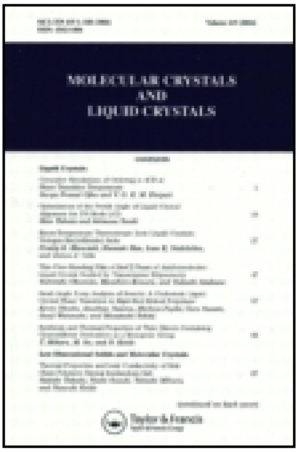

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Spin-crossover Phenomena of Iron Complexes in the NaTSM Intercalation Compounds

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Spin-crossover Phenomena of Iron Complexes in the NaTSM Intercalation Compounds

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The spin-crossover phenomena of iron complexes accompany with molecular deformations such as symmetric breathing and trigonal torsion. Thus they can serve as a sensitive probe to molecular surroundings. A confinement effect into interlayer spaces of a clay host compound, NaTSM (sodium fluorotetrasilicic mica), was studied for iron complexes by magnetic susceptibility and ^{57}Fe Mössbauer spectroscopy. Guest complexes examined are $[Fe^{II}(amp)_3]^{2+}$ (amp = 2-aminomethylpyridine), $[Fe^{III}(acpa)_2]^+$ (Hacpa = *N*-(1-acetyl-2-propylidene)-2-pyridylmethylamine), and $[Fe^{III}(sal_2trien)]^+$ (H_2sal_2trien = *N, N′*-disalicylidenetriethylenetetramine). A remarkable reduction of the high spin-low spin energy gap in the interlayer space was observed.

Keywords spin-crossover phenomena; intercalation; sodium fluorotetrasilicic mica; magnetic susceptibility; Mössbauer spectroscopy; DFT calculation

INTRODUCTION

Spin-crossover (SC) iron complexes exhibit remarkable spin-equilibrium behavior between high-spin (HS) and low-spin (LS) states[1]. These equilibria are very sensitive to the microscopic environment of each molecule, since SC phenomena accompany with small changes in molecular structures, especially in the distances between central metal atom and ligating atoms. We have examined the magnetic properties of some montmorillonite intercalation compounds including iron complexes and found that the accommodation into the interlayer space introduces inhomogeneity of the molecular environment of complexes as well as anisotropic constraint on the complex molecules giving rise to the depression of the SC temperature ($T_{1/2}$)[2]. Similar behaviors were also observed in another intercalation compound[3], while an opposite tendency was reported for a zeolite-encapsulated complex[4]. Montmorillonite contains, however, a small amount of iron contamination which obscure the characteristic SC, although the large ion-exchange capacity is favorable for the intercalation. In this paper we report the magnetic properties of NaTSM (sodium fluorotetrasilicic mica) intercalation compounds of some iron complexes without suffering from paramagnetic impurities.

EXPERIMENTAL

Sample preparations were carried out as described in the previous paper[2] except that NaTSM ($NaMg_{2.5}(Si_4O_{10})F_2 \cdot nH_2O$ sol; Topy Industries Ltd.) was used as a host layered material.

Physical measurements were also carried out following the previous methods[2].

RESULTS AND DISCUSSIONS

Magnetic susceptibilities and ^{57}Fe Mössbauer spectra of the intercalation compounds demonstrated that these iron species show the SC phenomena even in the intercalation compounds, although plural SC components were required to account for the findings.

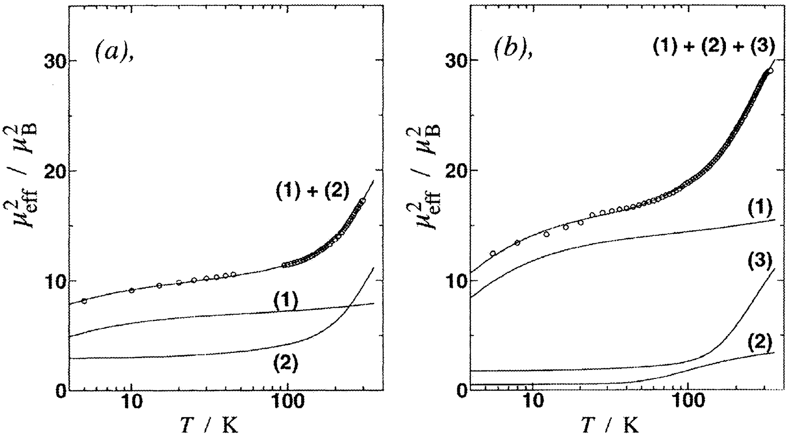

FIGURE 1 Effective magnetic moments of intercalation compounds (a), $[Fe(acpa)_2]^+$/NaTSM; *(b),* $[Fe(sal_2trien)]^+$/NaTSM, and their decomposition to plural components shown by thin curves (1), (2), and (3).

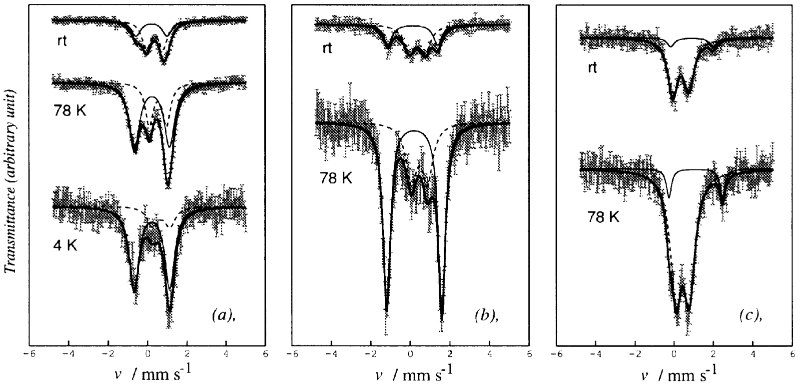

FIGURE 2 ^{57}Fe Mössbauer spectra for *(a),* $[Fe(acpa)_2]^+$/NaTSM; *(b),* $[Fe(sal_2trien)]^+$/NaTSM; *(c),* $[Fe(amp)_3]^{2+}$/NaTSM. Thin curves are quadrupole-splitting doublets from the LS species, while broken curves are from the HS species.

The magnetic properties were modeled by equations:

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

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

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

where $x = \zeta / k_B T$, ζ is the spin-orbit coupling, c_i is a molar fraction of the i-th component characterized by the SC enthalpy ΔH_i and entropy ΔS_i, f_i^{HS} is a HS fraction in the i-th component, and other symbols follow common notations. The effective moment of the HS species, $\mu_{HS}{}^2$, is given as a constant independent of temperature. The results of the analysis are compiled in TABLE 1.

Notable features of the spin equilibria in FIGURE 1 are: the existence of the high-spin residue component down to very low temperature and the depression of $T_{1/2}$ compared to that in solution. Both features should arise from the reduction of energy gap between the HS and LS states. Since the HS species has a larger molecular volume than the LS species, such a reduction of the energy gap is not expected in an isotropic compression similar to hydrostatic pressure. Thus the anisotropic deformation should be taken into account for the effect of confinement into the interlayer space.

TABLE 1 Thermodynamic parameters of spin equilibria for the spin-crossover iron complexes in different molecular environments.

complex	in montmorillonite			in NaTSM			in solution		
	c_i	ΔH_i	ΔS_i	c_i	ΔH_i	ΔS_i	ΔH	ΔS	ref.
$[\mathrm{Fe(amp)_3}]^{2+}$	0.72	0.08	6	0.50	0.1	25	21.3	71.1	8
	0.12	3.8	23	0.44	0.4	10		$(\mathrm{CH_3CN})$	
	0.16	9.4	36	0.06	8.6	40			
$[\mathrm{Fe(acpa)_2}]^{+}$	0.20	0.14	2	0.49	0.1	12	19.0	78.8	2
	0.32	4.9	13	0.51	5.5	2		(acetone)	
	0.48	19.9	52						
$[\mathrm{Fe(sal_2trien)}]^{+}$	0.36	0.07	21	0.56	0.04	2.2	21.4	65.7	9
	0.37	7.0	21	0.12	2.2	14		$(\mathrm{H_2O})$	
	0.27	28.6	47	0.32	7.0	23			

† ΔH values in the table are written in kJ $\mathrm{mol^{-1}}$ and ΔS values in J $\mathrm{K^{-1}\,mol^{-1}}$.

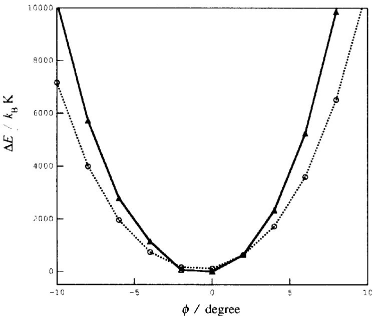

FIGURE 3 Adiabatic potential curves for the HS (O) and LS (Δ) states of the $[Fe(acpa)_2]^+$ complex under the acpa-ligand twisting(ϕ). Lines are for the sake of eye guide.

The effect of ligand torsion on the relative stability of the HS and LS states was examined by DFT calculations for the $[Fe(acpa)_2]^+$ model system. The molecular structures of $[Fe(acpa)_2](PF_6)$ were already solved for the LS state at 120 K and for the HS state at 290 K, in the same space group *P*2/*a*[5]. These X-ray structures were adopted as reference structures in the present calculations. Two acpa-ligand moieties in a molecule are related by a 2-fold axis on the iron atom, and the dihedral angle between two acpa ligands, defined around an axis perpendicular to the 2-fold axis, was taken as the molecular deformation coordinate since it is expected to be one of the most floppy modes and sensitive to an uniaxial stress imposed by host layers. In every 2 degrees of dihedral twisting, single-point unrestricted SCF calculations were run for both the HS and LS structures using Gaussian94 program suite with the B3PW91 hybrid energy functional and the LANL2DZ basis set implementing effective core potential[6]. The obtained SCF energies are plotted in FIGURE 3. These two adiabatic potential curves have roughly parabolic profiles. The acuteness of the LS curve is consistent with the fact that the skeletal vibration frequencies of the HS species are lower than those of the LS species having more compact molecular structure[7]. The LS state, which is more stable by *ca.* 100 k_B K under no distortion ($\phi = 0$), is destabilized with the ligand twisting and the ground state is switched from the LS to the HS state in the large distortion region ($|\phi| > 3°$). This tendency should explain the spin-equilibrium behavior of the complexes in the interlayer space of intercalation compounds.

In conclusion, several NaTSM intercalation compounds incorporating with SC complexes were synthesized and studied by magnetic susceptibility measurement and ^{57}Fe Mössbauer spectroscopy. Their SC behaviors were very similar to ones in montmorillonite analogs[2] and confirmed that the confinement into narrow interlayer spaces stabilizes the HS state relative to the LS state in spite of the larger molecular volume of the HS species. This tendency was rationalized by DFT calculations taking account of anisotropic molecular deformations under uniaxial pressure due to the host layer.

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