MAGNETIC INTERACTION IN THE SO-CALLED ZEROVALENT BERYLLIUM COMPLEX OF

2,2'-DIPYRIDYL, [Be(dipy)$_2$]

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The magnetic susceptibility and electronic absorption

spectrum of [Be(dipy)$_2$] indicate that two 2,2'-dipyridyl

radical anions are coordinated to a divalent beryllium ion

and that antiferromagnetic interaction (exchange integral,

J/k = -11.6°K) operates between two radical ions within the

molecule of [Be(dipy)$_2$].

A number of the so-called zerovalent metal complexes of 2,2'-dipyridyl,

[M(dipy)$_n$], have been prepared.[1,2] They attract attention because of the

anomalous valency of metals. It is expected that magnetic measurements can

provide significant information about the electronic structure of the compounds.

The magnetic moment of [Be(dipy)$_2$] was found to be 2.05-2.15 B.M. at room tem-

perature. The value is nearly equal to the effective magnetic moment, $\sqrt{2 \times 3}$

B.M., of a molecule having two independent unpaired electrons. This suggests

the formula [Be^{2+}(dipy$^-$)$_2$] rather than [Be^0(dipy^0)$_2$] because the latter repre-

sents diamagnetism. The ESR spectrum of [Be(dipy)$_2$] in a glassy matrix also

suggests that two 2,2'-dipyridyl radical anions are coordinated to a beryl-

lium(II) ion.[3] If the conclusion is correct, spin exchange interaction is

presumed to operate between two 2,2'-dipyridyl anions within [Be(dipy)$_2$]. The

present investigation has been undertaken in order to obtain some information

about spin exchange interaction as well as the oxidation state.

As shown in Fig. 1, the observed relative magnetic susceptibility exhibits

a maximum at about 14.5°K. The magnetic susceptibility of a compound having

two unpaired electrons in a molecule is given by the simple singlet-triplet

formula.

$$\chi = \frac{2cNg^2\beta^2}{3kT}\left[1 + \frac{1}{3}\exp(-2J/kT)\right]^{-1} \tag{1}$$

where apart from obvious notations, c is the fractional radical concentration

and J is the exchange integral. The latter can be evaluated directly from

the temperature, T_m, of the maximum susceptibility as $J/k = -0.80T_m$. Assuming
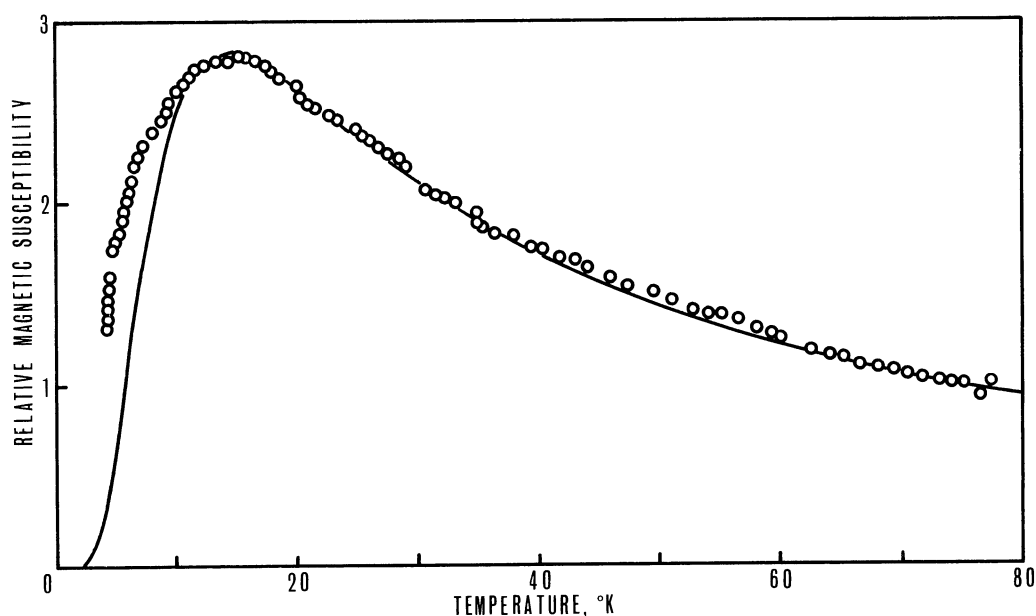

Fig. 1. Relative magnetic susceptibility of [Be(dipy)$_2$].

the validity of Eq. 1, one can calculate J/k to be equal to about -11.6°K.

The solid curve in Fig. 1 shows relative susceptibility calculated from Eq. 1

with J/k = -11.6°K. The curve agrees fairly well with the observed curve.

The absolute value of the susceptibility could not be determined accurately,

because the compound was very sensitive to atmospheric oxygen and moisture. The

magnetic moment at room temperature is estimated to be approximately 2.1 B.M.,

which agrees with the value cited in the literature.[2] From this value, the

radical concentration, c, is evaluated to be about 0.8 by use of Eq. 1 with J/k

= -11.6°K and g = 2.00, indicating the presence of additional diamagnetic sub-
stances in the sample. However, this does not affect the curve of relative
susceptibility versus temperature in any significant manner. The electronic
absorption spectra of [M(dipy)$_n$] provide a criterion to determine the oxidation
state.[4] Fig. 2 shows the spectrum of [Be(dipy)$_2$] observed in diethyl ether
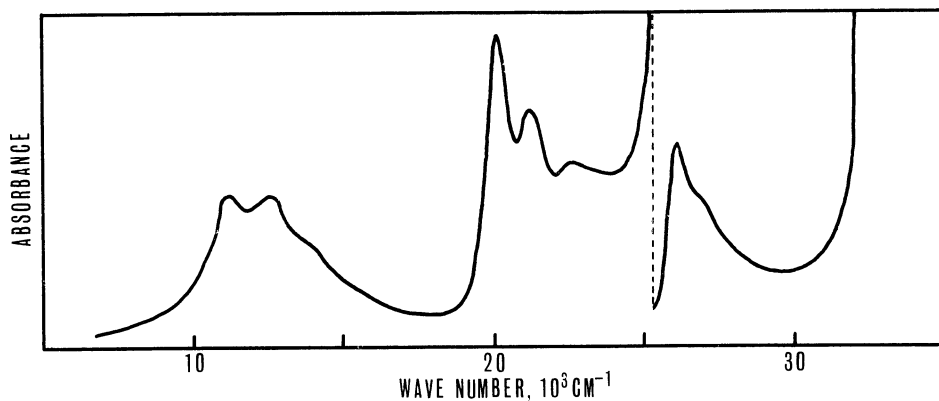solution between 5000 and 30,000 cm^{-1}. The spectrum resembles those of the

Fig. 2. Electronic absorption spectrum of [Be(dipy)$_2$].

corresponding alkali metal complexes,[5] suggesting that unpaired electrons are
mostly populated in the orbitals of 2,2'-dipyridyl. The magnetic and optical
properties indicate that the molecule of [Be(dipy)$_2$] contains two 2,2'-dipyridyl
radical anions interacting antiferromagnetically with each other and hence that
the ground state is a spin singlet.

References

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