Anomalous Temperature Dependence of the Magnetic Susceptibility of a Ni(II) Cyclam Complex with Iodide

Jun Yamauchi,* Hideyuki Tsuji,† Naoko Sakai, and Yoshiko Kawamura
Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-8501
†*Research and Development Center, Toshiba Electric Co. Ltd., Yokohama 135-8522*

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Magnetic susceptibility was studied on a Ni(II) cyclam complex with iodide, which exhibited an anomalous temperature variation. A diamagnetic spin state at room temperature made a transition into a paramagnetic state below ca. 50 K, and the magnetic susceptibility increased continuously toward a liquid helium temperature. An ESR observation was in good agreement with this magnetic behavior. This finding is unusual in spin crossover phenomena in transition metal ions.

Various complexes of 1,4,8,11-tetraazacyclotetradecane (cyclam) have been prepared and are of interest in connection with the stereochemical consequences of substitution in octahedral complexes. In particular, Ni(II) complexes exhibit interesting magnetic properties, such as a high spin state (S = 1) or a low spin state (S = 0) depending upon the anion moieties.[1] More recently, this complex has been found to be a very important constituent forming spatial magnetic networks in molecular magnetism.[2] The objective of this study, however, is concerned with the stereochemical influence of substituents at the apical position of the cyclam coordination. It has been reported that some halide complexes show remarkable variations in magnetic properties; chloride and bromide are in a high spin state, whereas iodide is diamagnetic.[3] In this communication, an unusual magnetic behavior of the Ni(II) cyclam complex with iodide (**1**) is reported, with an emphasis on a spin crossover phenomenon that results in a high spin state at a low-temperature region.

The sample was prepared following the synthetic methods described in the literature.[1,3] The elemental analysis indicated C, 23.6%; H, 4.2%; N, 10.9%; and I, 49.4%, which are compared with C, 23.4%; H, 4.7%; N, 10.9%; and I, 49.5%, based on the formula, $C_{10}H_{24}N_4I_2Ni$. The magnetic susceptibility measurement was carried out using a SQUID magnetometer (Quantum Design MPMS-2). The temperature was varied between 3 and 300 K at a magnetic field of 100 mT. The magnetic data obtained was corrected for a molecular diamagnetic contribution employing Pascal's constants, -2.62×10^{-4} cm^3/mol. Electron spin resonance (ESR) measurements were carried out using an X-band spectrometer (JEOL RE-3X) in a magnetic field of less than 1 T at a temperature of 300 down to 6 K.

The magnetic susceptibility in the region of 3 and 300 K is shown in Figure 1, which indicates a constant diamagnetism down to 60 K and a gradual increase below ca. 50 K, reaching the highest value at 3 K. The former behavior (a constant diamagnetism) is in good agreement with the previous report characterized at room temperature.[3] The abrupt increase of the magnetic susceptibility can be plotted distinctively in terms of the effective magnetic moment shown in Figure 2. The effective magnetic moment gradually increases below 60 K. After reaching a round maximum at 11 K, it starts to decrease in the low-temperature region. The important point here is that the effective magnetic moment gradually approaches 2.8 or 2.9 Bohr magnetons at zero degrees, which corresponds to the value of the spin quantum number $S = 1$ with an assumed g value of 2.0. This finding implies a high spin state of the 3d configuration of Ni^{2+} ion. The decrease of the effective magnetic moment at the low temperature side is probably due to antiferromagnetic interactions between the paramagnetic ions of $S = 1$.

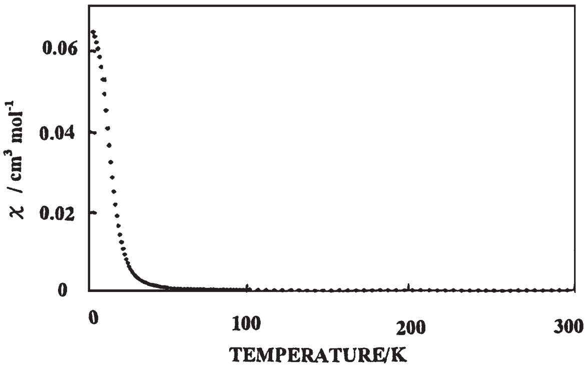

Figure 1. Magnetic susceptibility (χ).

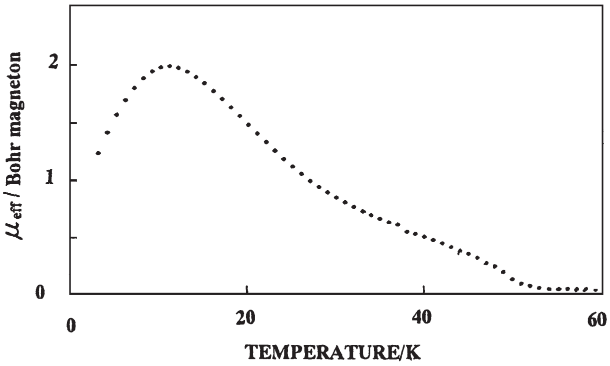

Figure 2. Effective magnetic moment (μ_{eff}).

The temperature dependence of the magnetic susceptibility of **1** mentioned above was ascertained by ESR observations. Some ESR spectra are shown in Figure 3 in the magnetic field range between 0 and 1 T. The ESR intensity grows up below 60 K and reaches its maximum at 12 K, in good agreement with the magnetic behavior. The resonance patterns are remarkably asymmetric around 325.6 mT (this magnetic field gives a g-value of 2.0) and spread out widely more than 1 T. These are the characteristics of transition metal ions in a high spin state. The

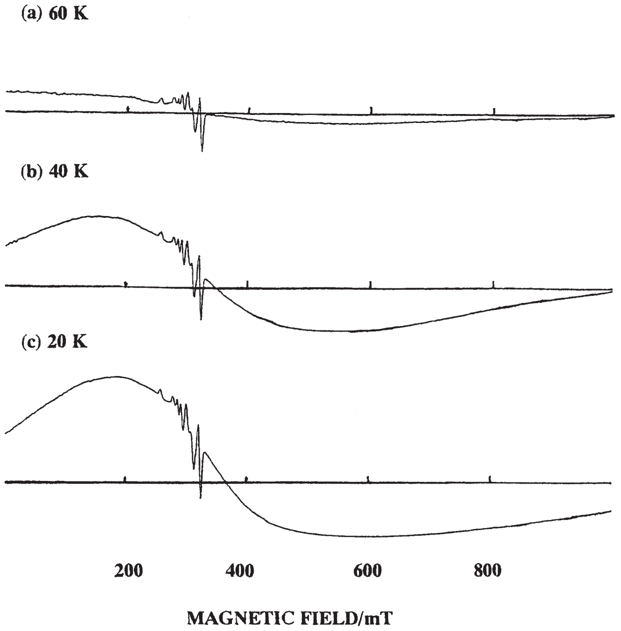

Figure 3. ESR spectra in a magnetic field range between 0 and 1 T at (a) 60 K, (b) 40 K, and (c) 20 K.

rough estimation of the linewidth was 400 mT, which, based on the spin state $S = 1$ expected from the effective magnetic moments, would be the magnitude of a zero-field splitting parameter, D, for $S = 1$. Therefore, the $2D$ components of the triplet absorption would amount to 800 mT, yielding plausible resonance patterns. The several weak absorptions around $g = 2$ are impurity signals, probably due to Mn^{2+} ions and others.

The magnetic data of Ni(II) cyclam complexes with halides and perchlorate show a remarkable change on altering the nature of the anion.[3] The effective magnetic moment at 20 °C was determined to be 3.09 and 3.06 Bohr magnetons for chloride and bromide salts, respectively. The 3d electronic configuration of the Ni(II) ions is a high spin state, $S = 1$. Although these values are somewhat lower than those normally encountered in octahedral complexes of Ni(II), a similar lowering of the moment was pointed out in bis(N,N'-dimethylethylenediamin) nickel(II) complexes.[1] On the other hand, iodide and perchlorate salts are diamagnetic at 20 °C. The changeover in magnetic behavior between bromide and iodide indicates that the axial distortion is sufficiently large to change the ground state from $^3A_{2g}$ to $^1A_{1g}$.[4] This finding was also exemplified identically between chloride and bromide by Goodgame and Venanzi.[1] In this context, the observation has shown a new classification of diamagnetic iodide salt into high spin multiplicity at low temperature, which is a spin crossover phenomenon.

A low-spin-high-spin (LS-HS) transition takes place in many transition metal ions of configuration d^n, $n = 4$ to 7, in octahedral surroundings, depending on a first approximation on the magnitude of the energy gap between e_g and t_{2g} orbitals relative to the mean spin pairing energy.[5] Experimental evidence was reported for an iron(II) complex by König and Madeja.[6] The spin crossover is an entropy-driven phenomenon, and LS is usually stabilized at a low temperature.[7] This finding is quite unusual with respect to stabilized HS at a low temperature. Temperature-induced spin crossover phenomena, which are currently widely accepted, are classified into two types: one is the so-called "abrupt type," and the other is the "gradual type."[7] Based on the effective magnetic moment of Figure 2, it could be concluded that complex **1** belongs to a gradual spin crossover phenomenon. A thermally induced LS-HS transition is characterized by an $x = f(T)$ curve, where x is the mole fraction of HS molecules and $(1 - x)$ is that of LS molecules.[5] The $x = f(T)$ curve can be deduced in a straightforward manner from the experimental effective magnetic moment. The case of **1** is simple because the LS state is diamagnetic. Thus, Figure 2 normalized by 2.8 or 2.9 Bohr magnetons directly represents an $x = f(T)$ curve except below ca. 15 K, where antiferromagnetic interactions between the complexes are dominant.

The molecular structure of chloride salt was determined by X-ray diffraction, indicating that the symmetry of the ligand field around the nickel ion is less than D_{4h}. The nickel–chlorine bond is considerably longer than usual for an undistorted octahedral complex, but there appears to be no distortion of the cyclic ligand. Compared with the chloride ion, the iodide ion may be too large to approach the metal closely. This estimation may conclude the diamagnetic state of **1** at room temperature because of an elongated octahedral ligand field. On decreasing the temperature, however, the distance between the nickel and the iodine is shrinking, and the iodide exerts more ligand field interaction from the apical direction. This contraction means approaching to a nearly octahedral symmetry from an elongated octahedral one. This mechanism tentatively explains the high spin state of **1** at low temperature. Many recent studies on the spatial magnetic network constructions using the Ni(II) cyclam complex has been concerned with the appropriate interaction between nickel ions through the apical positions, which always result in high-spin multiplicity.[2]

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