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MAGNETIC SUSCEPTIBILITY OF TRIS(2,2'-DIPYRIDYL)MANGANESE COMPLEXES HAVING AN ANOMALOUS VALENCY OF MANGANESE

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The magnetic susceptibility of tris(2,2'-dipyridyl)manganese complexes, $[Mn(dipy)_3]\cdot 2THF$ and $Li[Mn(dipy)_3]\cdot 4THF$ (THF: tetrahydrofuran), has been determined over a temperature range of 1.5-300 K. The susceptibility of $Li[Mn(dipy)_3]\cdot 4THF$ can be explained with a radical ion model, in which three 2,2'-dipyridyl radical ions are coordinated to a manganese(II) ion, suggesting the formula $[Mn^{2+}(dipy^-)_3]^-$ rather than $[Mn^-(dipy^0)_3]^-$. A similar model is applicable to $[Mn(dipy)_3]$-2THF as well.

The so-called zero-valent transition metal complexes of 2,2'-dipyridyl, $[M(dipy)_3]$, attract attention because of the anomalous valency of the central metal.[1)] In order to obtain some information about the oxidation state of manganese in this type of complexes, we have determined the magnetic susceptibility of $[Mn(dipy)_3]\cdot 2THF$ and $Li[Mn(dipy)_3]\cdot 4THF$ over a temperature range of 1.5-300 K. The observed reciprocal susceptibility is plotted against temperature in Figs. 1 and 2.

In the crystals of the manganese complexes, each manganese atom is reasonably assumed to have a distorted octahedral coordination of six nitrogen atoms from three dipyridyl molecules in accordance with the results of X-ray crystal analysis carried out on $[Ti(dipy)_3]$, $[V(dipy)_3]$, and $[Cr(dipy)_3]$.[2)] If manganese has a valence of -1 in the crystals of $Li[Mn(dipy)_3]\cdot 4THF$, the central metal has a $3d^8$ configuration, in which a $^3A_1$ term lies lowest in an octahedral ligand field. As shown in Fig. 1, the magnetic susceptibility of $Li[Mn(dipy)_3]\cdot 4THF$ does not obey the Curie-Weiss law over the temperature range investigated. In the high temperature region, the magnetic behavior cannot be explained by any theoretical susceptibility based on the ligand field theory, because the g-value of the $^3A_1$ term is independent of temperature. For this reason, we propose a tetranuclear cluster model or a radical ion model, in which three dipyridyl ions rather than neutral molecules are coordinated to a divalent manganese ion (see Fig. 3). For this model, the magnetic susceptibility can be formulated by use of the following Hamiltonian.

$$\mathcal{H} = -2J\sum_{i=1}^{3} S_m\cdot S_i - 2aJ\sum_{<1,2,3>} S_i\cdot S_j + g\beta H(S_m + \sum_{i=1}^{3} S_i) \qquad (1)$$

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where apart from obvious notations, <1,2,3> denotes all pairs among S_1, S_2, and S_3. Because $S_m = 5/2$ in high-spin manganese(II) complexes, the zero-field magnetic susceptibility is given by

$$\chi = \frac{2Ng^2\beta^2}{kT}\left[\frac{1 + 5x^4 + 10x^{7-3a} + 14x^{10} + 28x^{13-3a} + 30x^{18}}{3 + 5x^4 + 10x^{7-3a} + 7x^{10} + 14x^{13-3a} + 9x^{18}}\right] \qquad (2)$$

where $x = \exp(J/kT)$. If the g-value is assumed to be equal to 2.00, the theoretical equation with $a = 1.0$ and $J/k = -180$ K reproduces the observed curve fairly well except for the low temperature region (see Figs. 1 and 4). If $g = 1.90$ and $J/k = -160$ K, the equation gives the best fit with $a = 1.0$. The broad maximum of the susceptibility at about 5.5 K is attributable to a slight splitting of the degenerate ground level (triplet state) in a distorted coordination octahedron. If this effect is taken into account, the theoretical curve is expected to show a better agreement with experimental data. At low temperature, the magnetic behavior might involve magnetic interaction between the complex ions. At any rate, the magnetic susceptibility suggests the formula $[Mn^{2+}(dipy^-)_3]^-$ rather than $[Mn^-(dipy^0)_3]^-$.

The susceptibility of $[Mn(dipy)_3]\cdot 2THF$ obeys the Curie-Weiss law fairly well between 20 and 160 K. From the Curie constant, the magnetic moment is evaluated as μ = 3.9 B.M., suggesting that the ground state is a quartet (μ = 3.87 B.M.). When $S_m = 2$ and $S_1 = S_2 = S_3 = 1/2$ in the model shown in Fig. 3, a doublet state (μ = 1.73 B.M.) lies lowest in contradiction with the experimental result. If we assume that two dipyridyl anions and a neutral dipyridyl molecule are coordinated to a manganese(II) ion, i.e., $S_m = 5/2$, $S_1 = S_2 = 1/2$, and $S_3 = 0$, the theoretical magnetic susceptibility is formulated as

$$\chi = \frac{Ng^2\beta^2}{4kT}\left[\frac{10 + 35x^5 + 35x^{7-2a} + 84x^{12}}{2 + 3x^5 + 3x^{7-2a} + 4x^{12}}\right] \qquad (3)$$

With $g = 2.00$, $J/k = -200$ K, and $a = 1.0$, the theoretical formula reproduces the observed curve excellently as shown in Fig. 2. A magnetic anomaly appearing below about 10 K is probably due to the splitting of the degenerate ground level. If manganese is zero-valent, it has a $3d^7$ configuration, in which a $^4T_1$ term lies lowest in a weak octahedral ligand field, whereas a ^2E term represents the ground state in a strong field. The theoretical susceptibility of the $^4T_1$ term[3)] reproduces the observed curve fairly well (see Fig. 2). However, the absolute value of the spin-orbit coupling constant, $\lambda = -2000$ K (-1390 cm^{-1}), for the best fit is much greater than 100-1000 cm^{-1} normally observed for the first row transition metals.

Other models might be conceivable for the magnetic properties of the manganese complexes. However, only the radical ion model can explain consistently the magnetic susceptibilities of these complexes, suggesting that dipyridyl anions are coordinated to divalent ions. A detailed discussion will be presented elsewhere.

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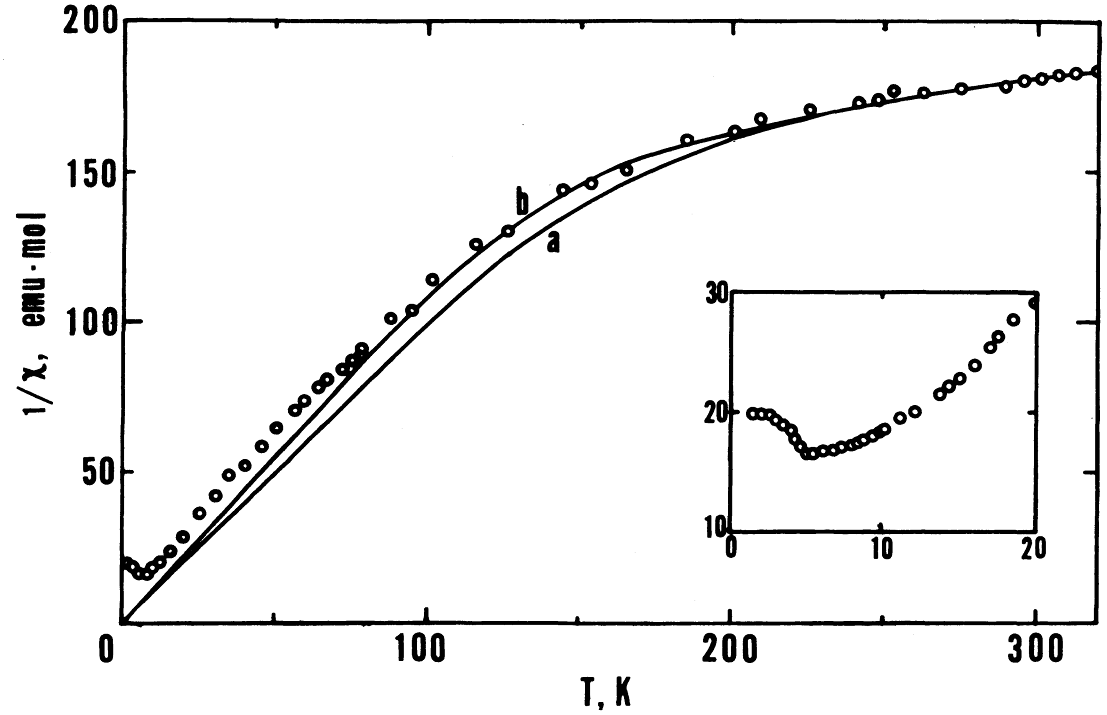

Fig. 1. Magnetic susceptibility of Li[Mn(dipy)$_3$]·4THF. Curve a shows theoretical susceptibility calculated by Eq. 2 with g = 2.00, J/k = -180 K, and a = 1.0. Curve b gives the best fit (g = 1.90, J/k = -160 K, and a = 1.0).

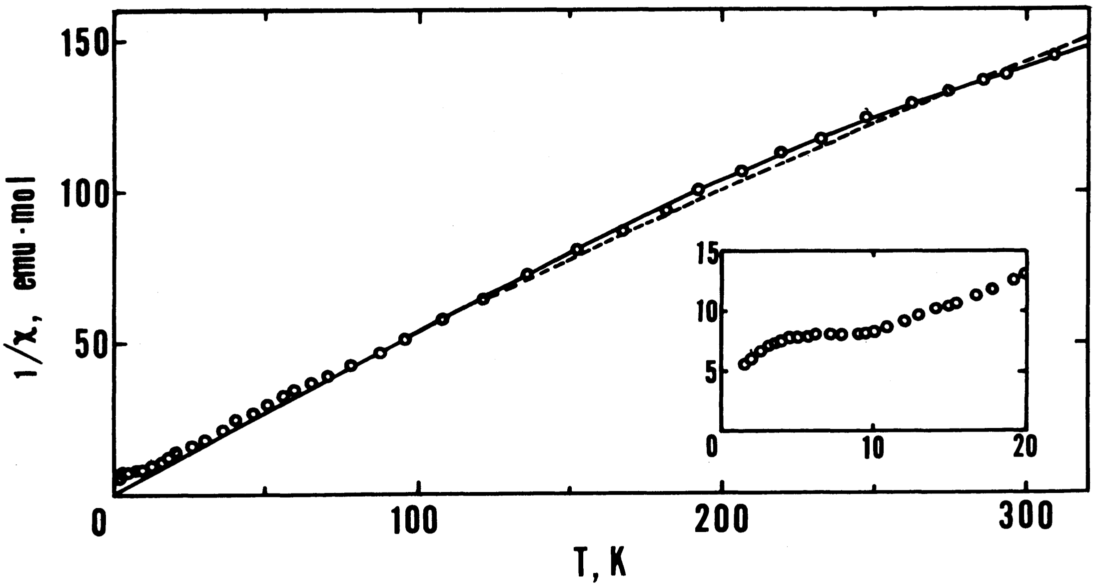

Fig. 2. Magnetic susceptibility of [Mn(dipy)$_3$]·2THF. The solid curve shows theoretical susceptibility calculated by Eq. 3 with g = 2.00, J/k = -200 K, and a = 1.0. The broken curve shows theoretical susceptibility for a 3d^7 configuration (λ = -1390 cm^{-1}).

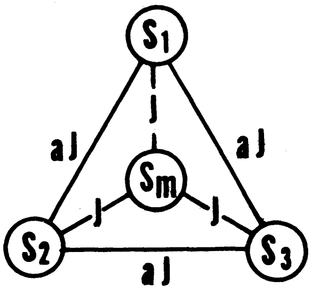

Fig. 3. A tetranuclear cluster model or a radical ion model. S_m and S_i (i = 1, 2, 3) represent the spin quantum numbers of the central metal and the ligands, respectively. J and aJ denote exchange integrals.

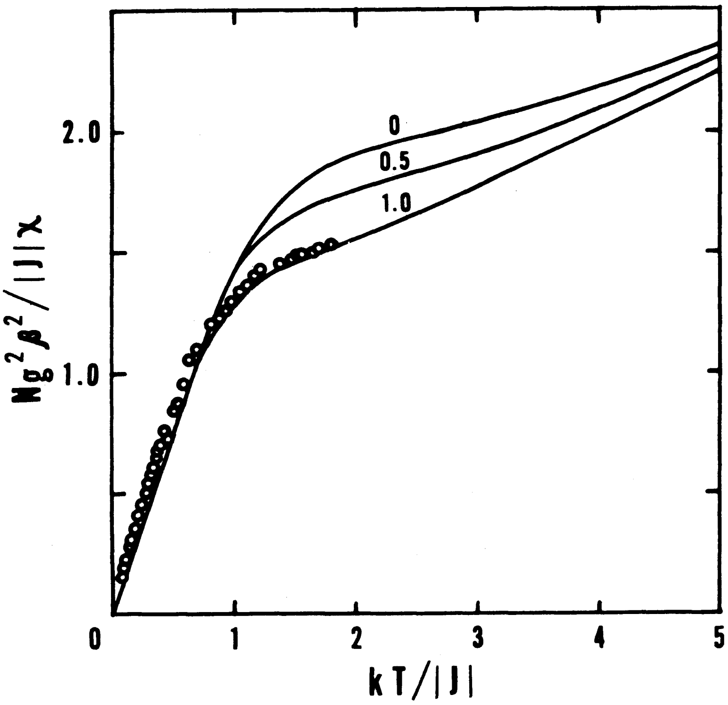

Fig. 4. Theoretical curves for a radical ion model (S_m = 5/2 and S_1 = S_2 = S_3 = 1/2) with a = 0-1 compared with observed data (J/k = -180 K and g = 2.00).

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