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Magnetic Susceptibility of the So-Called Zero-Valent Aluminium Complex of 2,2′-Bipyridine, $[Al(bpy)_3]^0 \cdot 1/2THF$

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Synopsis. The magnetic susceptibility of tris(2,2′-bipyridine)aluminium(0) was determined between 4.2 and 300 K. It can be explained by a radical ion model in which three 2,2′-bipyridine radical ions are coordinated to an aluminium(III) ion. Antiferromagnetic interaction operates between the radical ions with the exchange integral $J/k = -110$—115 K.

Tris(2,2′-bipyridine) complexes in apparently unusual valency states of metals have been prepared and characterized.[1)] An electronic-spectrum study of the so-called zero-valent aluminium complex $[Al(bpy)_3]^0$ showed that bpy^- ions are involved in the complex molecules.[2)] The magnetic susceptibility was found to obey the Curie-Weiss law between 80 and 300 K.[3)] The magnetic moment $\mu = 3.38$ B.M. evaluated from the Curie constant is inconsistent with the formula $[Al^0(bpy^0)_3]$, in which an unpaired electron exists in a molecule. From these, we can propose the formula $[Al^{3+}(bpy^-)_3]$ rather than $[Al^0(bpy^0)_3]$. If this is correct, magnetic interaction is presumed to operate between paramagnetic bpy^- ions within $[Al(bpy)_3]$. Thus, the proposed formula can be confirmed by getting information on the magnetic interaction. Therefore, we have determined the magnetic susceptibility down to 4.2 K, because the magnetic interaction may be effective at low temperatures.

Experimental

The material was prepared by the method reported by Herzog *et al.*[4)] Recrystallization from THF yielded deep green crystals. On heating *in vacuo* at about 90 °C, the crystals librated THF gas. Weight loss amounted to 8.0%, indicating that the crystals were those of a THF adduct, $Al(bpy)_3 \cdot 1/2$ THF (Found: Al, 4.8; THF, 8.0%. Calcd: Al, 5.1; THF, 6.8%). The effective magnetic moment 2.38 B. M. at 290 K agreed with 2.32—2.44 B. M. reported for $Al(bpy)_3$.[3,4)]

The magnetic susceptibility was determined by the Gouy method in the temperature range 80—300 K and by the Faraday method below 80 K. The molar magnetic susceptibility[5)] was corrected for diamagnetic contributions (10^{-6} emu mol^{-1}) from 2,2′-bipyridine (−93) and THF (−55).[6)]

Results and Discussion

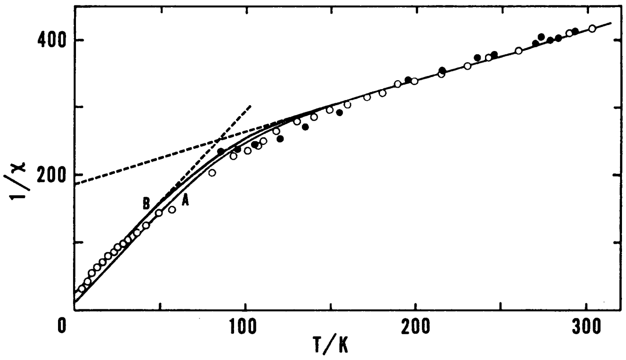

Fig. 1. Reciprocal magnetic susceptibility, $1/\chi$ in emu, (○) and relative ESR-signal intensity (●) of $[Al(bpy)_3]$ The curves A and B show theoretical susceptibilities calculated with the exchange integrals $J/k = -115$ K and -110 K, respectively, on the assumption of the formula $[Al^{3+}(bpy^-)_3]$.

The reciprocal molar susceptibility is plotted against temperature in Fig. 1. It obeys the Curie-Weiss law in the two temperature ranges, $T \gtrsim 180$ K and $T \lesssim 40$ K (broken lines in Fig. 1): the Curie and Weiss constants are determined as $C_h = 1.31$ emu K mol^{-1} and $\theta_h = -244$ K for the high temperature range, and $C_l = 0.37$ emu K mol^{-1} and $\theta_l = -9.7$ K for the low temperature range. Between 40 and 180 K, the magnetic susceptibility deviates from the Curie-Weiss law. This is confirmed by the temperature dependence of the signal intensity in the ESR powder spectrum (Fig. 1), which has an isotropic g factor equal to 2.003 and a peak-to-peak width equal to 1.5 mT.

The magnetic moment $\mu_h = 3.24$ B.M. evaluated from C_h is nearly equal to $(3 \times 3)^{1/2}$ B.M. of a molecule having three independent unpaired electrons. The moment $\mu_l = 1.72$ B.M. evaluated from C_l indicates that the ground state is doublet ($\mu_{S=1/2} = 1.73$ B.M). This shows that the magnetic unit of the complex consists of three spins interacting antiferromagnetically with each other, supporting the proposed formula $[Al^{3+}(bpy^-)_3]$, in which each bpy^- ion carries an unpaired electron and aluminium is diamagnetic. For the spin system, eight spin functions are derived. Four of them correspond to $S = 3/2 (m_s = \pm 3/2, \pm 1/2)$ and the remaining four functions can be divided into two sets each corresponding to $S = 1/2$ $(m_s = \pm 1/2)$. Because three bpy^- ions can be presumed to be equivalent with each other in a complex molecule, the magnetic susceptibility is given by[7)]

$$\chi = \frac{Ng^2\mu_B^2}{4kT}\left[\frac{1+5\exp(3J/kT)}{1+\exp(3J/kT)}\right], \tag{1}$$

where J is the exchange integral, the absolute value of which is equal to one third of the energy separation between the doublet and quartet states. When magnetic interaction operates between complex ions, Eq. 1 can be rewritten as[8)]

$$\chi = \frac{Ng^2\mu_B^2}{4k(T-\Delta)}\left[\frac{1+5\exp(3J/kT)}{1+\exp(3J/kT)}\right], \tag{2}$$

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where Δ denotes the Weiss constant that takes into account the interaction. The solid curve A in Fig. 1 shows the magnetic susceptibility calculated from Eq. 2 with $J/k=-115$ K, $\Delta=-5$ K, and $g=2.00$, yielding the best fit to the observed data. When the Weiss constant Δ is assumed to be equal to θ_1, the curve B calculated with $J/k=-110$ K agrees well with the observed χ-T curve (Fig. 1).

The antiferromagnetic interaction between bpy$^-$ ions takes place probably through aluminium atoms. Kobayashi *et al.*[9] propose a mechanism in which a charge transfer between bpy$^-$ ions yields the antiferromagnetic interaction: the unpaired electron of a bpy$^-$ ion can migrate to other bpy$^-$ ions within an [Al(bpy)$_3$] molecule through the vacant 3d orbitals of aluminium, and the resulting charge-transfer state stabilizes the doublet state rather than the quartet state. In this mechanism, aluminium 3d orbitals play an important part. Wulf and Herzog[3] determined the magnetic susceptibility of [Sc(bpy)$_3$]^0 between 80 and 350 K. It obeys the Curie-Weiss law in two temperature ranges: $\mu_h=3.67$ B.M. and $\theta_h=-667$ K for $T\gtrsim 220$ K, and $\mu_l=1.76$ B.M. and $\theta_l=-20$ K for $T\lesssim 134$ K. This magnetic behavior can be explained well with Eq. 2, the parameters being determined as $J/k=-200$ K, $\Delta=-20$ K, and $g=2.00$. Thus, three paramagnetic bpy$^-$ ions are coordinated to a diamagnetic scandium(III) ion also in [Sc(bpy)$_3$]^0. The absolute J value of the scandium complex is larger than that of the aluminium complex. This arises from difference in the nature of central-metal d orbitals, because 3d orbitals contribute to metal-nitrogen bonding to a greater extent in the scandium complex. This provides evidence for the important role of the d orbitals in the magnetic interaction.

In our previous papers,[8,10,11] we reported that the magnetic susceptibilities of the [M(bpy)$_n$]^0 type complexes of manganese, beryllium, and magnesium can be explained by radical ion models in which bpy$^-$ ions are coordinated to central-metal ions having normal oxidation states in the complexes. The present investigation along with the previous reports[8,10,11] has provided a convincing example in support of a conclusion that the "excess electrons" are localized mostly on the ligand molecules in the so-called zero-valent complexes of 2,2′-bipyridine.

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