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Magnetic Property and Electronic Structure of Tris(2,2′-bipyridine) Complexes of Manganese in Low Oxidation States

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The magnetic susceptibilities of tris(2,2′-bipyridine)manganese complexes, $[Mn(bpy)_3]\cdot 2THF$ and $Li[Mn(bpy)_3]\cdot 4THF$ (THF: tetrahydrofuran), have been determined over a temperature range of 1.6—320 K. The susceptibility of $Li[Mn(bpy)_3]\cdot 4THF$ can be explained with a radical ion model, in which three 2,2′-bipyridine radical ions are coordinated to a manganese(II) ion. A similar model is applicable to $[Mn(bpy)_3]\cdot 2THF$ as well. The presence of antiferromagnetic interaction indicates the formation of a weak covalent bond between manganese and bipyridine. This can be elucidated consistently by the molecular orbital theory.

A number of the so-called zerovalent transition metal complexes of 2,2′-bipyridine, $[M(bpy)_3]$, have been prepared.[1] Varieties of experimental studies including those of magnetic moment,[1] ESR,[2] optical spectra,[3,4] and IR spectra[5] have been carried out on the complexes at room temperature in an attempt to obtain information about the valency of central metals. However, no definite conclusions have been obtained as yet. The temperature dependence of magnetic susceptibility is expected to give a valuable information about the oxidation state of central metals in these complexes. In our previous paper,[6] we have briefly reported that the magnetic susceptibility of $[Mn(bpy)_3]\cdot 2THF$ and $Li[Mn(bpy)_3]\cdot 4THF$ suggests the presence of a divalent manganese ion coordinated by 2,2′-bipyridine radical ions. In this paper, we present a more detailed discussion on the magnetic property and the electronic structure of the manganese complexes.

Experimental

The materials were prepared by methods reported by Herzog and Schmidt.[7,8] $[Mn(bpy)_3]\cdot 2THF$ was obtained from a tetrahydrofuran solution as deep brown needle crystals. Calcd: Mn, 8.2%; THF, 21.6%. Found: Mn, 8.0%; THF, 22.4%. The observed effective magnetic moment, $\mu_{eff}=4.1_3$ B.M. (290 K), of $[Mn(bpy)_3]\cdot 2THF$ agrees with the value, 4.1_0 B.M., reported for the crystals of $[Mn(bpy)_3]$.[7] Deep red crystals of $Li[Mn(bpy)_3]\cdot 4THF$ were separated from a tetrahydrofuran solution. Calcd: Mn, 6.7%; THF, 35.2%. Found: Mn, 6.3%; THF, 33.2%. The effective magnetic moment, $\mu_{eff}=3.6_3$ B.M., at 290 K agrees with the value, 3.7_1 B.M., described in the literature.[8]

The susceptibility was determined in the temperature range of 1.6—20 K 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. Between 4.2 and 320 K, the susceptibility was determined by use of a magnetic balance already described.[9] The two different methods yielded data agreeing with each other within about ±2%. Each sample was sealed in a quartz cell with ambient helium because the compounds were very sensitive to atmospheric oxygen and moisture.

The molar susceptibilities were corrected for diamagnetic contributions (10^{-6} emu/mol) from 2,2′-bipyridine (−93) and THF (−55).[10] The contributions from manganese and lithium ions are negligible. The temperature-independent paramagnetism of manganese ions was disregarded because it is expected to be negligibly small in comparison with the observed susceptibility.

Results

Figures 1—4 show the observed susceptibility. The magnetic susceptibility of $Li[Mn(bpy)_3]\cdot 4THF$ does not obey the Curie-Weiss law in the temperature range investigated (see Fig. 1). On the other hand, that of $[Mn(bpy)_3]\cdot 2THF$ conforms to the Curie-Weiss law

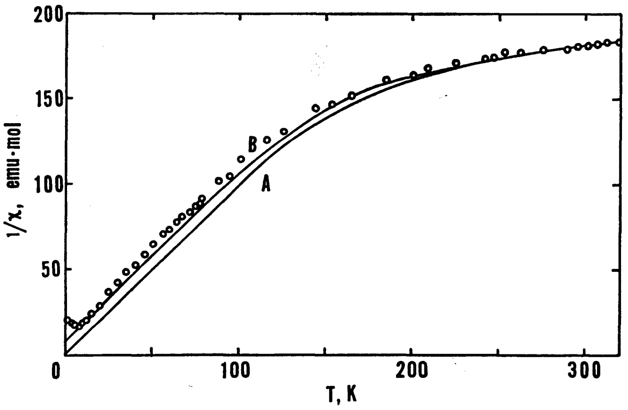

Fig. 1. Reciprocal magnetic susceptibility of $Li[Mn(bpy)_3]\cdot 4THF$. Curve A shows theoretical susceptibility calculated by Eq. (2) with $g=2.00$, $J/k=-180$ K, and $a=1.0$. Curve B represents susceptibility based on Eq. (6) with $g=2.00$, $J/k=-175$ K, $a=1.0$, and $\theta=-8$ K.

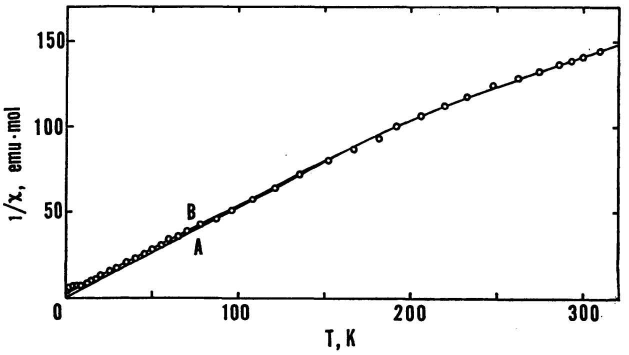

Fig. 2. Reciprocal magnetic susceptibility of $[Mn(bpy)_3]\cdot 2THF$. Curve A shows theoretical susceptibility calculated by Eq. (7) with $g=2.00$, $J/k=-200$ K, and $a=1.0$. Curve B represents modified susceptibility which takes into account magnetic interaction between complex molecules ($g=2.00$, $J/k=-200$ K, $a=1.0$, and $\theta=-4$ K).

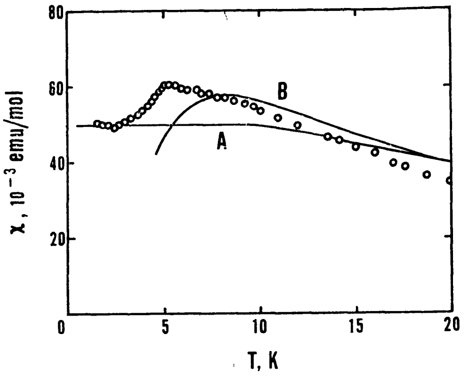

Fig. 3. Magnetic susceptibility of Li[Mn(bpy)$_3$]·4THF in a low temperature range and the theoretical susceptibility for the zero-field splitting. Curves A and B show the average susceptibility and the parallel susceptibility, respectively.

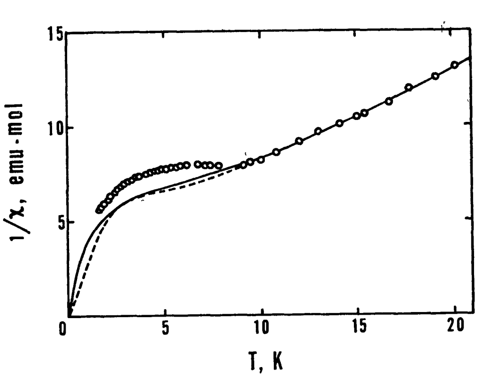

Fig. 4. Reciprocal magnetic susceptibility of [Mn(bpy)$_3$]·2THF in a low temperature range and the theoretical susceptibility for the zero-field splitting. The solid and broken curves show the average susceptibility and the parallel susceptibility, respectively.

fairly well between 20 and 160 K as is shown in Fig. 2. From the Curie constant, the magnetic moment was evaluated as $\mu=3.9$ B.M. It is noticeable that the susceptibility deviates from the Curie-Weiss law above about 160 K.

Discussion

The results of X-ray crystal analyses carried out on [Ti(bpy)$_3$], [V(bpy)$_3$], and [Cr(bpy)$_3$] have shown that each metal atom has a distorted octahedral coordination of six nitrogen atoms from three bipyridine molecules.[11] Therefore, the crystals of the manganese complexes are presumed to consist of discrete distorted octahedral units.

If the formula [Mn^{-1}(bpy^0)$_3$]$^-$ is assumed for Li[Mn(bpy)$_3$]·4THF, *i.e.*, if "excess electrons" are localized only on manganese, the central metal has a 3d^8 configuration, in which a $^3A_2$ term lies lowest in an octahedral crystal field. The deviation from the Curie-Weiss law in the high temperature range cannot be explained theoretically on the basis of the crystal field, because the *g*-value of the $^3A_2$ term is independent of temperature. Interpretation is infeasible also by contribution from the temperature-independent paramagnetism given by $8N\beta^2/10Dq$.[12] Assuming that $10Dq \sim 7000$ cm^{-1}, the paramagnetism is roughly estimated to be 3×10^{-4} emu/mol. This value is too small to interpret the deviation from the Curie-Weiss law. For these reasons, we have proposed a radical ion model,[6] in which three bipyridine ions are coordinated to a divalent manganese ion instead of neutral ligands coordinating to a monovalent negative manganese (see Fig. 5). This model represents an extreme case of excess electrons distributed only on the ligands. For this model, the susceptibility can be derived from the following Hamiltonian,

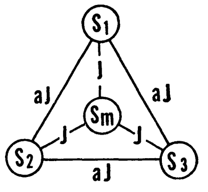

Fig. 5. Radical ion model. S_m and S_i (i=1, 2, 3) represent the spin quantum numbers of manganese and bipyridines, respectively. J and aJ denote exchange integrals.

$$\mathscr{H} = -2J\sum_{i=1}^{3}\mathbf{S}_m\cdot\mathbf{S}_i - 2aJ\sum_{\langle 1,2,3\rangle}\mathbf{S}_i\cdot\mathbf{S}_j + g\beta\mathbf{H}(\mathbf{S}_m+\sum_{i=1}^{3}\mathbf{S}_i) \quad (1)$$

where apart from obvious notations, J and aJ represent exchange integrals and $<1,2,3>$ denotes all pairs among $\mathbf{S}_1$, $\mathbf{S}_2$, and $\mathbf{S}_3$. Because $S_m=5/2$ in high spin manganese(II) complexes and $S_1=S_2=S_3=1/2$, the zero-field magnetic susceptibility is given by

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

where $x=\exp(J/kT)$. If the *g*-value is assumed to be equal to 2.00, the observed susceptibility can be reproduced by the theoretical equation with $a=1.0$ rather than with $a=0$ or 0.5 as reported in our previous paper.[6] Curve A in Fig. 1 represents the theoretical curve with $a=1.0$ and $J/k=-180$ K, showing a fairly good agreement with the observed data except for a low temperature range. Evidently, the disagreement is related to the anomaly at about 6 K. A broad maximum of susceptibility at the temperature (see Fig. 3) is attributable to a slight splitting of the degenerate ground level (triplet state) in a distorted coordination octahedron. The susceptibilities due to this zero-field splitting have been formulated as[13]

$$\chi_{\parallel} = \frac{2Ng_{\parallel}^2\beta^2}{kT}\left[\frac{\exp(-D/kT)}{1+2\exp(-D/kT)}\right] \quad (3)$$

$$\chi_{\perp} = \frac{2Ng_{\perp}^2\beta^2}{kT}\left[\frac{1-\exp(-D/kT)}{1+2\exp(-D/kT)}\right] \quad (4)$$

$$\chi_{av} = \frac{1}{3}(\chi_{\parallel}+2\chi_{\perp}) \quad (5)$$

where $\chi_{\parallel}$ and $\chi_{\perp}$ are the parallel and perpendicular susceptibilities, respectively, χ_{av} is the average susceptibility, and D denotes the zero-field splitting constant. Curve A in Fig. 3 shows χ_{av} calculated with $g=2.00$ and $D/k=40$ K. The curve exhibits no maximum and consequently does not explain the observed data. If only the parallel susceptibility is taken into account, the observed curve can be reproduced fairly well by Eq. (3) with $g=2.00$ and $D/k=12$ K (see Fig. 3). An alternative explanation is conceivable for the behavior at about 6 K. The magnetic behavior might involve magnetic interaction between complex ions at very low temperature. If interaction between complex ions is much weaker than that within an ion, Eq. (2) can be modified as

$$\chi = \frac{2Ng^2\beta^2}{k(T-\theta)}[F(x)] \tag{6}$$

where θ denotes the Weiss constant that takes into account the interaction between complex ions,[14] and $F(x)$ stands for the expression bracketed in Eq. (2). As shown in Fig. 1, curve B calculated by Eq. (6) with $g=2.00$, $J/k=-175$ K, and $\theta=-8$ K reproduces very well the observed curve at temperatures above about 6 K.

The magnetic moment, $\mu=3.9$ B.M., of $[\mathrm{Mn(bpy)_3}]\cdot$2THF indicates that the ground state is a quartet ($\mu=3.87$ B.M.). When three bipyridine anions are coordinated to a manganese(III) ion ($S_m=2$ and $S_1=S_2=S_3=1/2$), a doublet state (1.73 B.M.) lies lowest in contradiction to the experimental result. If two bipyridine anions and a neutral bipyridine molecule are coordinated to a divalent manganese ion, *i.e.*, $S_m=5/2$, $S_1=S_2=1/2$, and $S_3=0$, the ground state is a quartet. In this case, the theoretical susceptibility is formulated as

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

This formula reproduces the observed curve excellently with $g=2.00$, $J/k=-200$ K, and $a=1.0$ as shown in Fig. 2, except for a very low temperature range. If excess electrons are localized only on manganese, the metal has a 3d^7 configuration, in which a $^4\mathrm{T}_1$ level lies lowest in a weak octahedral field, whereas a $^2\mathrm{E}$ level represents the gound state in a strong field. As the theoretical magnetic moment of the $^4\mathrm{T}_1$ term shows temperature dependence owing to spin-orbit coupling,[15] it is possible to explain the observed curve qualitatively. However, the absolute value of the spin-orbit coupling constant, $\zeta=4170\ \mathrm{cm}^{-1}$ ($\lambda=-1390\ \mathrm{cm}^{-1}$), for the best fit[6] is much greater than 239—402 cm^{-1} normally observed for manganese.[12] These suggest that the radical ion model is applicable to the so-called zero-valent manganese complexes as well. A magnetic anomaly appearing below about 10 K is due probably to the zero-field splitting of the ground level ($S=3/2$), which yields theoretical susceptibilities given by[13]

$$\chi_{\parallel} = \frac{Ng_{\parallel}^2\beta^2}{4kT}\left[\frac{1+9\exp(-2D/kT)}{1+\exp(-2D/kT)}\right] \tag{8}$$

$$\chi_{\perp} = \frac{5Ng_{\perp}^2\beta^2}{4D}\left[\frac{1-\exp(-2D/kT)}{1+\exp(-2D/kT)}\right] \tag{9}$$

The solid and broken curves in Fig. 4 represent the average susceptibility ($g=2.00$ and $D/k=10$ K) and the parallel susceptibility ($g=2.00$ and $D/k=4.8$ K), respectively; they show a good agreement with the observed curve. Magnetic interaction between complex molecules also may contribute to the aforementioned anomaly at low temperature. Equation 7 can be modified by introducing the Weiss constant in the same manner as for Eq. (6). Curve B in Fig. 2 shows modified susceptibility calculated with $g=2.00$, $J/k=-200$ K, and $\theta=-4$ K. It reproduces the observed curve excellently.

The radical ion model can explain the magnetic susceptibilities of the manganese complexes consistently, indicating that the excess electrons are localized for the most part on the ligands rather than on the central metal in agreement with the results of optical spectra.[3] However, the presence of antiferromagnetic interaction ($J<0$) suggests also the formation of weak covalent bonds between bipyridine anions and a manganese(II) ion. Therefore, the radical ion model has been treated by the molecular orbital theory for coordination compounds. The molecular orbital scheme has been proposed for tris(2,2′-bipyridine) complexes.[16,17] Figure 6 shows an energy diagram associated with 3d orbitals in a D_3 field. The bonding σ levels of the complex are completely filled with electrons from the σ orbitals of the ligands. When manganese in $[\mathrm{Mn(bpy)_3}]^0$ is in a divalent high-spin state, the degenerate σ^* levels are occupied by two electrons from the dγ orbitals of a manganese ion. The π level is filled with three electrons from dε orbitals of manganese and two electrons from the antibonding π orbitals of bipyridine ions, leading to a $\sigma^{12}\pi^5\pi^{*0}\sigma^{*2}$ configuration as shown in Fig. 6. Because the π, π^*, and σ^* orbitals are orthogonal to one another, the ground state is a quartet ($\mu=3.87$ B.M.) in conformity with the observed magnetic moment. If the central metal has a valence of 3, the ground state has a $\sigma^{12}\pi^6\pi^{*0}\sigma^{*1}$ configuration ($\mu=1.73$ B.M.) in contradiction to the experimental result. A $\sigma^{12}\pi^6\pi^{*1}\sigma^{*0}$ configuration corresponding to a low-spin manganese(II) complex also conflicts with the observed moment. For the ground state having the configuration $\sigma^{12}\pi^5\pi^{*0}\sigma^{*2}$, the first excited state has a $\sigma^{12}\pi^4\pi^{*1}\sigma^{*2}$ configuration, which yields a total spin quantum number and degeneracy consistent with those derived from Eq. (1) for the radical ion model. The spin multiplicity of higher excited states also is in conformity with that for the radical ion model. In the molecular orbital

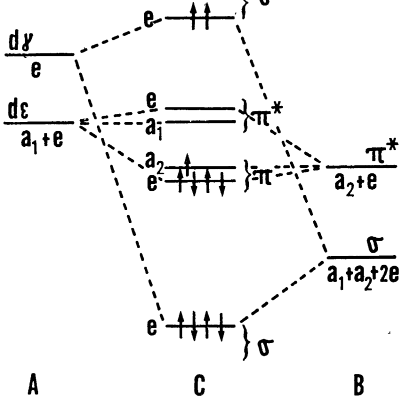

Fig. 6. Energy diagram of $[\mathrm{Mn(bpy)_3}]^0$. A: 3d orbitals of a manganese ion. B: Combined orbitals of bipyridines. C: Molecular orbitals of the complex. The σ levels associated with the s and p orbitals of the metal are not shown.

system of $[Mn(bpy)_3]^-$, the σ^* level is occupied by two electrons from the dγ orbitals of a manganese(II) ion while the π level is filled with six electrons from the dε orbitals of manganese and the π^* orbitals of bipyridine ions, leading to a $\sigma^{12}\pi^6\pi^{*0}\sigma^{*2}$ configuration (μ=2.83 B.M.). Excited states, *i.e.*, $\sigma^{12}\pi^5\pi^{*1}\sigma^{*2}$ ($S=2$), $\sigma^{12}\pi^4\pi^{*2}\sigma^{*2}$ ($S=3$), and $\sigma^{12}\pi^3\pi^{*3}\sigma^{*2}$ ($S=4$), have magnetic moments and degeneracies consistent with those based on the radical ion model. Strictly speaking, energy separation between *a* and *e* levels should be taken into account. However, this does not affect essentially the foregoing discussion, especially when the energy separation is very small in comparison with the π-π^* separation.

As discussed above, the magnetic properties of the manganese complexes can be interpreted consistently by the molecular orbital theory as well as by the radical ion model involving antiferromagnetic interaction. This indicates that weak dπ-π^* bonds are formed between manganese and bipyridine but that excess electrons are mostly localized in the antibonding π orbitals of bipyridine rather than in the orbitals of manganese. The π-π^* energy separation can be approximated with the value of $4|J|$ or $5|J|$ expressing an energy separation between the ground state and the first excited state in the radical ion model (see Eqs. (2) and (7)). The value may be nearly equal to an energy difference between the π^* of bipyridine anions and the dε of a manganese ion, because the π^* and dε orbitals are suspected to interact with each other only to a small extent.

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