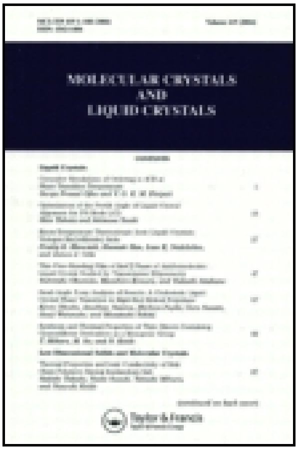

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Spin-Crossover Phenomena of Iron Complexes in the Montmorillonite Interlayer Space

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SPIN-CROSSOVER PHENOMENA OF IRON COMPLEXES IN THE MONTMORILLONITE INTERLAYER SPACE

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Abstract Spin-crossover phenomena of four iron complexes, $[Fe(amp)_3]^{2+}$ (amp = 2-(aminomethyl)pyridine), $[Fe(acac_2trien)]^+$ (H_2acac_2trien = *N,N'*-bis(1-methyl-3-oxobutylidene)triethylenetetramine), $[Fe(sal_2trien)]^+$ (H_2sal_2trien = *N,N'*-disalicylidenetriethylenetetramine), and $[Fe(acpa)_2]^+$ (Hacpa = *N*-(1-acetyl-2-propylidene)-2-pyridylmethylamine), intercalating into the montmorillonite interlayer space were examined by the magnetic susceptibility measurement and ^{57}Fe Mössbauer spectroscopy. Confinement of the complexes in the 2D space brings some dispersion and drop of the spin-crossover temperature in comparison with those for their spin equilibria in solution. Twisting deformation of the complexes was proposed to be responsible for the observed variation of the relative stability between high-spin and low-spin species.

INTRODUCTION

Spin-crossover complexes are known to possess a couple of tautomeric electronic structures, high-spin (HS) and low-spin (LS) states, and reveal the molecular bistability between them. This property suggests interesting applications, for example optical recording materials, and gave rise to extensive works.[1,2] The bistability between the HS and LS states appears as thermal equilibria in dilute systems (solutions and mixed crystals), while as cooperative phenomena in crystalline states.

In the dilute systems the major problem is on the crossover temperature ($T_{1/2}$), where the LS state stabilized in the lower temperatures switches into the HS state. Several attempts to regulate the switching characteristics by chemical modifications of complex molecules were carried out.[3-5] Kläui *et al.*[4] classified the effects of the modifications into two groups. One is a steric effect and the other is an electronic effect. The latter is reasonably understood as electron-inductive and/or resonance properties of substituents, which modulate ligand field strength in the complexes. In turn, the steric effect of substituents is difficult to be examined solely because the electron-induction effect is inevitably mixed in it.

In the present work we have concentrated in the aspect of the steric effect by means of the intercalation of the complexes into a layered host compound. Such an outer constraint is favorable to investigate the steric effect without suffering from the electronic effect. As a host layer compound, montmorillonite has been chosen because of its great intercalation capacity for bulky molecules such as octahedral metal complexes.

EXPERIMENTAL

The guest complexes, [Fe(amp)$_3$] Cl$_2$·EtOH, [Fe(acac$_2$trien)] PF$_6$, [Fe(sal$_2$trien)] PF$_6$, and [Fe(acpa)$_2$] PF$_6$·H$_2$O, were prepared according to the literatures.[6-9] Na$^+$-exchanged montmorillonite (Kunipia F) was supplied from Kunimine Kogyo Co., Japan. Intercalation compounds were synthesized by reactions of ethanol-acetone solutions of the iron complexes with microcrystalline montmorillonite under argon atmosphere at room temperature for 24 h. Completion of the reaction was confirmed by monitoring the (001) reflection of unreacted montmorillonite using a Shimadzu XD-3A X-ray diffractometer. Elemental analyses of the products were carried out by conventional combustion microanalysis for C, H, and N, and ICP emission spectroscopic analysis was adopted for Fe, Al, and Si contents. The results are tabulated in Table I with interlayer expansions of the intercalation compounds.

Magnetic susceptibilities of the intercalation compounds **1-4** were measured by the Gouy method at room temperature and the temperature dependence of them was determined by use of the Faraday balance at the temperature range of 4-300 K. Obtained raw susceptibilities were resolved into both contributions from the montmorillonite host layer and from the paramagnetic guest complexes. Since the montmorillonite contained a small amount of the paramagnetic Fe(II) ion, the host layer contribution was completely removed. All the raw susceptibilities were normalized into the quantities per silicon atom which was a constant ingredient of the host skeleton, and then subtracted by the susceptibility of the untreated montmorillonite. Then a diamagnetism correction for the complex molecule was performed according to Pascal's law.

Temperature dependence of the UV-Vis absorption spectrum for [Fe(acpa)$_2$] PF$_6$ was measured in acetone using a Shimadzu UV-2200 spectrophotometer equipped with Oxford

TABLE I Elemental analyses and interlayer distances of the intercalation compounds.

compound		C(%)	H(%)	N(%)	Si(%)	Fe(%)	d/Å	Δd/Å†
intact montmorillonite		-	-	-	26.9	1.41	12.1	2.5
[Fe(amp)$_3$]$^+$ / montmorillonite	(1)	7.58	1.83	2.86	24.8	3.98	16.1	6.4
[Fe(acpa)$_2$]$^+$ / montmorillonite	(2)	9.46	2.10	1.94	23.6	3.58	17.3	7.7
[Fe(acac$_2$trien)]$^+$ / montmorillonite	(3)	8.43	2.13	2.32	22.5	3.61	17.0	7.4
[Fe(sal$_2$trien)]$^+$ / montmorillonite	(4)	7.00	1.91	1.98	22.9	3.39	17.3	7.7

† Δd stands for interlayer expansions from the anhydrous-montmorillonite value, 9.6 Å.[10]

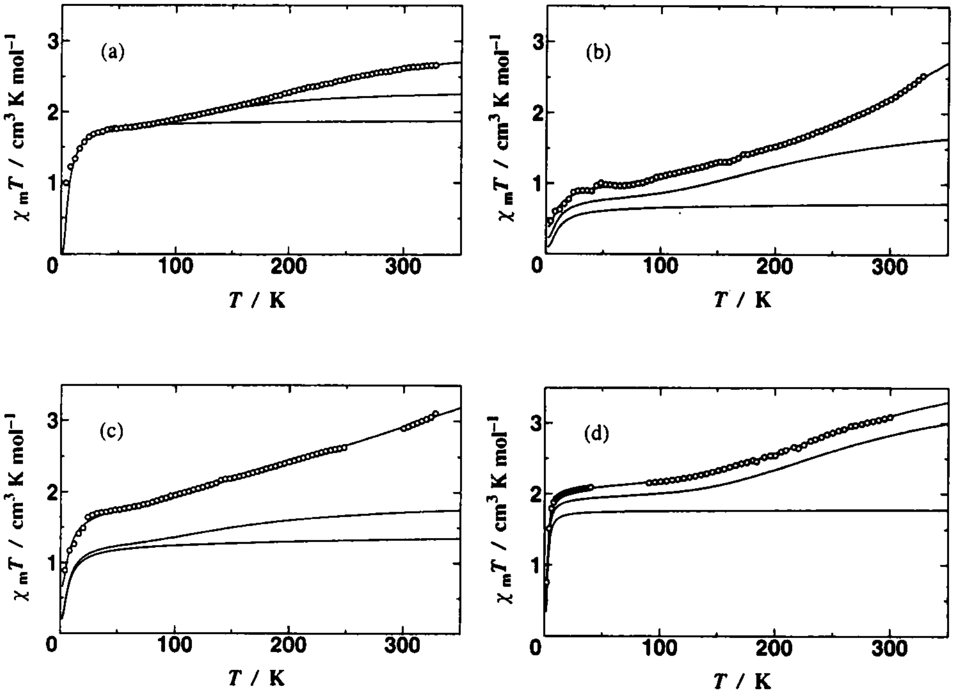

FIGURE 1 Temperature dependence of $\chi_{m}T$ for the intercalation compounds. (a), for compound **1**; (b), for compound **2**; (c), for compound **3**; (d) for compound **4**.

DN1704 cryostat in the temperature range of 200-300 K to obtain thermodynamic parameters for the spin equilibrium in solution.

^{57}Fe Mössbauer spectra for compounds **1**, **2** and **4** were measured at room temperature, 200 K, and 78 K using metallic iron foil as a standard. The observed spectra were deconvoluted with Lorentzian functions corresponding to the HS Fe(III), the LS Fe(III) species, and the Fe(II) ion of the host lattice.

RESULTS AND DISCUSSION

Temperature-dependent effective magnetic moments of $[Fe(amp)_3]^+$, $[Fe(acac_2trien)]^+$, $[Fe(sal_2trien)]^+$, and $[Fe(acpa)_2]^+$ complexes intervening between the montmorillonite layers are shown in Figure 1. All the curves exhibit the positive dependence of magnetic moments on temperature, indicating spin-crossover phenomena from the LS to the HS states. This is also confirmed by the Mössbauer spectra of compound **4** (Figure 2). However, these curves of the magnetic moments could not be reproduced by assuming a singe-step equilibrium between the LS and the HS states. Thus, multi-component fitting was attempted by

$$\chi_m T = \frac{N_0 \mu_0}{3 k_B} \sum_i c_i \left[(1 - f_i^{HS}) \mu_{LS}^2 + f_i^{HS} \mu_{HS}^2\right] \qquad (1)$$

$$f_i^{HS} = \left\{1 + \exp\left[\Delta H_i / k_B T - \Delta S_i / k_B\right]\right\}^{-1} \qquad (2)$$

where χ_m stands for molar susceptibility of the iron complex, μ_{LS} and μ_{HS} are magnetic moments of the iron complexes in the HS and the LS states, respectively, c_i is a mole fraction of the i-th equilibrium component characterized by the enthalpy ΔH_i and the entropy ΔS_i of spin equilibrium, and N_0 is the Avogadro number, μ_0 the permeability of vacuum, k_B the Boltzmann constant, and T temperature. The relation, μ_{LS}^2 (or μ_{HS}^2) = $g^2 S(S+1) \mu_B^2$, with corresponding spin quantum number S was used, where g is Lande's g-value and μ_B the Bohr magneton. For the LS state of the Fe(III) complex, Kotani's equation,

$$\mu_{LS}^2 = \frac{3x + 8 + 8\exp(-3x/2)}{x\,[1 + 2\exp(-3x/2)]}\, \mu_B^2 \qquad (3)$$

was adopted, where $x = \zeta / k_B T$ and ζ is a spin-orbit coupling equal to 600 k_B K. In all the cases the application of two components provided poor curve-fittings, successful fittings being performed by three components. Thermodynamic quantities of spin equilibria of each component in the interlayer space are summarized in Table II.

TABLE II Thermodynamic parameters of spin equilibria for the iron complexes in the montmorillonite interlayer space.

compound	component	fraction	$T_{1/2}$ / K	ΔH / kJmol^{-1}	ΔS / JK^{-1}mol^{-1}
$[Fe(amp)_3]^+$ / montmorillonite	1	0.72	14	0.08	6
(1)	2	0.12	168	3.8	23
	3	0.16	264	9.4	36
$[Fe(acpa)_2]^+$ / montmorillonite	1	0.20	92	0.14	2
(2)	2	0.32	369	4.9	13
	3	0.48	382	19.9	52
$[Fe(acac_2trien)]^+$ / montmorillonite	1	0.28	43	0.08	2
(3)	2	0.07	216	3.3	15
	3	0.65	872	9.5	11
$[Fe(sal_2trien)]^+$ / montmorillonite	1	0.36	3	0.07	21
(4)	2	0.37	328	7.0	21
	3	0.27	610	28.6	47

TABLE III Thermodynamic parameters of spin equilibria for the iron complexes in solution.

compound	solvent	$T_{1/2}$ / K	ΔH / kJmol^{-1}	ΔS / JK^{-1}mol^{-1}	references
$[Fe(amp)_3]^+$	CH_3CN	300	21.3	71.1	13
$[Fe(acpa)_2]^+$	acetone	241	19.0	78.8	this work
$[Fe(acac_2trien)]^+$	pH 10 buffer	335	16.7	49.9	14
$[Fe(sal_2trien)]^+$	H_2O	326	21.4	65.7	14

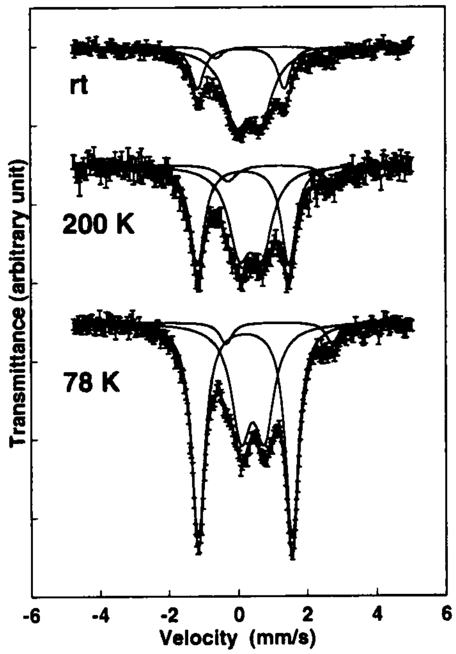

FIGURE 2 ^{57}Fe Mössbauer spectra of compound 4. Broad doublet peaks centered at 1.5 mm s^{-1} arise from the Fe(II) ion in the host lattice. Inner and outer quadrapole-split doublets around 0.5 mm s^{-1} correspond to the HS and the LS states of the $[Fe(sal_2trien)]^+$ complex, respectively.

Obviously the thermodynamic parameters of component 1 were calculated to be meaningless values, suggesting that the origin of the crossover behavior observed below 20 K for component 1 is not ascribed to the spin equilibrium. Component 1 seems to be identical with so-called "HS residue" reported for the ground crystals.[11,12]

Thermodynamic parameters for spin equilibria of the iron complexes in solution are listed in Table III. Remarkable difference is found for ΔH_i values in the intercalating state and in solution. For the major components in the intercalation compounds the energy differences between the HS and the LS states are reduced compared with those in solution, which indicate that the HS species in the interlayer space are more preferred to in solution. Such unexpected preference of the HS species was also observed for the spin-crossover complexes in the adsorption system[15] and in the zeolite encapsulated system.[16]

Reduction of the energy difference between the HS and the LS states in the interlayer space suggests that intercalation gives rise to a deviation of local symmetry about the iron center instead of an isotropic dilational/compressive deformation of the complexes. A dilation of the coordination sphere scales the ligand field strength by a scalar factor and all energy terms are monotonously shifted to higher energies as the metal-ligand distances contract. Thus, for the iron complexes it would induce an increase of the HS-LS energy splitting rather than the observed reduction. On the other hand, a molecular deformation accompanied with lowering of the symmetry causes a reduction of the HS-LS splitting.[17] It was evidently demonstrated by a model calculation for the $[Fe(amp)_3]^{2+}$ complex adopting a twist deformation about the pseudo-C_3 axis as an illustrative example. By the angular overlap method (AOM)[18] the variation of energy terms was examined as a function of a deformation coordinate, θ. It was taken as the twisted angle from octahedral to trigonal prismatic coordination. Interelectron repulsion was accounted for through Racah's B and C parameters, which were set equal to the value of the free Fe(II) ion, whether the spin-orbit coupling was neglected for simplicity. Details of the calculation will be reported elsewhere.

In conclusion, spin-crossover phenomena in the interlayer space are explained assuming the plural spin-equilibrium components whose enthalpy change have smaller values compared with those in solution. This reduction of the energy separation between the HS and the LS states through the intercalation is attributed to the asymmetrical deformation of the coordination sphere, *e.g.* the twisting deformation.

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