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HEAT CAPACITY AND DUAL SPIN-TRANSITIONS IN THE CROSSOVER SYSTEM $[Fe(2\text{-}pic)_3]Cl_2 \cdot EtOH$*

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ABSTRACT

The heat capacity of $[Fe(2\text{-}pic)_3]Cl_2 \cdot C_2H_5OH$ Crystal (2-pic: 2-picolylamine) has been measured with an adiabatic calorimeter between 13 and 315 K. Two phase transitions centered at 114.04 and 122.21 K were observed. This finding accords with recent prediction of possible existence of two-step spin-conversion (H. Köppen et al., Chem. Phys. Lett., 91 (1982) 348). The total transition enthalpy and entropy amounted to ΔH = 6.14 kJ mol^{-1} and ΔS = 50.59 J K^{-1} mol^{-1}. The transition entropy consists of the magnetic contribution (13.38 J K^{-1} mol^{-1}), the orientational order-disorder phenomenon of the solvate ethanol molecule (8.97) and the change in the phonon system, in particular the change in stretching and deformation vibrations of the metal-ligand (28.24).

INTRODUCTION

The spin-crossover behavior in tris(2-picolylamine)iron(II) halids, $[Fe(2\text{-}pic)_3]X_2$ (X = Cl, Br or I), is of interest in various aspects. (i) The spin-transition is affected by the noncoordinating halogen ion: $[Fe(2\text{-}pic)_3]Cl_2$ and $[Fe(2\text{-}pic)_3]Br_2$ exhibit a discontinuous low-spin ($^1A_1$) $\rightleftharpoons$ high-spin ($^5T_2$) transition while $[Fe(2\text{-}pic)_3]I_2$ remains in a continuous or equilibrium type (ref.1). (ii) A variety of solvent molecules can be stoichiometrically amalgamated in the crystal lattices of $[Fe(2\text{-}pic)_3]Cl_2$ (refs.2,3) and $[Fe(2\text{-}pic)_3]Br_2$ (ref.4). Those noncoordinating solvent molecules critically influence the spin-crossover behavior. Interestingly, the compounds solvated with ethanol (EtOH) or methanol (MeOH) undergo a complete spin-transition between the pure low-spin and the pure high-spin species (refs.2-4) although the nonsolvated moieties involve a residual paramagnetic fraction at low temperatures (ref.1). On the other hand, $[Fe(2\text{-}pic)_3]Cl_2 \cdot H_2O$ gives rise to a first-order spin-transition accompanied by a large hysteresis of 91 K while $[Fe(2\text{-}pic)_3]Cl_2 \cdot 2H_2O$ remains in the low-spin state without any spin-crossover phenomenon (ref.3). (iii) $[Fe(2\text{-}pic)_3]Cl_2 \cdot EtOH$ can form complete solid solutions with the diamagnetic zinc analogue to give $[Fe_xZn_{1-x}(2\text{-}pic)_3]Cl_2 \cdot EtOH$, and they bring about the complete spin-crossover: the transition temperature, T_C, follows the following

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empirical relation (ref.2),

$$T_C(x)/K = 40x + 82 \qquad (0.2 \leqq x \leqq 1.0).$$

Surprisingly, the spin-transition is still observable even at an extremely low iron concentration of $x = 0.0009$ (ref.5).

These remarkable features inherent in the tris(2-picolylamine)iron(II) halide systems seemed to have their origins in the unique ligand capable of forming hydrogen-bonding (refs.2,3,5). In fact, X-ray diffraction analyses revealed the existence of a two-dimensional hydrogen-bonding network linking all amine hydrogen atoms of the ligands, the noncoordinating halogen ions and the hydroxy-groups of the solvent molecules (refs.4,6-11). Interesting new aspect found for $[Fe(2\text{-}pic)_3]Cl_2 \cdot EtOH$ and $[Zn(2\text{-}pic)_3]Cl_2 \cdot EtOH$ from X-ray diffraction (refs.8,9, 11) is orientational disorder of the ethanol molecule at high temperatures. This finding strongly suggests a coupling between the spin-transition and the order-disorder phenomenon of the solvate ethanol molecule.

Recently, an additional new aspect of the spin crossover in $[Fe(2\text{-}pic)_3]Cl_2 \cdot EtOH$ was elucidated by close reinvestigations of ^{57}Fe Mössbauer spectroscopy and magnetic susceptibility measurements (ref.12). A two-step spin-conversion in the crossover region with transition temperatures at 114.0 K and 120.7 K was detected: this kind of unusual spin-transition has never been reported for any other spin-crossover system.

The objective of the present paper is to examine, on the basis of heat capacity measurements, whether the two-step spin-conversion would be accompanied by two distinct phase transitions, and to clarify the relationship between the spin-transitions and the order-disorder phenomenon of the solvate ethanol molecule. As already recognized in the case of the typical spin-crossover systems, $[Fe(phen)_2X_2]$ (phen = *o*-phenanthroline, X = NCS or NCSe) (refs.13,14), heat capacity measurements provide important informations concerning the energetic and entropic aspects which are not detectable from spectroscopic and magnetic measurements or structural analyses.

EXPERIMENTAL

The complex was prepared as described previously (ref.2). The product was recrystallized from absolute ethanol and dried in a vacuum for 3 h at room temperature. All handling was carried out in a dry nitrogen atmosphere. *Anal.* calcd. for $Fe(C_{20}H_{30}N_6OCl_2)$: C, 48.31% (found, 48.39%); H, 6.08 (6.09); N, 16.90 (16.95); Fe, 11.23 (11.39).

The heat capacity measurements between 13 and 315 K were made with an adiabatic calorimeter workable in the range 13-530 K (ref.15). A calorimeter cell made of gold-plated copper (ref.16) contained the specimen of 15.1218 g ($\hat{=}$

0.030411 mol) and a small amount of helium gas to aid the heat transfer inside the cell.

RESULTS AND DISCUSSION

The results of calorimetric measurements are shown in Fig. 1 in terms of molar heat capacity at constant pressure, C_p. Two sharp peaks due to phase transitions were observed at T_{C2} = 114.04 K and T_{C1} = 122.21 K. The peak height at T_{C1} was much higher than that at T_{C2}. The present calorimetric value of T_{C1} agrees well both with the temperature (122 K) at which the high-spin fraction (x_{HS}) deduced from the Mössbauer spectrum becomes equal to the low-spin fraction ($x_{LS} = 1 - x_{HS}$) (ref.2), and with the temperature (120.7 K) at which the temperature derivative of x_{HS} derived from the magnetic susceptibility (dx_{HS}/dT) shows a maximum value (ref.12). On the other hand, the present T_{C2} coincides with the temperature (114.0 K) of the second peak of dx_{HS}/dT (ref.12). As a conclusion, the two heat capacity anomalies might be caused by the two-step spin conversion.

As seen in Fig. 1, two peaks due to the phase transitions appear in a narrow temperature interval and hence it involves a large ambiguity to estimate independently the enthalpies and entropies of these phase transitions. We shall, therefore, determine the overall quantities by estimating normal heat-capacity curve on the basis of an effective frequency distribution method (ref.17). Normal heat capacity principally consists of the contributions from a continuous phonon distribution and many discrete intramolecular optical vibrational modes. The latter contribution can be well approximated by the Einstein model. A borderline between the continuous and discontinuous frequency distributions was assumed here to be located at 700 cm^{-1}. Since the present compound consists of 60 atoms, its number of degrees of freedom is 180. Among them, thirty six modes (108 degrees of freedom) were assigned from the infrared absorption spectra. In accordance with the fact that the spin-transition of the present complex occurs over a wide temperature region (refs.2,5,12), the excess heat capacity due to the phase transitions extends its tails far below T_{C2} and far above T_{C1} (see Fig. 1). Therefore, determination of the normal heat capacities for the low (LT) and high temperature (HT) phases was made by use of 41C_p values below 60 K and 19C_p data above 260 K, respectively. The normal heat capacities estimated from the 'best' frequency spectra are shown in Fig. 1 by broken lines. The normal heat capacities for the LT- and HT-phases are switched at T_{C1}. This procedure made a heat capacity jump of ΔC_p = 7.76 J K^{-1} mol^{-1}.

The total transition enthalpy and entropy amounted to ΔH = 6.14 kJ mol^{-1} and ΔS = 50.59 J K^{-1} mol^{-1}, respectively. It is noticeable that the present value of ΔS is very close to 48.78 and 51.22 J K^{-1} mol^{-1} found for the spin-crossover

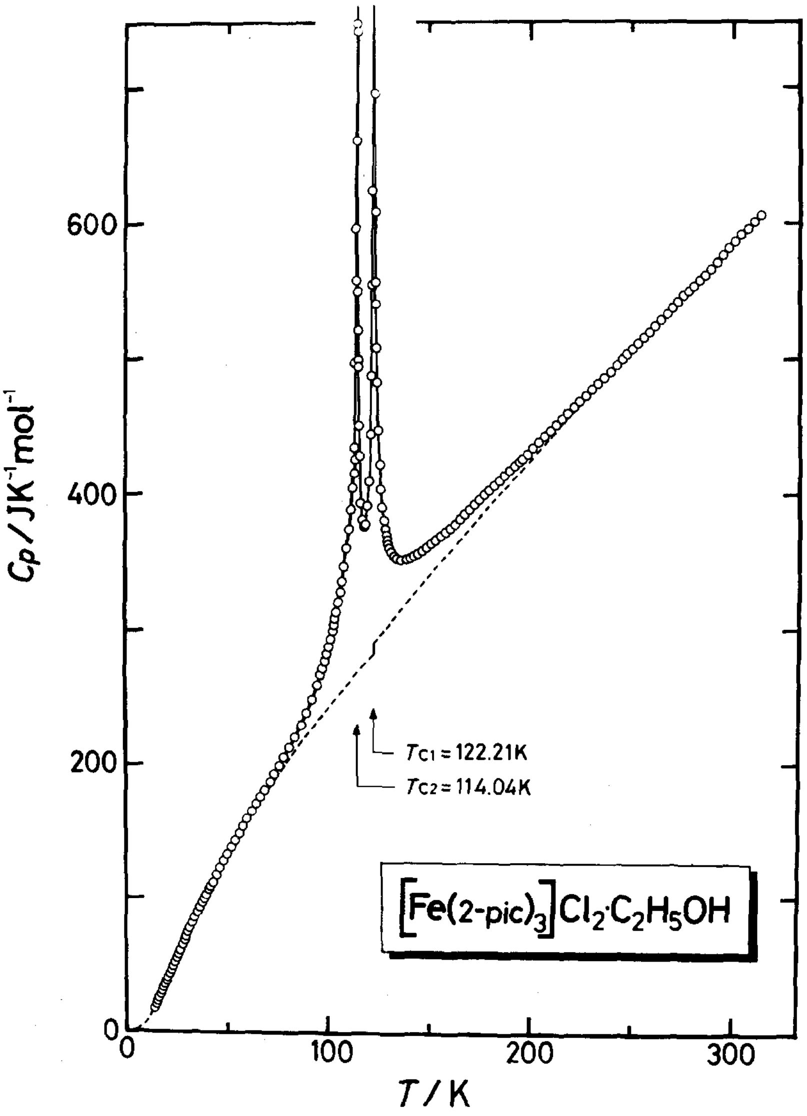

Fig. 1 Molar heat capacity of $[Fe(2\text{-pic})_3]Cl_2\cdot EtOH$. Broken lines indicate the estimated normal heat capacities.

complexes of $[Fe(phen)_2(NCS)_2]$ and $[Fe(phen)_2(NCSe)_2]$, respectively (refs.13,14) although the transition mechanism of the present complex would be different from that of these two compounds. The transition entropy of the present complex consists mainly of (i) a change in the spin states, (ii) the order-disorder phenomenon of the solvate molecule, and (iii) a change in the phonon system, in particular drastic changes in the bond lengthes between the central iron ion and the ligands.

As to (i), we need not take into account the contribution from the degeneracy of the electron orbitals because the orbital degeneracy of the high-spin state $^5T_2$ has been already lifted under a lower site symmetry to give either $^5B_2$ or $^5A_1$ (ref.5). The magnetic entropy is, therefore, $R\ln 5$ (= 13.38 J K^{-1} mol^{-1}), where R is gas constant.

The entropy arising from the order-disorder phenomenon amounts to $\sim R\ln 2.94$ (= 8.97 J K^{-1} mol^{-1}) as the population ratio of three ethanol sites is 3 : 2 : 2 at 298 K and 1 : 0 : 0 at 90 K (ref.9).

The contribution from the item (iii) corresponds to the remaining entropy of 28.24 J K^{-1} mol^{-1} (= 50.59 - 13.38 - 8.97). The X-ray diffraction analyses for the present complex revealed a considerable contraction of the Fe-N bond length by as much as 0.2 Å on going from the high-spin to the low-spin state, and thereby an expansion of the N-Fe-N bond angle by about 6° (refs.8,9). These drastic changes in the molecular geometry can contribute to the transition entropy through changes in the normal mode frequencies of Fe-N stretching and N-Fe-N deformation vibrations. In the case of $[Fe(phen)_2(NCS)_2]$ and $[Fe(phen)_2(NCSe)_2]$, the entropy acquisition due to the Fe-N stretching mode was 17.4 and 22.5 J K^{-1} mol^{-1}, respectively (ref.14). Therefore, we can expect an entropy gain of more or less 20 J K^{-1} mol^{-1} for the Fe-N stretching vibrations of the present complex. If this is the case, the remaining entropy of about 8 J K^{-1}

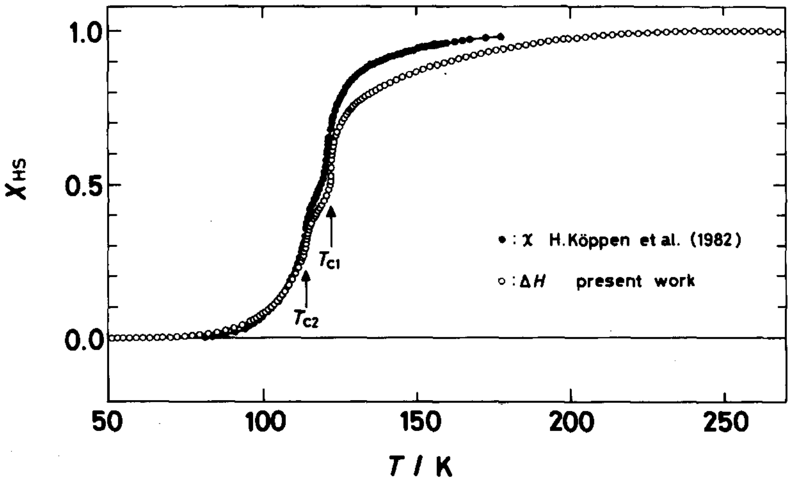

Fig. 2 Temperature dependence of the high-spin fraction, x_{HS}, estimated from the magnetic susceptibility (●) (ref.12) and the calorimetric measurements (○).

mol^{-1} would be ascribed to the change in the metal-ligand deformation vibrations and a minor change in the hydrogen bonding system between the low-spin and the high-spin state. Anyhow, complete assignments of IR and Raman spectra of the present complex are urgent to check the validity of the phonon entropy.

Along with the entropic aspect discussed above, the enthalpic aspect can be obtained from the calorimetric measurements. We attempted to estimate the high-spin fraction, x_{HS}, according to the relation, $x_{HS} = \Delta H(T)/\Delta H$, where $\Delta H(T)$ implies the enthalpy gain at temperature T and ΔH corresponds to the total transition enthalpy. Temperature dependence of the calorimetric x_{HS} is compared in Fig. 2 with the x_{HS} derived from the magnetic susceptibility (ref.12). Agreement between the two seems to be satisfactory if we take into account the fact that magnetic susceptibility directly reflects only the magnetic property while the enthalpy consists of both the magnetic and the nonmagnetic contributions.

Based on this good agreement as well as the entropic argument, we can safely conclude that the spin-transition in the present complex is actually coupled both with the phonon system and with the orientational order-disorder phenomenon of the solvate ethanol molecule. The surprising finding that the spin-transition is still observable even at an extremely low iron concentration of $x = 0.0009$ in the $[Fe_xZn_{1-x}(2\text{-pic})_3]Cl_2 \cdot EtOH$ system (ref.5) seems to be well accounted for in terms of this coupling scheme. Further calorimetric study on the mixed systems is of particular interest in this regard. Such study is now going on.

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