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Notes

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Electron Spin Resonance Investigation of the Mixed-Valence Dinuclear Tetra(μ-1,8-naphthyridine-*N*,*N'*)-bis(bromonickel) Tetraphenylborate Complex

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The interest in the magnetic interactions among metal atoms in polymeric transition-metal complexes is increasing,[1-11] from both an experimental and a theoretical point of view. By far, the most common examples of reported complexes are those where an even number of electrons are present. Recently, we reported the synthesis and the characterization of some mixed-valence nickel complexes with the ligand 1,8-naphthyridine (napy),[12] where a copper acetate-type dimer is present containing three unpaired electrons.

We report now the single-crystal ESR spectra of one of these complexes and interpret the magnetic interactions between the metal ions using an angular overlap parameterization of the orbital energies we have suggested recently.[13]

Experimental Section

The $[Ni_2Br_2(napy)_4]B(C_6H_5)_4$ complex was prepared as previously described.[12] Single crystals were obtained by slow evaporation of acetone solutions. The crystals were found by Weissenberg techniques to conform to the X-ray structure report.[12] They can be described as prisms, with the (100) face most developed.

X-band (9-GHz) ESR spectra were run with the apparatus described previously,[14] and Q-band (35-GHz) ESR spectra were run with a Varian V-4651 microwave bridge.

Results

The room-temperature polycrystalline powder spectra of $[Ni_2Br_2(napy)_4]B(C_6H_5)_4$ recorded at Q-band and X-band frequencies are shown in Figure 1.[33] They are quite similar to each other as regards both the position and the shape of the lines. They can be interpreted by using an effective Hamiltonian with $S = {}^1/_2$ and axial symmetry. The corresponding g' values are shown in Table I. We recorded also X-band frozen-solution spectra, by pouring directly the chloroform solution into liquid nitrogen, in order to prevent crystallization.[15] The close similarity of the latter spectra to the powder spectra suggests that the crystal g' values correspond quite closely to the molecular g' values.

Table I. g' Values for $[Ni_2Br_2(napy)_4]B(C_6H_5)_4$

	X band		Q band
	powder	glass	powder
$g'_{\parallel}$	2.19 ± 0.03	2.20 ± 0.03	2.22 ± 0.03
$g'_{\perp}$	4.30 ± 0.03	4.30 ± 0.03	4.27 ± 0.03

The single-crystal spectra showed only one signal for most orientations in the magnetic field, and the line shape was found to be Lorentzian to a good approximation. In the case of spectra recorded with the static field in the (010) plane, in some orientations at X-band frequency the line appeared markedly asymmetric and unusually broad. Q-band spectra showed that the origin of this behavior is the presence of two signals of differing intensities. In the original structure report it was observed that the X-ray reflections were split into two separate peaks largely different in intensity,[12] as a consequence of the poor quality of the crystals, and we interpret the appearance of two signals in the ESR experiment as due to the same cause. Repeated attempts to find better crystals were unsuccessful. The best results were obtained with small crystals, 0.05 × 0.3 × 0.7 mm being the typical dimensions of the ones we used.

The spectra recorded with the magnetic field parallel to the monoclinic b crystal axis yielded the g_{yy}' value of 4.25 ± 0.02 at X-band frequency and 4.12 ± 0.02 at Q-band frequency. The main origin of the large uncertainty on the value of g' is associated with orientation errors of the crystal in the magnetic field. By rotating around the b axis a dramatic dependence of the line width on the orientation in the magnetic field was observed. At Q-band frequency it was observed to vary between 16 and 120 mT, the narrower line being observed in correspondence to the higher g' value, $g_{xx}' = 4.28 \pm 0.02$, while the wider line was observed in correspondence to the lowest g' value, $g_{zz}' = 2.26 \pm 0.03$. In the X-band spectra the signal could be followed only in a range of about ±60° from the x direction. Approaching closer to the z direction caused washing out of the signal. We interpret the difference observed at the two different frequencies as due to the higher sensitivity of the Q-band experiment, which allowed us to detect the signals of small crystals. The g_{zz}' value in the X-band experiment was obtained by extrapolating the angular dependence of the g'^2 values at the z direction. It is $g_{zz}' = 2.24 \pm 0.03$ that is in accord with both the powder and the Q-band spectra.

At X-band frequency the spectra were run also down to liquid helium temperature, and although a sharpening of the lines was observed, it was not possible to record any signal in the z direction. Spectra were run also up to 400 K, and no

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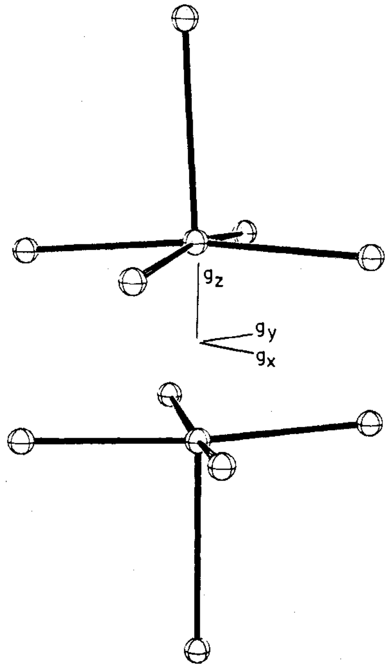

Figure 2. The orientation of the g' principal directions in the dimer. The g_x' and g_y' directions make an angle of 45° to the plane of the paper.

anomalous change in the intensities of the signals was observed in the range 4.2–400 K.

The orientation of the g' principal directions within the molecule is shown in Figure 2. It is interesting to note that although the crystals are monoclinic and no symmetry element is present in the dimer, the Ni–Ni vectors of different molecules are to a good approximation in the (010) plane. Therefore, they are all parallel to each other. We feel confident to assume that although intermolecular exchange interactions may be present, the observed g' values and directions are quite close to the molecular ones. The z direction is within error parallel to the nickel–nickel vector, while the x and y directions almost exactly bisect the twist angle between the two coordinate planes.

Discussion

The ESR spectra of $[Ni_2Br_2(napy)_4]B(C_6H_5)_4$ can be considered as due to a spin quartet ground level, in accord with the magnetic susceptibility data, which were found to follow Curie–Weiss behavior in the range 77–400 K.[12,16] If the properties of the dimer are interpreted using the exchange Hamiltonian,[17] it must be concluded that a large ferromagnetic coupling is operative between the two nickel atoms, one with $S = 1$ and the other with $S = {}^1/_2$. The separation of the ground quartet from the first excited doublet is $3J$. The constancy of the intensities of the ESR signals in the range 4.2–400 K, and the fact that no inflections were observed in the magnetic susceptibility curve up to 400 K, suggests a lower limit to the value of J of 300 cm^{-1}. Such large values of the ferromagnetic coupling constant are by no means common for transition-metal dimers.[1-8] The observed nickel–nickel distance is very short, 241.5 pm, and a direct mechanism of magnetic interactions cannot be excluded. In this case there would be a parallel interaction[7] between the electrons in the $x^2 - y^2$ orbitals and a perpendicular interaction for the electrons in the $x^2 - y^2$ and z^2 orbitals. In this scheme there is no way to decide which of the two interactions is stronger, thus determining the sign of J. On the other hand, the magnetic interactions in copper acetate type dimers have been interpreted on a weakly coupled chromophore approach, and we will attempt a similar one for the present compound.

Recently, several MO-based approaches to the electronic and magnetic properties of transition-metal dimeric complexes have been proposed.[19-28] In particular, Hoffmann[19] suggested that the ferromagnetic and antiferromagnetic contributions to the metal–metal coupling could be expressed as a sum of terms depending on exchange integrals and orbital energy differences, respectively.

In order to evaluate a theoretical expression for J in our case it is required to have a knowledge of the energy levels of the dimer. Recently, we suggested that the orbital energies of the dimer complex could be evaluated by using an extension of the angular overlap formalism from one to two metal centers[13] and applied the model to copper(II) dimers.

In the angular overlap treatment every donor atom must be considered as shared by the two metal atoms, and this can determine the splitting of the otherwise degenerate levels which are mainly d metal in character. In the present complex, each donor atom can be considered as shared in a highly unsymmetrical fashion by the two metal centers. In particular, the nitrogen atoms of the naphthyridine ligands are bound to a metal, with an average bond distance of 210.5 pm, while they are on the average 310 pm from the other metal atom. Although the latter distance is too long to assume that a normal bond is formed, it cannot be excluded that some kind of interaction is still operative. As a matter of fact, Smith suggests a value of e_σ of 250 cm^{-1} for a copper metal with a nitrogen donor at 300 pm.[29] Therefore, in the present case, for a ligand close to metal atom A, e_{iA} must be large, while e_{jB} is small, and the reverse is true for a ligand close to metal B. e_{iA} and e_{jB} are the angular overlap parameters of the metal A and B, respectively. However, unless e_{jB} is set to zero, the model[13] predicts a splitting of the metal orbitals. Sample calculations were performed using the reported formulas,[13] and the effect of different ligands was considered as additive.

In Figure 3 is shown the effect of including a σ perturbation, $e_{\sigma I}$, of the far ligand on the orbitals of the metal. It is apparent that a large splitting is predicted for the $x^2 - y^2$ orbitals and a smaller one for the z^2 orbitals. Including $e_{\pi I}$ would have caused a splitting of the xy orbitals and, in general, an increase of the splitting of the other levels. The energy levels of Figure 3 show an increased splitting of the $x^2 - y^2$ and a decreased splitting of the z^2 orbitals as compared to the pattern of the levels suggested by Ballhausen[20] for copper acetate.

If the energy level pattern of Figure 3 is considered to provide a reasonable approximation of the molecular orbitals which are mainly d metal in character for our mixed-valence complex, an extension of the method of Hoffmann[19] (see Appendix 1[33]) allows us to express the difference in energy between the ground quartet and the first excited doublet level as

$$E_{3/2} - E_{1/2} = -3J = -(3/4)K_{ab} - (3/2)K_{bd} - (3/4)K_{bc} + (3/4)\frac{(\epsilon_3 - \epsilon_4)^2}{J_{dd} - J_{bd}}$$

where the symbols have the same meaning as in Hoffmann's paper[19] and as redefined in Appendix 1. It is apparent that the fourth term is responsible for the antiferromagnetic coupling, while the first three yield the ferromagnetic interaction. The main difference from the cases of two and four electrons previously reported[19] is that now among the ferromagnetic terms there is a one-center exchange integral (K_{ab}), whose value must be large. Consequently, a large ferromagnetic coupling is predicted, in accord with the observed behavior of our mixed-valence compound.

It is possible also to use the above ground-state functions in order to evaluate the expected g values by standard

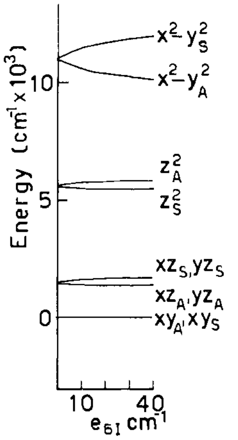

Figure 3. Energy level diagram for a dimer having the copper acetate structure. The parameters used are $e_\sigma{}^N = 3700$ cm^{-1}, $e_\pi{}^N = 0$ cm^{-1}, $e_\sigma{}^{Br} = 2030$ cm^{-1}, and $e_\pi{}^{Br} = 1390$ cm^{-1}, the geometrical parameters corresponding to the structure report.

techniques, the details of which are reported in Appendix 2,[33] modified to allow for two-center orbitals.

The principal g values, assuming tetragonal symmetry for the sake of simplicity, are calculated as

$$\Delta g_\parallel = \frac{8}{3}\zeta\left[\frac{1}{\Delta(x^2-y^2{}_S \rightarrow xy_S)} + \frac{1}{\Delta(x^2-y^2{}_A \rightarrow xy_A)}\right]$$

$$\Delta g_\perp = \frac{2}{3}\zeta\left[\frac{1}{\Delta(z^2{}_A \rightarrow yz_A)} + \frac{1}{\Delta(x^2-y^2{}_S \rightarrow yz_S)} + \frac{1}{\Delta(x^2-y^2{}_A \rightarrow yz_A)}\right]$$

where the Δ's are defined in Appendix 2. In order to guess the values of g, we can set $\zeta = 600$ cm^{-1}, close to the value obtained from Ni^0, Ni$^{\rm I}$, and Ni$^{\rm II}$ atomic spectra.[30] The transitions from the $x^2 - y^2$ orbitals to xy and yz are expected to be close in energy (see Figure 3). If one sets them at about 10 000 cm^{-1}, in correspondence to an observed transition,[12] a higher limit to g is set at 2.3. The transition from z^2 should be lower in energy than the previous ones. Using the values of the energies which can be obtained from Figure 3, it can be concluded that $g_\parallel$ and $g_\perp$ must be close to each other, perhaps with $g_\perp$ slightly lower than $g_\parallel$.

The values of g' shown in Table I are in accord with a quartet ground level split by a large zero-field splitting. The Q-band spectra set a lower limit to the zero-field splitting of about 1.5 cm^{-1}. The close correspondence of the g' values for the X-band and the Q-band experiments suggests that the zero-field splitting is larger.

Assuming axial symmetry for the powder ESR spectra and using the spin Hamiltonian for a spin quartet, $g_\parallel = 2.20$, $g_\perp = 2.14$, and $D \geq 30$ cm^{-1}. The values were calculated considering that the $\pm{}^1/_2$ levels lie lower in energy at zero field. The single-crystal values show that there is a deviation from tetragonal symmetry, suggesting that a completely anisotropic spin Hamiltonian should be used. Attempts were made to calculate g_x, g_y, g_z, D, and E, using the reported matrices.[31] It appears, however, that the large uncertainties on the experimental values do not allow us to obtain accurate values of the spin Hamiltonian parameters, since a small variation of the experimental data causes large shifts in the calculated values.

The g values obtained from the powder spectra can be considered as in substantial agreement with the theoretical provisions above. Further, using the values of g and D to calculate the magnetic susceptibility yields values which are in good agreement with the experimentally observed ones.

Finally, the observed line widths deserve some comments. First of all, the observation of ESR signals at room temperature for a spin quartet is common only for metal ions which have orbital singlet ground states largely separated from the excited levels.[32] According to our model in the present case, the ground level is orbitally nondegenerate and the first excited level, quite close in energy, is that which can be obtained by excitation of one electron to the $z^2{}_S$ orbital. Since this level is expected to mix into the ground level via a magnetic field parallel to the z axis, it can determine an effective relaxation path, thus yielding broad lines in the parallel direction. In the x and y directions the excited levels which can interact with the ground level are the yz, and xz orbitals, which are expected to be about 10 000 cm^{-1} higher in energy. In this case, therefore, the relaxation is far less effective and relatively narrow lines can be observed. In this respect the present pattern of energy levels appears to be better suited to describe the spectral and magnetic properties of the complex than the scheme by Ballhausen,[20,12] which predicts a larger splitting of the z^2 orbitals.

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Supplementary Material Available: Figure 1, showing EPR spectra of [$Ni_2Br_2(napy)_4$]$B(C_6H_5)_4$, and Appendixes 1 and 2, showing methods of expressing the difference in energy between a ground quartet and the first excited doublet level and of evaluating the principal g values (4 pages). Ordering information is given on any current masthead page.

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