N1	170.0 (3)
N3–Cu1–N2	88.0 (3)	O1–Cu1–N1	84.9 (2)
O1–Cu1–N2	166.2 (3)	O1–Cu1–N3	104.0 (2)
O2–Cu1–N1	87.3 (2)	O2–Cu1–N2	88.1 (3)
O2–Cu1–N3	95.9 (2)	O2–Cu1–O1	97.1 (2)

[a] Primed atoms are related to the unprimed ones through an inversion center at (1, 1, 1).

Results

Structure. The structure is formed by centrosymmetric dinuclear Cu_2L^{2+} cations, BPh_4^- anions, and acetone solvate

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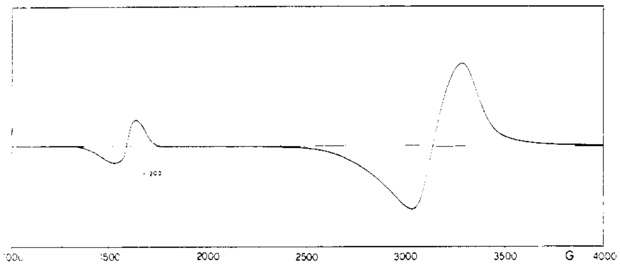

Figure 2. Room-temperature polycrystalline powder EPR spectrum of $Cu_2L(BPh_4)_2{\cdot}2(CH_3)_2CO$ at X-band frequency.

molecules. A view of the dinuclear species is shown in Figure 1. Each of the copper atoms, which are bridged by the oxamide moiety, is coordinated by one oxygen, one amidic nitrogen, and two aminic nitrogen atoms, which form a distorted-square-planar environment. At a longer distance, approximately on the perpendicular to the coordination plane, there is an oxygen of an acetone molecule. Values of bond distances and angles about the metal atoms are listed in Table III. Bond lengths and angles within the ligand molecule and in the anion are listed in Table SIII.[21]

The copper–amidic nitrogen distance of 1.899 (6) Å is shorter than those found in two analogous copper complexes with oxamides:[22,23] 1.933 Å in (μ-oxamido)bis(2,2′-bipyridylamine)bis(nitrato)dicopper(II) and 1.924 Å in (μ-oxamido)bis(2,2′-bipyridyl)bis(nitrato)dicopper(II) trihydrate. The copper–oxamide oxygen distance, 1.988 (5) Å, is intermediate between those, 2.007 and 1.962 Å, found for the above complexes, respectively. The present copper–oxygen distance also compares well with the distances observed for dinuclear oxalato-bridged copper(II) complexes.[24,25] The copper–amine nitrogen bond lengths, 1.994 (6) and 2.008 (7) Å, are larger, as expected, than that of the copper–amide nitrogen bond. The metal atom lies 0.087 Å from the best plane through the four closest donor atoms, on the side of the acetone molecule. In view of the rather large Cu–O distance formed by the acetone oxygen atom (2.609 (8) Å) the copper coordination environment may be described as essentially square planar with a weak axial perturbation. The copper–copper distance, 5.189 (2) Å, is the shortest so far reported for copper complexes bridged by substituted oxalato ligands. The least-squares plane through the four closest donor atoms is essentially parallel to the oxamide plane.

The bond angles about the metal atom are largely asymmetric, the N1–Cu–N2 angle being much smaller than 90° (82.6 (3)°) and the opposite angle N3–Cu–O1 much larger than this value (104.0 (2)°). The N1–Cu–O1 angle is in the range usually found for this sort of ligand.

EPR Spectra. The polycrystalline powder EPR spectra of the complex are shown in Figure 2. Single-crystal spectra were recorded by rotating the static magnetic field in the (100), (010), and (001) planes. Four $\Delta M = \pm 1$ lines are seen for a general orientation of the static magnetic field in the (100) and (001) planes, while only two are present in the (010) plane, in agreement with the monoclinic symmetry of the crystals.[27] The lines are rather broad, as shown in Figure 3, so that a detailed analysis of the spectra is difficult. We tried to use a curve-fitting procedure, by computing the experimental spectra as sums of Lorentzian curves, but in any case the standard deviations of the spectral parameters were fairly high, and for hardly overlapping lines also large correlation coefficients of the parameters were found. The best results were obtained for the spectra in the (010) plane, where only two lines are seen, and also the copper hyperfine splitting remains small and totally unresolved. In the other planes only the g values could be reasonably obtained because they can be evaluated from the intersection of two partially overlapping lines with the zero line. The angular dependence of the g^2 values in the three planes and of D in the (010) plane is shown in Figure 4. It is apparent that the **g** and **D** tensors, defined in the spin Hamiltonian $H = \mu_B\mathbf{B}{\cdot}\mathbf{g}{\cdot}\mathbf{S} + \mathbf{S}{\cdot}\mathbf{D}{\cdot}\mathbf{S}$, are not parallel. The principal g values and directions obtained by the Schonland procedure[28] are given in Table IV. The spectra where the largest g value is recorded yield also a hyperfine splitting which can be interpreted as the sum of two seven-line patterns, with A = 95 G and D = 45 G.

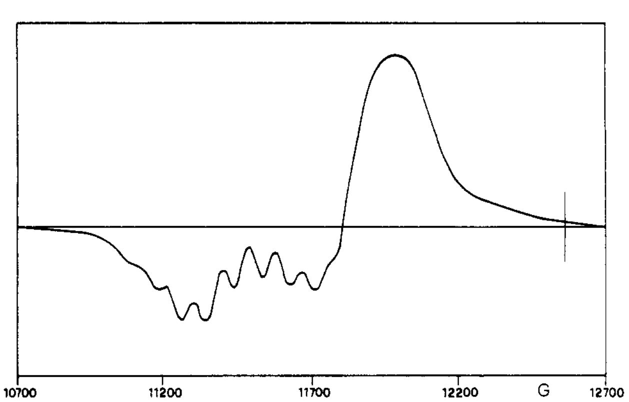

Figure 3. Room-temperature single-crystal EPR spectrum of $Cu_2L(BPh_4)_2{\cdot}2(CH_3)_2CO$ at Q-band frequency. The static magnetic field is in the (001) plane, making an angle of 20° with b.

Table IV. Principal g Values and Directions[a] of $Cu_2L(BPh_4)_2{\cdot}2(CH_3)_2CO$

g_x	2.0450	0.4237	−0.0836	−0.9019
g_y	2.0397	−0.8258	−0.4446	−0.3467
g_z	2.1966	0.3720	−0.8918	0.2574

[a] Direction cosines relative to the a^*, b, c crystal axes.

Discussion

The experimental **g** tensor, which is expected to be identical with that of a mononuclear copper(II) complex,[6] can be assigned to either magnetically nonequivalent site in the monoclinic unit cell. According to one choice g_z is within error orthogonal to the O1, N1, N2, N3 mean coordination plane, with g_x and g_y lying close to the bond directions. The values are typical for square-planar copper(II) complexes with a fairly strong in-plane ligand field.[27] Also, the hyperfine splitting of 90×10^{-4} cm^{-1} is in agreement with this view since it is expected to be roughly half the value of a corresponding mononuclear copper(II) complex.[6]

The analysis of the zero-field splitting tensor is less satisfactory since D could be meaningfully followed only in the (010) plane. In particular, the largest observed zero-field splitting, 90 G, is seen roughly halfway between the directions of maximum and minimum g values in that plane. The direction of maximum zero-field splitting corresponds nicely to the projection of the Cu–Cu direction in the (010) plane, indicating that the magnetic dipolar interaction between the two paramagnetic centers is dominating the zero-field splitting

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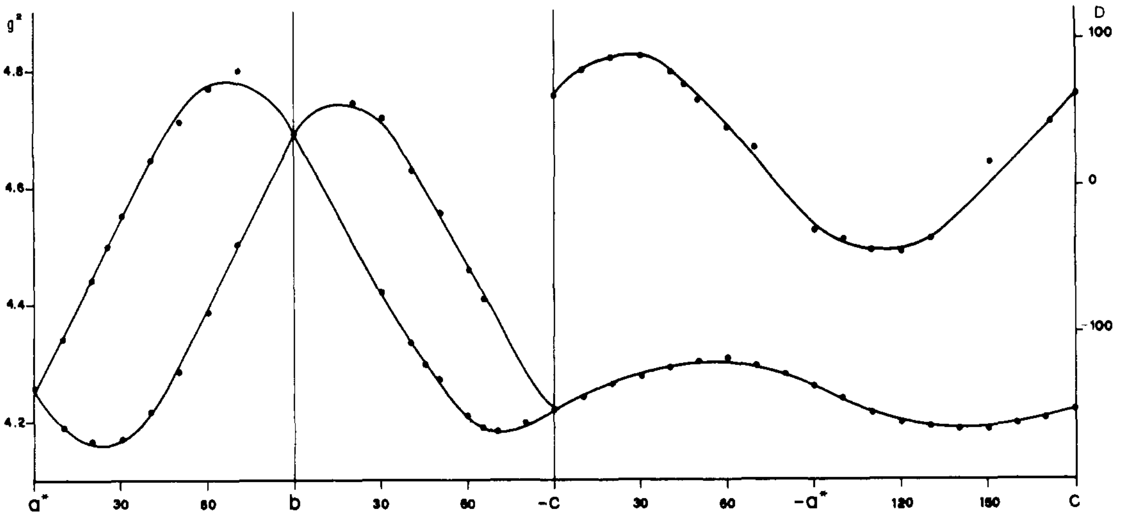

Figure 4. Angular dependence of the g^2 values of $Cu_2L(BPh_4)_2 \cdot 2(CH_3)_2CO$ in the (100), (010), and (001) planes and of the D values in the (010) plane.

tensor. If for the sake of simplicity we assume that the Cu–Cu direction is making an angle of 45° with the bond directions (it actually makes an average angle of 43°), we can use the reported formulas[1] to calculate the zero-field splitting tensor in the point dipole approximation. Using the experimental g values and the copper–copper distance seen in the crystal structure, we calculate $D_{x'x'} = -133 \times 10^{-4}$ cm^{-1}, $D_{y'y'} = +61 \times 10^{-4}$ cm^{-1}, and $D_{z'z'} = +72 \times 10^{-4}$ cm^{-1}, where x' is parallel to the Cu–Cu direction and z' parallel to z. With these principal values we calculate for the direction r along which we experimentally see the largest zero-field splitting a value of 125 G, which is slightly higher than the experimental value. Parallel to the direction where we experimentally read the largest g value we observe D = 44 G and predict D = 72 G. The differences between observed and calculated values many be due to (i) experimental error, (ii) inadequacy of the approximation of point dipoles, (iii) neglect of ligand-centered dipolar contribution, and (iv) exchange contributions. Of the four possibilities (iii) and (iv) seem to be the most probable. It is not possible to conclude whether an exchange contribution is operative, but in any case it must be small. It must be mentioned here that the exchange coupling constant J relative to the interaction between the two ground magnetic orbitals was found to be 550 cm^{-1}.[16] In fact we have shown[1] that for some planar copper(II) complexes bridged through two equatorial ligands the exchange contributions to the zero-field splitting tensor are given by

$$D^{ex} = 1/48(\Delta g_z^2)J_{x^2-y^2,xy}$$

$$D^{ex} = -1/96(\Delta g_x^2)J_{x^2-y^2,xy}$$

where $\Delta g_z = g_z - 2.0023$ and $J_{x^2-y^2,xy}$ is the exchange coupling between an electron in a $x^2 - y^2$ orbital and one in a xy orbital. Even if we attribute all the difference between the experimental and the calculated zero-field splitting tensor components to the exchange contribution, we find that $J_{x^2-y^2,xy}$ is still smaller than 0.1 cm^{-1}.

The present finding is much different from what we observed in bis(μ-hydroxo)-bridged copper(II) complexes,[1] where we evaluated $J_{x^2-y^2,xy}$ to be ferromagnetic and on the order of 10^2 cm^{-1}. The different behavior in the present case must be due to the extended bridge (Figure 5), which makes the ferromagnetic coupling between the xy and $x^2 - y^2$ magnetic orbitals almost ineffective. We wish to recall that a similar behavior was previously observed by us in the ground-state interaction between an octahedral nickel(II) and an octahedral cobalt(II) ion.[29,30] We found larger ferromagnetic contribution when the bridge was formed by two oxygen atoms, while it was almost negligible where the N–N grouping of a phthalazine molecule was bridging the two metal ions.

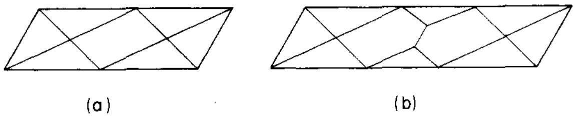
(a) (b)

Figure 5. Sketch of two bridged complexes: (a) monoatomic bridge; (b) substituted oxalato type bridge.

In conclusion it seems possible to state that, when two $x^2 - y^2$ magnetic orbitals are coupled, a fairly large exchange contribution, and consequently a fairly large zero-field splitting in the EPR spectra, can be expected when the bridge is monoatomic, allowing efficient overlap of $x^2 - y^2$ and xy magnetic orbitals, while the exchange contribution is substantially quenched when the bridge is an extended one.

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Registry No. $Cu_2L(BPh_4)_2 \cdot 2(CH_3)_2CO$, 89579-62-4; *N,N'*-bis(6-ethyl-3,6-diazaoctyl)oxamide, 89579-63-5; diethyl oxalate, 95-92-1; *N,N*-diethyldiethylenetriamine, 24426-16-2.

Supplementary Material Available: Tables of thermal parameters (Table SI), positional parameters of hydrogen atoms (Table SII), bond lengths and bond angles (Table SIII), and structure factors for $Cu_2L(BPh_4)_2 \cdot 2C_3H_6O$ (17 pages). Ordering information is given on any current masthead page.

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