CHEMISTRY LETTERS, pp. 1055-1058, 1973. Published by the Chemical Society of Japan

MAGNETIC SUSCEPTIBILITY OF LITHIUM 2,2'-DIPYRIDYLIDE IN ITS DIETHYL ETHER ADDUCT

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The magnetic susceptibility of the diethyl ether adduct of lithium 2,2'-dipyridylide was determined at temperatures between 4.2 and 300 K. The magnetic susceptibility conforms to the alternating linear Heisenberg model (alternation parameter, a = 0.8) and indicates that strong antiferromagnetic interaction (J/k = -80 K) operates between anion radicals.

Various so-called zero-valent metal complexes of 2,2'-dipyridyl (dipy) have been prepared.[1] The magnetic property of the beryllium complex, $Be(dipy)_2$, has shown the presence of two dipyridyl radical ions in a molecule of the complex,[2] suggesting the formula $Be^{2+}(dipy^-)_2$ rather than $Be^0(dipy^0)_2$. The magnetic property of lithium 2,2'-dipyridylide attracts attention because the lithium salt is expected to contain typical radical ions. A number of studies carried out on the magnetic properties of Wurster's blue cations and tetracyanoquinodimethanide anions have shown that these radical salts show magnetic properties characteristic of the arrangement of radical ions.[3] The present investigation has been undertaken in order to obtain information about the arrangement of dipyridyl ions in crystals as well as magnetic interaction between the anion radicals.

Experimental Section

Herzog and Lühder[4] isolated lithium 2,2'-dipyridylide as a tetrahydrofurane (THF) adduct, Li(dipy)·1.84THF, using a mixture of THF and diethyl ether as a solvent. However, samples obtained by the method showed fluctuations in magnetic data. Hence, we prepared the lithium salt by modifying the method described by Herzog and Lühder. Dipyridyl (1.6 g) dissolved in diethyl ether (200 ml) was reduced with excess metallic lithium to $dipy^{2-}$ for two days. The reaction product was poured through a filter on the powder of dipyridyl (1.5 g). The mixture was stirred for about two hours and then concentrated. Deep purple crystals of the diethyl ether adduct, $Li(dipy)\cdot(C_2H_5)_2O$, were obtained (Calcd: $(C_2H_5)_2O$, 31.2%. Found: 30.1%).

The magnetic susceptibility was determined by means of magnetic balances described in our previous paper.[5] As the compound is very sensitive to atmospheric oxygen and moisture, samples have been maintained in a dry argon or helium atmosphere. Each sample was sealed in a quartz cell for magnetic measurements. For this reason, the absolute values of magnetic susceptibility were difficult to determine accurately. The accuracy was estimated to be about ±5%. The molar susceptibility was corrected for diamagnetic contributions (in 10^{-6} emu/mol) from lithium ions (-0.6), 2,2'-dipyridyl (-93), and diethyl ether (-55).[6] The value of 2,2'-dipyridyl is based on the observed susceptibility of pyridine.

Results and Discussion

Figure 1 shows the temperature dependence of the corrected susceptibility, χ, and the effective magnetic moment, $\mu = 2.83(\chi T)^{1/2}$. In the crystals of ion radical salts, radical ions are usually stacked face to face in a one-dimensional array.[3] For a one-dimensional lattice of spin S_i, the Hamiltonian of exchange interaction is generally given by

$$\mathcal{H} = -2J \sum_{i=1}^{N/2} (S_{2i-1}\cdot S_{2i} + aS_{2i}\cdot S_{2i+1}) + g\beta \sum_{i=1}^{N} S_i\cdot H$$

where apart from obvious notations, J stands for the exchange integral and a denotes the alternation parameter ($0 \le a \le 1$). The g-value is assumed to be equal to 2.00 for organic radicals. Duffy and Barr[7] have calculated the magnetic susceptibilities of alternating rings involving 10 spins (N = 10) and discussed the magnetic properties of infinite chains (see Fig. 2).

The observed magnetic susceptibility versus temperature curve can be fitted to a theoretical curve with a = 0.8 except for a region of very low temperature. Whereas the theoretical curve tends to zero at very low temperature, the observed susceptibility assumes a finite value almost independent of temperature below about 10 K. Bonner and Fisher[8] have shown that the susceptibility of a regular lattice (a = 1) consisting of even number of spins tends to zero at very low temperature and that the susceptibility of an infinite regular chain tends to a finite value at 0 K. When a is nearly equal to unity, the susceptibility of an infinite alternating chain is expected to tend to a finite value smaller than that for a regular chain at 0 K in agreement with the observed magnetic susceptibility at very low temperatures. At high temperatures, the observed curve agrees fairly well with the theoretical curve for an infinite regular chain (a = 1) as well. A conceivable reason for the discrepancy at low temperatures is the presence of magnetic interaction between chains. Therefore, the existence of regular chains in crystals is not necessarily ruled out. However, it is suppposed to be more probable that the crystals contain alternating chains, because the theoretical curve with a = 0.8 shows a better agreement with the observed data than does the curve with a = 1. In any case, there is no doubt that Li(dipy)·$(C_2H_5)_2O$ has linear chains rather than isolated binuclear clusters as crystal units.

The strong antiferromagnetic interaction in the lithium salt is probably due to a charge-transfer mechanism which has already been proposed for

Wurster's blue radical salts.[9] The exchange integral, $|J|/k$ = 80 K, is much larger than 11.6 K for $Be(dipy)_2$,[2] in which the plane of a dipyridyl ion is perpendicular to that of the nearest neighboring ion because each beryllium ion has a tetrahedral coordination of four nitrogen atoms from two dipyridyl ions. Therefore, it is expected that a charge-transfer interaction as well as the overlap of π-orbitals between dipyridyl ions is smaller than in the lithium salt in agreement with the present experimental results.

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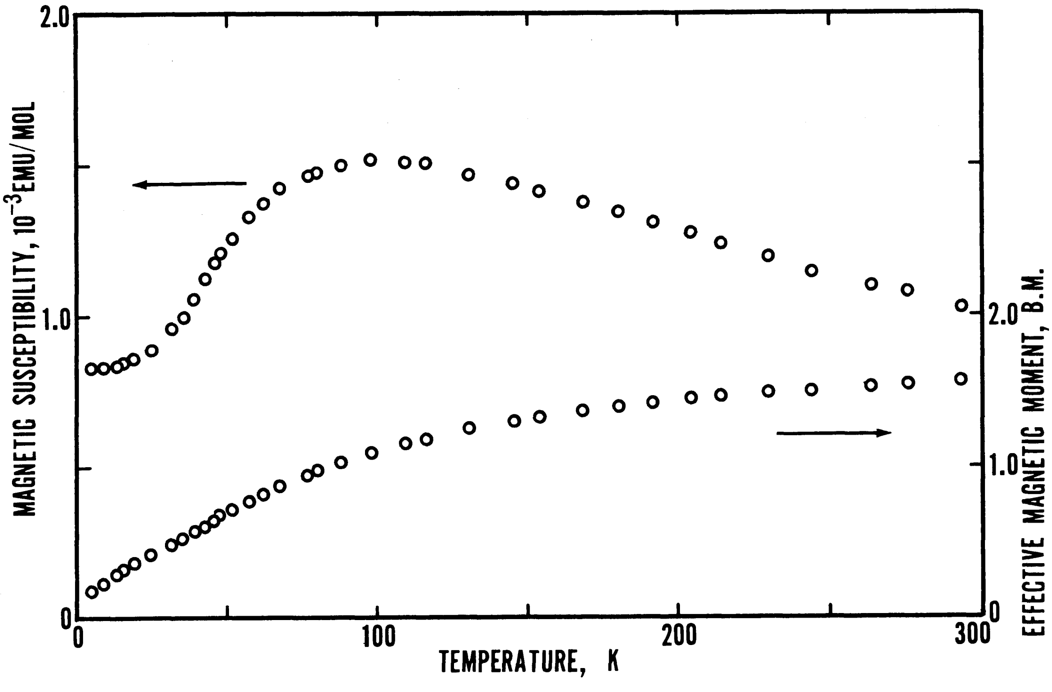

Fig. 1. Magnetic susceptibility and the effective moment of $Li(dipy)\cdot(C_2H_5)_2O$.

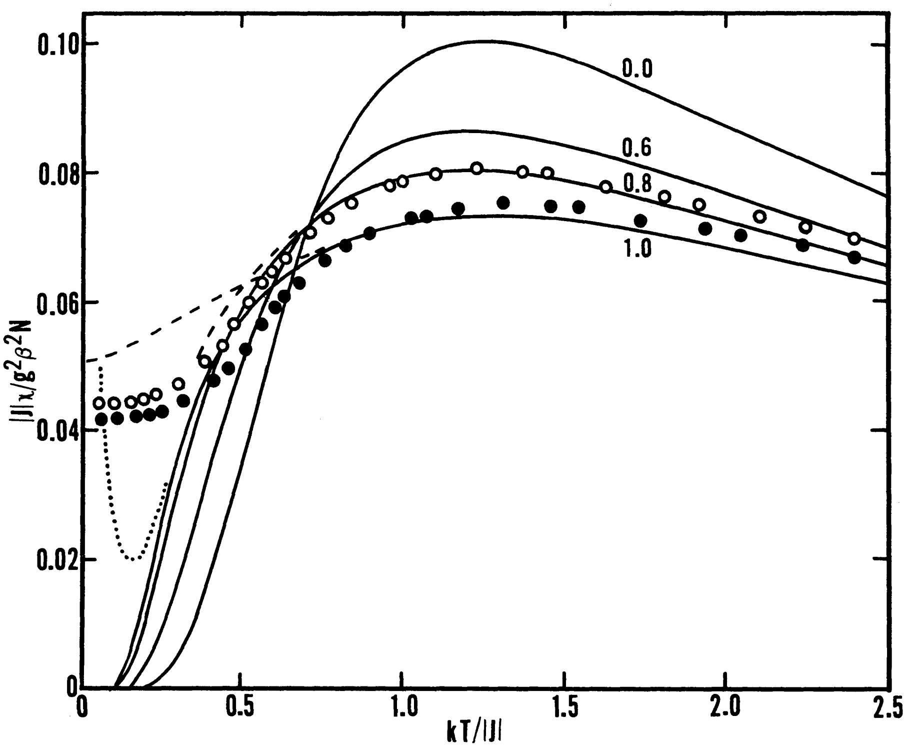

Fig. 2. Theoretical susceptibility of alternating linear chains each having 10 spins with α = 0-1 (solid curves) and the observed susceptibility (o: J/k = -80 K, ●: J/k = -70 K). The dotted curve shows the susceptibility of alternating chains (N = 10, α = 0.8) containing 1.0 mole percent of an additional paramagnetic impurity. Broken curves are asymptotic curves extrapolated to $N = \infty$.

(Received July 23, 1973)