excited state would be premature, although we note that a LMCT transition from ligand σ orbitals is calculated to occur in this region.[13]

Vogler and Kunkely proposed that photooxidation of M(mnt)$_2^{2-}$ complexes occurs via a CTTS state.[3] However, it is likely that additional excited states are reactive for the following reasons: (1) $E_{1/2}$ values do not correlate with the quantum yields (Table I); (2) quantum yields in 24:1 (v/v) CHCl$_3$/CH$_3$CN are significantly lower than in CHCl$_3$ (compare our values to those in ref 3), whereas the redox potentials of these solvents should be almost identical. Decreased quantum yields in the presence of coordinating solvents has previously been observed in the charge-transfer photochemistry of dithiocarbamate complexes in chlorocarbons and attributed to quenching of either the excited state or a reactive intermediate.[11,17] Both LMCT and CTTS states are thought to be involved in the chlorine-abstraction reactions of dithiocarbamate complexes in chlorocarbon solutions.[11] In view of the fact that redox reactions in M(mnt)$_2^{2-/-}$ complexes are primarily ligand localized, we suggest that excited states with *decreased* bonding electron density on the ligands (relative to the ground state) are potentially reactive, although other factors (e.g., energy, lifetime, etc.) clearly must influence the reactivity as well. We are currently carrying out both spectroscopic and photochemical experiments designed to identify the reactive excited states and to explore further aspects of the redox photochemistry of dithiolene complexes.

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Registry No. Ni(mnt)$_2^{2-}$, 14876-79-0; Pd(mnt)$_2^{2-}$, 37562-15-5; Pt(mnt)$_2^{2-}$, 15152-99-5; Co(mnt)$_2^{2-}$, 40706-01-2; Cu(mnt)$_2^{2-}$, 19562-26-6; CHCl$_3$, 67-66-3; CH$_3$CN, 75-05-8; CCl$_4$, 56-23-5.

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Contribution from the Department of Applied Science,
Faculty of Engineering, Kyushu University,
Fukuoka 812, Japan

Magnetic Susceptibility of Dimers with Anisotropic Exchange Interactions

Seiji Nakatsuka, Keiji Osaki, and Norikiyo Uryû*

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As was demonstrated by a typical example of hydrated copper acetate,[1] there have been reported many dimeric compounds with antiferromagnetic Heisenberg exchange interactions between pairing spins of $S = {}^1/_2$. Most of their magnetic properties such as the susceptibility and specific heat have been explained by assuming an isotropic or Heisenberg Hamiltonian:

$$H' = -2J\mathbf{S}_1\cdot\mathbf{S}_2 \qquad (1)$$

Then, the so-called Bleaney-Bowers formula, namely, the magnetic susceptibility per mole of dimers, is calculated as

$$\chi = \frac{2Ng^2\mu_B{}^2}{3kT}[1 + {}^1/_3 \exp(-2J/kT)]^{-1} \qquad (2)$$

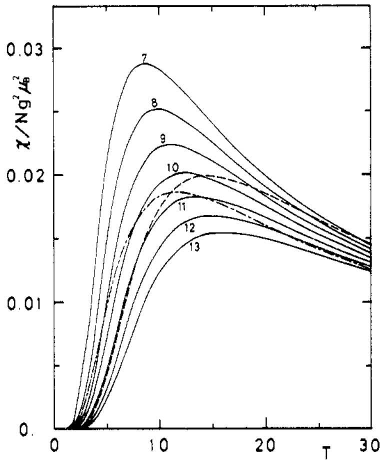

Figure 1. Magnetic susceptibility of dimers of spin $^1/_2$ ions coupled antiferromagnetically in the Heisenberg (—), *XY* (---), and Ising (-·-·) approximations. The values of $|J|/k$ are shown for each curve of the Heisenberg case. For the *XY* and the Ising cases, the curves have been calculated for $|J|/k$ = 22.5 K and $|J|/k$ = 15 K, respectively.

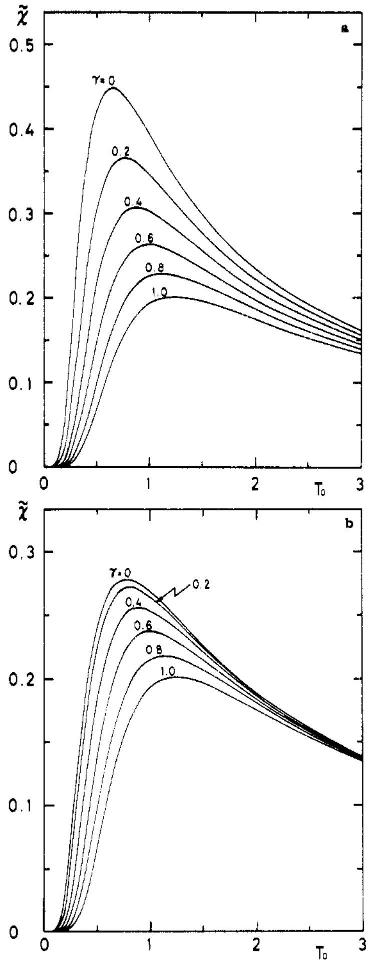

Figure 2. Behavior of the reduced magnetic susceptibility $\tilde{\chi} = \chi|J|/Ng^2\mu_B{}^2$ vs. reduced temperature $T_0 = kT/|J|$ for various values of the anisotropy parameter γ: (a) the *XY*-Heisenberg case; (b) the Ising-Heisenberg case.

where N is Avogadro's number, μ_B is the Bohr magneton, g is the g factor, and k is the Boltzmann constant. If the g factor has been settled, for instance, by ESR experiment, the only adjustable parameter is the separation $2J$ between the ground singlet and the excited triplet. Usually, the J value has been assumed to be constant, and the experimental behavior of the susceptibility vs. temperature in most of the dimeric copper

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compounds has been explained in reasonable agreement with theory.

Some cases, however, have been reported where the Bleaney–Bowers formula is unable to explain the behavior of the susceptibility unless the exchange parameter J is assumed to vary with temperature.[2-4] Whether the exchange interaction originates in the direct-exchange or superexchange mechanism, the value of the exchange parameter J depends on the separation between magnetic ions as well as on the angle between bonding paths at the intervening anion in the latter case. As has been demonstrated by Lines,[5] thermal lattice vibrations modulate the exchange integral and give rise to the striction mechanism which gives the main contribution to the temperature-dependent part of J.

For the analysis of the magnetic properties of copper dimers, an isotropic form of the exchange interaction (1) has been assumed customarily. The combined action of the crystal field potential and the spin–orbit interaction, however, is able to modify the exchange interaction to have an anisotropic form, which assumes the form of the XY or Ising model in the extreme cases. In the present note, we should like to point out that the behaviors of the susceptibility given by the Bleaney–Bowers formula with an apparent temperature-dependent exchange parameter can be reconciled with those calculated for the dimer model with a constant exchange parameter and with the XY or Ising character to some extent. In the case of binuclear complex salts with spins $S > 1$, an alternative explanation may be made by an introduction of the biquadratic exchange interaction as has been done for chromium binuclear complex salts.[6] The biquadratic exchange Hamiltonian, however, reduces to a bilinear exchange term in the case of $S = {}^1/_2$.

For an external magnetic field applied along the z axis of the dimer, the Hamiltonian will be taken as

$$H_1 = -2J[\mathbf{S}_1\cdot\mathbf{S}_2 + (\gamma - 1)S_{1z}S_{2z}] + g\mu_B H(S_{1z} + S_{2z}) \quad (3)$$

for the XY-Heisenberg case and

$$H_2 = -2J[\gamma\mathbf{S}_1\cdot\mathbf{S}_2 + (1 - \gamma)S_{1z}S_{2z}] + g\mu_B H(S_{1z} + S_{2z}) \quad (4)$$

for the Ising-Heisenberg case. In both cases, $\gamma = 1$ corresponds to the isotropic Heisenberg model, and $\gamma = 0$ in H_1 and H_2 corresponds to the XY model and the Ising model, respectively. The parameter γ may change from 1 to 0, reflecting the XY or the Ising character in the exchange interactions.

The diagonalization of the Hamiltonian H_1 or H_2 can easily be done by the use of the vector model, and the magnetic susceptibility χ is calculated as follows. For the XY-Heisenberg case

$$\chi_1 = \frac{Ng^2\mu_B^2}{|J|T_0}[1 + \exp(\gamma/T_0)\cosh(1/T_0)]^{-1} \quad (5)$$

and for the Ising-Heisenberg case

$$\chi_2 = \frac{Ng^2\mu_B^2}{|J|T_0}[1 + \exp(1/T_0)\cosh(\gamma/T_0)]^{-1} \quad (6)$$

where $T_0 = kT/|J|$.

As a demonstration that the XY or Ising character introduced into the Heisenberg exchange interaction may be reflected in the susceptibility behavior as if the exchange parameter varies with temperature, the susceptibilities of the pure Heisenberg model ($\gamma = 1$) for several values of J have been shown in Figure 1 and compared with those of the XY model and the Ising model ($\gamma = 0$). As can be seen, the susceptibility of the XY model with a fixed J value simulates those of the Heisenberg model with different J values at any intervals of the temperature. In other words, the XY model simulates the Heisenberg model, whose $|J|$ value decreases with increasing temperature. The susceptibility behavior of the Ising model is in a similar situation, provided that in the corresponding Heisenberg model $|J|$ increases with increasing temperature.

In both the XY-Heisenberg and the Ising-Heisenberg cases, the magnetic susceptibility takes its maximum value, χ_{max}, at the temperature T_{max}. In order to see the γ dependence of T_{max} and χ_{max}, we can examine the reduced susceptibility $\tilde{\chi} = \chi|J|/Ng^2\mu_B^2$ as a function of the reduced temperature T_0. As can be seen from eq 5 and 6, $\tilde{\chi}$ is independent of $|J|$ and only depends on the anisotropy parameter γ. In Figure 2, parts a and b, the results of calculation of $\tilde{\chi}$ vs. T_0 for various values of γ in the XY-Heisenberg and Ising-Heisenberg cases are shown, respectively. The results also enable us to plot the behavior of $\tilde{\chi}_{max}$ vs. γ for both cases. From the values of χ_{max} and T_{max} experimentally obtained, let us make the product $T_{max}\chi_{max}k/(Ng^2\mu_B^2)$, which is equal to $T_0(\mathrm{max})\tilde{\chi}_{max}$ from their definitions, is independent of $|J|$, and only depends on γ. From the results shown in Figure 2, the γ dependence of $T_0(\mathrm{max})\tilde{\chi}_{max}$ in the XY-Heisenberg and Ising-Heisenberg cases can be obtained, and the parameter γ can be fixed unambiguously. Therefore, we may estimate the value of $\tilde{\chi}_{max}$ and so the exchange integral $|J|$.

It should be noted, however, that eq 5 and 6 represent the parallel susceptibility $\chi_\parallel$, so to speak, and may be employed for comparison with the experimental data on a single crystal. In most cases of dimeric copper compounds, the susceptibility measurements were done on powder samples and so the comparison should be made with the relevant formula. The expression of the powder susceptibility is given by $\chi_P = (\chi_\parallel + 2\chi_\perp)/3$, where $\chi_\perp$ denotes the perpendicular susceptibility. With an external magnetic field applied along the x axis, the perpendicular susceptibility is shown to be given by

$$\chi_\perp = [4Ng_x^2\mu_B^2/(1-\gamma)|J|] \times \{\sinh[(1-\gamma)/2T_0]\}/\{\exp[(1-\gamma)/2T_0] + \exp[(3+\gamma)/2T_0] + 2\cosh[(1-\gamma)/2T_0]\} \quad (7)$$

for the XY-Heisenberg case and by

$$\chi_\perp = [4Ng_x^2\mu_B^2/(1-\gamma)|J|] \times \{\sinh[(1-\gamma)/2T_0]\}/\{\exp[(\gamma-1)/2T_0] + \exp[(1+3\gamma)/2T_0] + 2\cosh[(1-\gamma)/2T_0]\} \quad (8)$$

for the Ising-Heisenberg case.

As an example of the application of the present theory, let us analyze the experimental data on $\mathrm{Cu}(n\text{-}\mathrm{C_3H_7nso})\mathrm{NO_3}$ given in ref 2. With the use of a computing facility, the least-squares fit with the experimental values has been done for the powder susceptibility expressions of the XY-Heisenberg (eq 5 and 7) and the Ising-Heisenberg (eq 6 and 8) cases. The best fit is obtained for the Ising–Heisenberg case with $J/k = -345.50$ K, $\gamma = 0.217$, and $g = g_x = 2.02$, and the result of the calculation of χ_P is shown in Figure 3. Needless to say, for the present example we may employ the conventional Bleaney–Bowers formula and obtain a fit with the experiment, provided that the exchange integral J is assumed to vary with temperature. We have estimated the J value as a function of temperature by this fitting procedure, and the result is also shown in Figure 3. In this way, the magnetic susceptibility of the $S = {}^1/_2$ dimers may well be analyzed theoretically.

As one of the other possible effects to explain the deviation from the Bleaney–Bowers formula, the interdimer interactions may be a most probable candidate. If we take the interdimer

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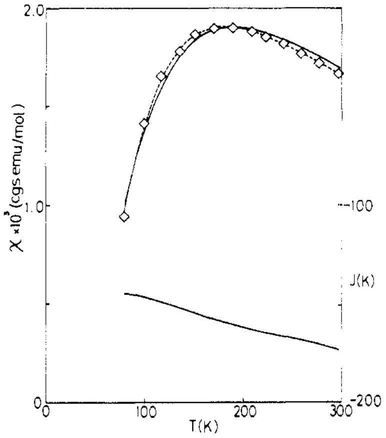

Figure 3. Magnetic susceptibility behavior of spin $^1/_2$ dimers with Ising-Heisenberg coupling. The upper solid curve shows the powder susceptibility calculated by the use of eq 6 and 8 with $J/k = -345.50$ K, $\gamma = 0.217$, and $g = g_x = 2.02$, and the dashed curve shows the parallel susceptibility, eq 6, with $J/k = -213.50$ K and $\gamma = 0.282$. Both curves are compared with the experimental data on $Cu(n\text{-}C_3H_7\text{-nso})NO_3$ given by Mikuriya et al. The lower solid curve shows the temperature dependence of the exchange integral J estimated from the comparison of the Bleaney–Bowers formula, eq 2, with the experimental data.

interactions into account, the system necessarily becomes that of many spins interacting among themselves. However, the exact solution for such a many-spin system of the Heisenberg exchange is not yet known, and we have to be satisfied by an approximate solution such as the mean-field theory. As can easily be shown, the mean-field approximation modifies the magnetic susceptibility χ_0 for the system of isolated dimers as

$$\chi = \chi_0 \Big/ \left[1 - \frac{2zJ'}{Ng^2\mu_B{}^2}\chi_0 \right] \tag{9}$$

where J' denotes the exchange coupling constant of the interdimer interaction and z is the number of nearest dimers. Apparently, the effect of this type of correction is an upward ($J' > 0$) or downward ($J' < 0$) shift of the suceptibility curve and is different from that of the anisotropic exchange proposed in the present note. Therefore, the susceptibility behavior of the present example cannot be explained solely by the interdimer interactions. An extension of the present analysis including the interdimer interactions will be able to give an overall fitting with a more resonable anisotropy parameter γ, which is usually of the order of a few percent.

Contribution from the Department of Structural Studies,
Research Laboratory for Inorganic Chemistry,
Hungarian Academy of Sciences, Budapest, H-1431, Hungary

Trigonal-Bipyramidal Molecular Structures and the VSEPR Model

I. Hargittai

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The compatibility of a molecular structure with the VSEPR model[1] has to be judged by examining *all* angles characterizing the configuration of all electron pairs in the valence shell of the central atom. Usually, only the variations of the bond angles are considered as they are determined directly from experiment while the angles made by the lone pairs of electrons are not always attainable from the experimental data. For example, the E–P–F angle of PF_3, where E is the lone pair, can be calculated from the F–P–F bond angle by virture of C_{3v} symmetry; on the other hand, the angles of E–S–E and E–S–F of the C_{2v} symmetry SF_2 molecule cannot be calculated from the F–S–F bond angle.

For some time a series of tetrahedral structures has seemed to provide incompatible variations with the VSEPR model. While originally it has been stated[1] that in the series CH_4, NH_3, and H_2O the bond angles decrease as the number of nonbonding pairs increases, for several analogous series this was not entirely the case.[2] While it was invariably observed that in going from AX_4 to BX_3E, with E being a lone pair of electrons, the bond angles decreased, the replacement of yet another bond by a second lone pair did not lead to further decrease of the bond angle in CX_2E_2, except for the hydride molecules.

As the "bond angles" made by the lone pairs of electrons in the tetrahedral systems under consideration were not available from experimental data, ab initio molecular orbital calculations have been carried out[3] for a series of molecules. The structural variations in the resulting geometries showed complete agreement with the predictions of the VSEPR model when *all* angles have been considered. In the series SiF_4, PF_3, SF_2, for example, these angles were[4]

SiF_4	PF_3	SF_2
F-Si-F 109.5°	F-P-F 96.9°	F-S-F 98.1°
	E-P-F 120.2°	E-S-F 104.3°
		E-S-E 135.8°

While the F–S–F bond angle is indeed smaller than the F–P–F bond angle, the E–P–F angle is much larger than the E–S–F angle, and the origin of this difference is decisive as the relative strength of the repulsive interactions decrease in the order

$$E/E > E/b > b/b$$

where b is a bonding pair.

It appeared to be particularly useful to characterize the general space requirements of various bonds and lone pairs by the so-called triple-average angles[5] that were shown to be rather constant for single bonds and double bonds as well as for lone pairs of electrons.[3]

Following the success of this approach, the so-called quadruple-average angle[6] $\bar{\alpha}_Y$ was introduced by Hargittai[7] to characterize the general space requirements of bonds, lone pairs, and double bonds in YAX_4 trigonal-bipyramidal molecules. The consideration of the relatively constant values of the quadruple-average angles for lone pairs and double bonds has facilitated the selection of one or two of the four models of $O{=}SF_4$ that had been reported from experimental studies displaying considerable differences in the bond angles.[8] The results of ab initio calculations[9] and further experimental

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[4] The position of the lone pair was characterized by the center of its charge distribution.

[5] The triple-average angle is the mean of the three angles made by a bond or a lone pair in a tetrahedral configuration.[3]

[6] The quadruple-average angle, $\bar{\alpha}_Y$, is the mean of the four angles made by A–Y in YAX_4, where Y may be a ligand or a lone pair and the X ligands may be the same or may be different.

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