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Magnetic Susceptibility of Magnesium 2,2′-Dipyridylide in its THF Adducts

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The magnetic susceptibility of magnesium 2,2′-dipyridylide has been determined in its THF (tetrahydrofuran) adducts in a temperature range of 1.6—20 K. The susceptibility of Mg(dipy)$_2$·THF exhibits two maxima at about 3.9 and 9.5 K due to short range and long-range interactions, respectively. The observed susceptibility conforms to the alternating linear Heisenberg model above about 6 K. Mg(dipy)$_2$·3THF shows no definite maximum of magnetic susceptibility. The magnetic behavior of these complexes different from that of Be(dipy)$_2$ is attributable to the difference in the ionic character between Mg–N and Be–N bonds.

The magnetic susceptibility of beryllium 2,2′-dipyridylide, Be(dipy)$_2$, conforms to an equation for isolated binuclear clusters, indicating that antiferromagnetic interaction operates between two 2,2′-dipyridyl radical anions within a molecule.[1] The tetrahydrofuran adduct of magnesium 2,2′-dipyridylide, Mg(dipy)$_2$·3THF, was found to show an effective magnetic moment of 2.73 B.M. at room temperature.[2] This value is nearly equal to $(2\times3)^{1/2}$ B.M. for a biradical having two independent unpaired electrons, indicating the presence of two dipyridyl ion radicals in a molecule. However, magnesium 2,2′-dipyridylide is suspected to show a magnetic property different from that of Be(dipy)$_2$ at low temperature, because beryllium and magnesium compounds differ from each other in bond nature. One may expect to obtain information about magnetic interaction by comparing the magnetic properties of the beryllium and magnesium complexes. Therefore, we have undertaken to determine the magnetic susceptibility of magnesium 2,2′-dipyridylide.

Experimental

Preparation of Materials. Excess metallic magnesium was mixed with a solution of 2,2′-dipyridyl in THF. On adding a small quantity of iodine to the solution, deep red crystalline precipitate separated. Recrystallization from THF yielded the crystals of Mg(dipy)$_2$·3THF[2] (Calcd: Mg, 4.5%. Found: Mg, 4.4%). When the precipitate was recrystallized from benzene, deep red needle crystals were obtained. On heating in vacuum at about 90 °C, weight loss amounted to 19.2%. The liberated gas did not freeze even at dry-ice temperature, indicating that the crystals were those of a THF (mp, −108.5°) adduct, Mg(dipy)$_2$·THF, rather than a benzene adduct (Calcd: Mg, 5.9%; THF, 17.6%. Found: Mg, 5.6%; THF, 19.2%). As the compounds were very sensitive to atmospheric oxygen and moisture, they were preserved in an atmosphere of argon or helium.

Magnetic Measurement. The magnetic susceptibility was determined by means of a Hartshorn bridge operating at 90 Hz with a field strength equal to about 10 Oe. Iron(III) alum was employed as a standard. The molar susceptibility was corrected for diamagnetic contributions (10^{-6} emu/mol) from 2,2′-dipyridyl (−93) and THF (−55). The values were calculated on the basis of the observed susceptibility of pyridine and the Pascal constants.[3]

Electronic Spectra. Electronic spectra were recorded in solutions by means of a Model 323 recording spectrophotometer from Hitachi Ltd.

Results and Discussion

The magnetic susceptibility *versus* temperature curve of Mg(dipy)$_2$·THF exhibits two maxima at about 3.9 and 9.5 K as shown in Fig. 1. The broad maximum at the higher temperature is undoubtedly due to a short-range magnetic interaction. An ESR study carried out on magnesium 2,2′-dipyridylide in a glassy 2-methyltetrahydrofuran matrix has indicated that each metal ion has a tetrahedral coordination comprising four nitrogen atoms from two dipyridyl ions.[4] From the result, the biradical molecules of Mg(dipy)$_2$ are expected to exist as units in the crystals of Mg(dipy)$_2$·THF. This suggests that the magnetic behavior due to a short-range interaction can be explained by the binuclear cluster model. However, the observed curve can be reproduced with difficulty by the theoretical formula for weakly coupled biradicals[5] as well as by isolated biradicals. For the coupled dimer model or the alternating linear Heisenberg model, the Hamiltonian is given by

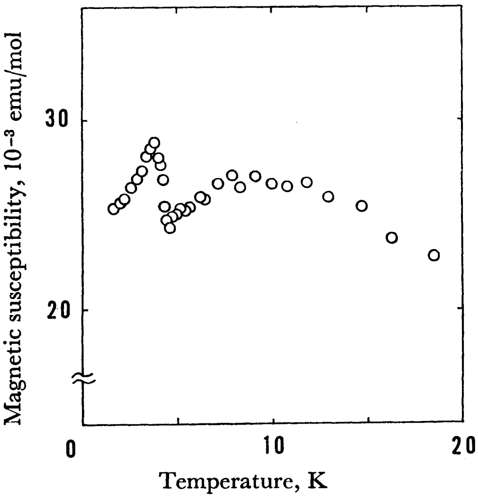

Fig. 1. Magnetic susceptibility of Mg(dipy)$_2$·THF.

$$\mathcal{H} = -2J\sum_{i=1}^{N/2}(\mathbf{S}_{2i-1}\cdot\mathbf{S}_{2i}+a\mathbf{S}_{2i}\cdot\mathbf{S}_{2i+1}) + g\beta\sum_{i=1}^{N}\mathbf{S}_i\cdot\mathbf{H}$$

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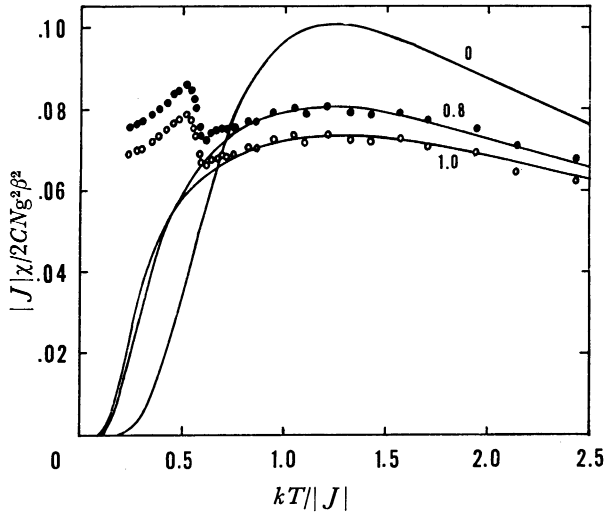

Fig. 2. Theoretical magnetic susceptibility of alternating linear chains with a=0—1 and the observed curves of Mg(dipy)$_2$·THF (○: $J/k=-7.6$ K, C=0.93; ●: $J/k=-7.6$ K, C=0.85).

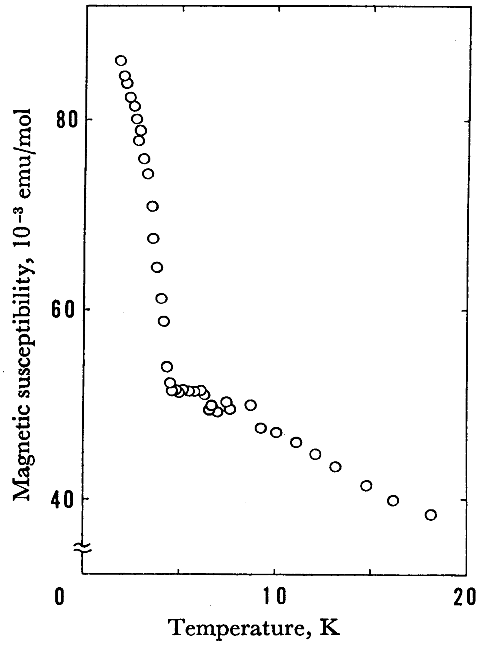

Fig. 3. Magnetic susceptibility of Mg(dipy)$_2$·3THF.

where apart from obvious notations, J denotes the exchange integral and a is the alternation parameter ($0\leq a\leq 1$). Duffy and Barr[6] have calculated the theoretical curve of $|J|\chi/Ng^2\beta^2$ *versus* $kT/|J|$ for various a values using the Hamiltonian with N=10. The result is applicable to the susceptibility of Mg(dipy)$_2$·THF, when $|J|\chi/Ng^2\beta^2$ is rewritten as $|J|\chi/2CNg^2\beta^2$ (C denotes the fractional radical concentration and g is reasonably assumed to be equal to 2.00 for organic radicals). As shown in Fig. 2, the theoretical curves with a=0.8 and 1.0 agree well with the observed data except for a region below about 6 K. The exchange integral was evaluated as $J/k=-7.6$ K. As described above, the curve for isolated binuclear clusters (a=0) does not reproduce the observed curve even in a region above the temperature of the maximum susceptibility.

The magnetic susceptibility exhibits another maximum at about 3.9 K. The appearance of the second peak in a susceptibility *versus* temperature curve has been observed for some metal complexes having one-dimensional lattices,[7,8] but no quantitative discussion has been given. Undoubtedly, the maximum at the lower temperature is due to a three-dimensional ordering existing below the temperature.

The magnetic behavior of Mg(dipy)$_2$·3THF resembles that of Mg(dipy)$_2$·THF to some extent, but no definite maxima were observed in the temperature range investigated (see Fig. 3). Below about 4.5 K, the susceptibility *versus* temperature curve shows a sharp increase and a gradual diminution of the slope with decreasing temperature, suggesting the appearance of a peak at still lower temperature. The almost constant susceptibility between 4.5 and 6 K is due to a short-range interaction. Although accurate analysis is difficult owing to the absence of any definite maximum, the susceptibility conforms to the alternating linear chain model rather than to the isolated binuclear cluster model.

From the result of an ESR study carried out on the magnesium salt in a glassy matrix,[4] the biradical molecules of Mg(dipy)$_2$ are expected to be present as crystal units. However, the observed value of the alternation parameter, a=0.8—1.0, shows that alternating linear chains rather than binuclear clusters should be regarded as magnetic units. The appearance of long-range ordering also suggests the presence of alternating linear magnetic chains interacting with one another. On the other hand, Be(dipy)$_2$ shows magnetic properties conforming to theoretical susceptibility for isolated binuclear clusters. The quite different magnetic properties are evidently due to the difference in crystal structure between the magnesium and beryllium compounds, because the electronic absorption spectrum of the magnesium salt in a diethyl ether solution bears a strong resemblance to those of the corresponding lithium and beryllium salts[1,9] (see Table 1). Beryllium occupies a unique position among group IIA elements and readily forms covalent bonds.[10] This favors the regular tetrahedral arrangement of Be–N bonds. Because Mg–N bonds are essentially ionic in the crystals of some magnesium salts, 2,2′-dipyridyl anions are presumably stacked face to face to form a one-dimensional array, which exists commonly in the crystals of

TABLE 1. ABSORPTION MAXIMA (10^{-3} cm^{-1}) IN THE ELECTRONIC SPECTRA OF 2,2′-DIPYRIDYLIDES

Mg(dipy)$_2$ (in diethyl ether)	Be(dipy)$_2$ (in diethyl ether)	Li(dipy)$^{a)}$ (in THF)
10.9	11.2	10.6
12.2	12.6	12.0
13.5$^{b)}$	14.3$^{b)}$	13.0
19.2	20.0	18.2
20.1	21.2	19.2
	22.5	
26.2	26.1	26.0
26.8	26.7$^{b)}$	

a) Ref. 9. b) Shoulders.

radical ion salts.[11,12] Even if a tetrahedral arrangement comprising Mg–N bonds exists in crystals, the tetrahedral coordination is suspected to be distorted to a great extent. Probably the distortion facilitates the presence of magnetic interaction between the biradicals. The magnitude of exchange interaction ($J/K=-7.6$ K) is smaller than those in Be(dipy)$_2$ (-11.6 K) and Li(dipy)·$(C_2H_5)_2O$ (-80 K).[1,11] If interaction takes place through the sp^3 orbitals of the central metal in the beryllium complex, ferromagnetic interaction ($J>0$) must be dominant because the sp^3 orbitals are orthogonal to one another. This contradiction to the experimental results suggests the intervention of a more complicated mechanism. A charge-transfer mechanism proposed for Wurster's salts is applicable also to beryllium 2,2′-dipyridylide. When a charge-transfer state, Be^0(dipy^0)$_2$, interacts with the ground state, Be^{2+}(dipy$^-$)$_2$, to some extent, the singlet state in the degenerate ground state is stabilized, whereas the triplet state is unaffected. This mechanism leads to an antiferromagnetic interaction, which masks the ferromagnetic interaction through the sp^3 orbitals as experimental results indicate. In the magnesium salts also, only the singlet state of Mg^{2+}(dipy$^-$)$_2$ can interact with a charge-transfer state, Mg^0(dipy^0)$_2$ or Mg^{2+}(dipy^0)(dipy^{2-}). Evidently, the magnitude of exchange interaction depends on the ionization potential and the distance between radical ions.

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