Effects of the Encapsulation of Alkali Ions into Iron(III) Complexes with a Macrocyclic Ring on Magnetic Properties

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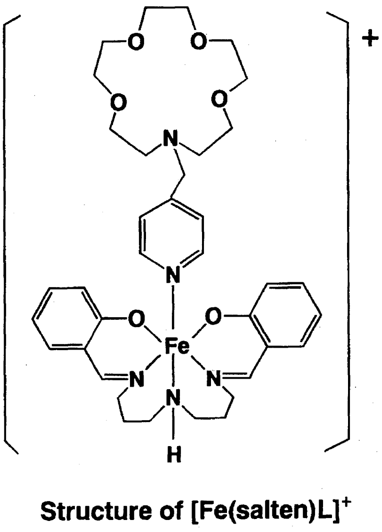
New spin-crossover iron(III) complexes [FeM(salten)L]X with an alkali ion in a macrocycle have been prepared, and the magnetic properties of the complexes in the solid and in acetonitrile solution have been examined, where M is Li^+, Na^+, K^+, or Rb^+, H_2salten is 4-aza-heptamethylene-1,7-bis(salicylideneiminate) and L is *N*-(4-picolyl)-aza-15-crown-5-ether. The spin-crossover behaviors of the iron(III) complexes dependent on temperature in the solid are observed on the Mössbauer spectra and magnetic susceptibilities, and those in acetonitrile on the electronic spectra. The magnetic properties of the complexes in the solid are changed with the species of alkali metal ions included in a macrocycle. Li-complexes show the magnetic moment of 4.00 B.M. at 300 K and 2.19 B.M. at 80 K, and Na-complexes 5.03 B.M. at 300 K and 4.21 B.M. at 80 K. The Mössbauer spectra of Li-complexes show that the interexchange rates of the spin-state transition between high-spin and low-spin states are as fast as the reciprocal of the lifetime of the excited state of ^{57}Fe(10^{-7}s) above 110 K. The magnetic behaviors of all of the complexes in acetonitrile are similar.

Spin-crossover iron(II) and iron(III) complexes, and other transition metal complexes of d^4–d^7 have been intensively studied because the change in the electronic ground state is combined with chemical reactions in vivo.[1—5] Recently, the application of spin-crossover complexes to various electronic devices (optical information storage, display devices, molecular switches, and so on) has been noticed.[6,7] The bistable character expected for spin-crossover complexes in useful because the magnetic properties of the spin-crossover complexes are changed with temperature, pressure, or electromagnetic radiation, which induce structural change at the molecular and lattice levels. Gütlich et al.[8—12] and Hauser et al.[13,14] have developed LIEST (light-induced excited-spin-state trapping), and Zarembowitch et al.[15,16] have developed LD-LISC (ligand-driven light-induced spin-change). In the former case, samples are irradiated with light of 550 nm to induce the $^1A_1 \rightleftarrows {}^1T_1$ transition and in the later case, the photochemical isomerization of ligands from *trans* to *cis* with light of 360 nm is induced. Hendrickson et al. have reported light-induced electronic state and species.[17,18] LIEST experiments using VTFTIR measurement[19,20] and spin state transition via field excitation[21] have been reported. Real et al.[22] have attempted to clarify the nature of the cooperative mechanism of a catenane supramolecule in spin crossover systems by correlating the structural change with magnetic susceptibility.

It is of significance to do research on other external triggers which drive spin-state transition. A number of supramolecular systems have been studied and some of them have been developed as a sensor for ion-recognition and as intelligent materials,[23,24] and there have been numerous reports on the interaction within crown ether-alkali metal systems.[25,26] Recently macrocyclic polyethers containing metal cations in intramolecular cavities have been reported.[27—33] We tried to trigger the electronic spin-state transition of metal-ions of the complexes in solution by ion-recognition. In this work the iron(III) complexes with aza-crown ether shown in Scheme 1 are prepared, and the magnetic properties of the complexes in the solid and in acetonitrile solution, and the effects of encapsulation of alkali metal ions into the aza-crown ether of [Fe(salten)L]ClO_4 on the magnetic properties are examined



Structure of [Fe(salten)L]$^+$

Scheme 1.

using magnetic measurement, Mössbauer spectroscopy, absorption spectroscopy, and EPR. Preliminary results on the magnetic and spectroscopic properties in the absence and presence guest substrates are reported.

Experimental

Preparation of the Ligands. ***N*-(4-Picolyl)-aza-15-crown-5-ether:** A water solution containing 0.46 mmol of 4-chloromethylpyridine hydrochloride was neutralized by an excess of a solution of saturated potassium carbonate with mixing, the green oil produced was extracted from the water phase with chloroform, and the organic solvent was evaporated to dryness. The oily residue was added to 1-aza-15-crown-ether (0.46 mmol; 1.0 g) in 100 ml of acetonitrile. The mixed solution was refluxed with anhydrous calcium carbonate (2.3 mmol) for 18 h and then was chromatographed with silica gel 60 and acetonitrile. The ligand *N*-(4-picolyl)-aza-15-crown-5-ether was obtained as a yellow oil and is abbreviated as L. Yield was 77%. Calcd for *N*-(4-picolyl)-aza-15-crown-5-ether 2: C, 74.38; H, 6.90; N, 5.03%. Found: C, 73.90; H, 6.57; N, 5.13%. FAB Mass spectrum *m/z* 311 ($M+H^+$); ^{1}H NMR (CD_3CN) δ = 2.80 (4H, t), 3.66 (54H, m), 7.31 (2H, d), 8.51 (2H, q).

Salten: Salten was prepared by the reported method.[34)]

Preparation of the Complexes. **Li-Complexes:** Dipropylenetriamine (3.5 mmol) was added to salicylaldehyde (7 mmol) in methanol (100 ml) and the solution was stirred for 1 h. To the solution iron perchlorate (3.5 mmol) was added with a little 2, 2′-dimethoxypropane and the solution was stirred. After 30 min, ligand L (3.5 mmol) in methanol (5 ml) was added and then $LiBPh_4$ (3.5 mmol) in methanol (30 ml) was added slowly. The precipitated materials were recrystallized five times from dichloromethane and a mixed solution of acetone and ethanol. Final products show blue-purple color at room temperature and green at 78 K.

Other complexes were prepared using $NaBPh_4$, $KBPh_4$ or $RbBPh_4$ in terms of $LiBPh_4$, respectively and showed a reddish purple color at room temperature and dark green at 78 K. Iron complexes without guest ions were prepared in a similar manner using $Fe(ClO_4)_3\cdot 6H_2O$. The complexes were obtained as powder and contained many impurities. The pure complexes were obtained from many times repeated crystallization from dichloromethane and a mixed solution of acetone and ethanol. Anal. Calcd for [FeLi(salten)(L)]$(BPh_4)_2$ **1**: C 74.26; H, 6.95; N, 5.04; Fe, 4.12; Li, 0.51%. Found: C, 73.80; H, 6.65; N, 5.19; Fe, 4.14; Li, 0.53%. Calcd for [FeNa(salten)(L)]$(BPh_4)_2$ **2**: C, 74.38; H, 6.90; N, 5.03; Fe, 3.96; Na, 1.68%. Found: C, 73.90; H, 6.57; N, 5.13; Fe, 4.09; Na, 1.62%. Calcd for [FeK(salten)(L)]$(BPh_4)_2$ **3**: C, 73.73; H,6.94; N, 4.79; Fe, 4.15; K, 2.83%. Found: C, 73.00; H, 6.50; N, 5.07; Fe, 4.04; K, 2.74%. Calcd for [FeRb(salten)(L)]$(BPh_4)_2$ **4**: C, 71.40; H, 6.68; N, 4.61; Fe, 3.87; Rb, 5.99%. Found: C, 70.70; H, 6.28; N, 4.91; Fe, 3.91; Rb, 6.10%. Calcd for [Fe(salten)(L)]$(ClO_4)_2\cdot 2H_2O$ **5**: C, 51.52; H, 6.37; N, 8.35; Fe, 6.66%. Found: C, 51.89; H, 6.18; N, 8.02; Fe, 6.53%.

Fast atom bombardment (FAB) mass spectra were obtained using a JMS-SX/SX 102A tandem mass spectrometer. A mixture of glycerin–DMF was used as a matrix. The complex **2** shows significant peaks at m/z = 1045.70 and 1023.70 as shown in Fig. 1. The former peak is assigned to $\{[FeNa(salten)(L)]BPh_4\}^+$ and the latter peak to $\{[FeH(salten)(L)]BPh_4\}^+$. The FAB mass spectrum of complex **5** shows a peak at m/z = 703.60 assigned to $[Fe(salten)L]^+$. Although the observation of these data supports the idea that the stoichiometries of the complexes are in agreement with those estimated from the analytical data, the complexes may contain other molecules, i.e. water, or the solvent molecules used. The compounds of large crown ethers and aza-crown ethers often have a "sandwich" structure in which metal ions are inserted between crown rings. Although such structures were not suggested from the FAB mass spectra, the chemical structure of the complexes should be confirmed further.

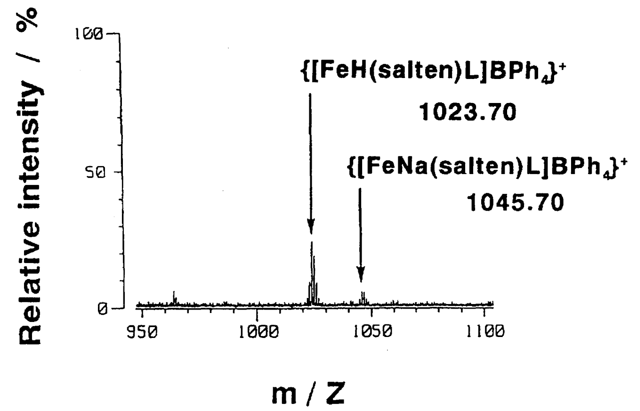


Fig. 1. FAB mass spectrum of Na-complexes.

Physical Measurements. The magnetic susceptibilities of the polycrystalline samples were measured by the Faraday method using a type 2002 (Cahn Instrument) electrobalance with an electromagnet (0.8 T). Temperature was controlled over the range 78—300 K by a digital temperature controller, model 3700 (Scientific Instruments). Heating rates were controlled manually and magnetic data for one heating measurement were collected in about 5 h. $HgCo(NCS)_4$ was used as a calibration standard. Effective magnetic moments were calculated by use of the formula $\mu_{\mathrm{eff}} = (8\chi_{\mathrm{m}}T)^{1/2}$, where χ_{m} is the molar susceptibility after applying a diamagnetic correction. The values of magnetic susceptibility of the complexes in acetonitrile were measured by the Gouy method.

Mössbauer spectroscopy was done with a constant-acceleration spectrometer (Austin Science Associates (ASA)). Data were stored in a 1024-channel pulse height analyzer, Type 5200 (Inotech, Inc.). The temperature was monitored with a calibrated copper vs. constantan thermocouple within a variable-temperature cryostat, DN1726 liquid nitrogen cryostat (Oxford). A cobalt-57 source of 10 mCi diffused into palladium foil was used for the absorption measurement. The spectra were fitted to a Lorentzian line shape by using a software of IGOR Pro (Wave Metrics, Inc.) on a personal computer. Isomer shifts are reported with respect to the centroid of the spectrum of iron foil enriched with ^{57}Fe.

Electronic spectra of an acetonitrile solution containing the samples (5×10^{-5} mol l^{-1}) and reflection spectra were recorded using a UV-3100PC UV-vis-NIR scanning spectrophotometer (Shimadzu) in the region from 350 to 700 nm. ESR spectra were measured on a X-band spectrometer [FEX (JEOL) calibrated with MnO in MgO].

Results and Discussion

Magnetic Susceptibility. Iron complexes [Fe(salten)(py)]BPh_4 and [Fe(salten)(2Me-im)]BPh_4 have been reported to be spin-crossover complexes by Matsumoto et al.,[35)] and the crystal structures for some of them have been identified. Salten is a pentadentate ligand and the sixth coordination of the moiety of an iron atom is occupied by the nitrogen atom of ligand L. The moiety of iron atoms of the complexes prepared here is assumed to be similar to that of [Fe(salten)(4me-py)]BPh_4 of which the structure has been analyzed. The temperature dependence of the magnetic moment of complex **5** is plotted in Fig. 2 with those for other complexes. Alkali metal ions in the aza-crown of the complexes are not encapsulated, but H_2O molecules may be. The value of the magnetic moment of complex **5** is 4.20 B.M. at 80 K, and 4.85 B.M.at 300 K, supporting the possibility of an incomplete spin-state transition in the temperature range studied. The values of the magnetic moments of the complexes at 80 and 300 K are listed in Table 1 with those in acetonitrile.

It has been known that Li^+ and Na^+ preferentially form complexes with 15-crown-5-derivatives and that Li^+ and Na^+ ions selectivities are also observed for several modified 1-aza-15crown-5-derivatives.[28] Aza-15-crown-5-derivatives, lariat ethers having a pyridylmethyl group as its sidearm, have excellent Ag^+ ion selectivity.[28] Alkali metal ions form complexes with aza-crown ethers mainly by electrostatic interactions and have no strict stereochemical demands for a specific co-ordination geometry. Therefore the encapsulation of alkali metal ions into L is expected to bring about a weak change in the co-ordination geometry of the iron sites. The values of the magnetic moments of Li-complexes are lower than those of the others in the temperature range observed, which may be due to a packing effect in solid state.

The crystal ionic radii (co-ordination number is six) for Li^+, Na^+, K^+, and Rb^+ ions are 0.78, 1.03, 1.39, and 1.52 Å, respectively, and the cavity of the aza-crown ether is estimated to be 1.7—2.2 Å in diameter. The size ratio of metal ion/cavity size in consideration of crystal packing and the interaction between solvent and metals in solution become important.

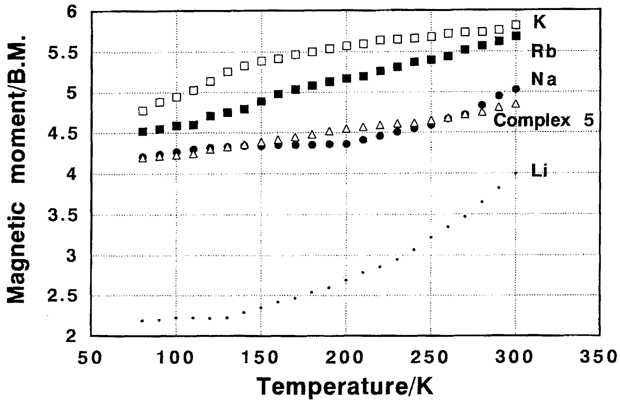


Fig. 2. Temperature dependence of the magnetic moment for the complexes. Li; Li-complex, Na; Na-complexes, K; K-complexes, Rb; Rb-complexes.

Table 1. Magnetic Moments for the Complexes at 80 and 300 K, and in Acetonitrile (B.M.)

	B.M.		
Complexes	at 80 K	at 300 K	in Acetonitrile[a]
1	2.19	4.00	5.4
2	4.21	5.03	4.9
3	4.78	5.82	5.4
4	4.52	5.68	4.9
5	4.20	4.85	4.3

a) Measured at 293 K.

The magnetic susceptibilities of the complexes in acetonitrile were measured and those for Li-, Na-, Rb-, and K-complexes in acetonitrile are 5.4, 4.9, 5.4, and 4.9 B.M. at 293 K, respectively and that for complex **5** is 4.3 B.M. The complexes including alkali metal ions in a crown ether show similar values to that of the complexes including no alkali metal ions.

Mössbauer Spectra and EPR. The temperature dependence of Mössbauer spectra was measured for the complexes. Figure 3 shows the Mössbauer spectra for Li-complexes at various temperatures. The Mössbauer spectrum at 78 K shows a large doublet with quadrupole splitting $\Delta E = 2.92$ mm s^{-1} and isomer shift $\delta = 0.20$ mm s^{-1}, which are characteristic of low-spin complexes, and a weak high-spin doublet with $\Delta E = 0.50$ mm s^{-1} and $\delta = 0.25$ mm s^{-1}, in accordance with the value of 2.19 B.M. at 80 K. The species showing the high-spin doublet may be impurities because the value of the quadrupole splitting observed is small compared with those observed for the other complexes. The spectrum at 298 K is not one characteristic of high-spin complexes in accordance with the value of 4.00 B.M; the spectrum shows a large doublet with the value of isomer shift close to that for the low-spin state. This observation suggests that the spin-state interexchange between high-spin and low-spin states is fast at high temperature and then the average spectrum is

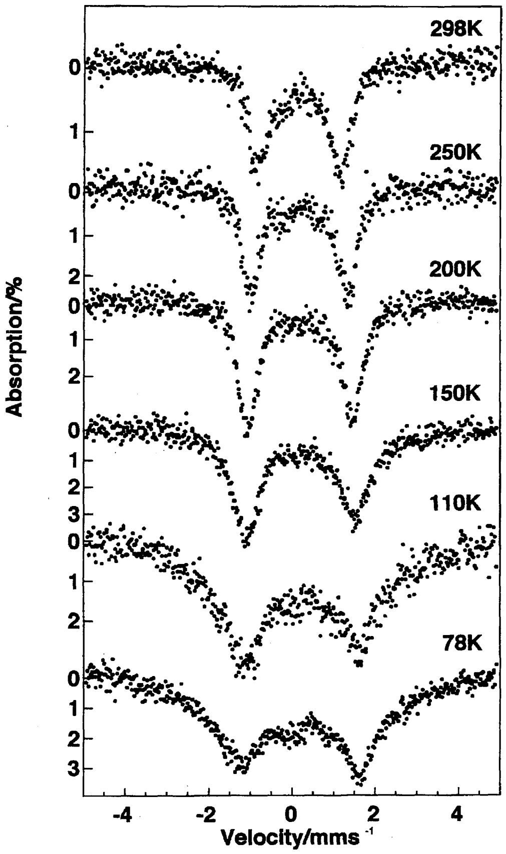


Fig. 3. Mössbauer spectra for Li-complexes at various temperatures.

observed. The interexchange rate is probably faster than the reciprocal of the lifetime of the excited state of a Mössbauer nuclide ^{57}Fe (10^{-7} s) and the rates are at least faster than 10^7 s above 110 K. A similarly rapid interexchange has been observed for [Fe(salten)(2Me-im)]BPh$_4$.[34]

Absorptions due to high-spin and low-spin species are observed for the other complexes at 78 K. The absorption of high-spin state is observed for K- and Rb-complexes at 298 K in accordance with the result of the magnetic susceptibilities. The Mössbauer parameters for the complexes are collected in Table 2. The values of isomer shifts for K- and Rb-complexes are 0.36 and 0.35 mm s^{-1} at 298 K, larger than those for the other complexes. The quadrupole splitting of Na-complexes is larger than those of K- and Rb-complexes at 298 K, supporting the idea that Na-complexes show rapid interexchange between high- and low-spin states and that Na-complexes are richer in the low-spin state than K- and Rb-complexes, in accordance with the value of the magnetic moment of 5.03 B.M. at 300 K. The full widths at half maximum (FWHM) observed for the complexes were larger than the theoretically observed value 0.20 mm s^{-1}. The reasons for the broadening of the width are complex. First, the complexes show relaxation spectra due to rapid spin-state interexchange between high-spin and low-spin states, and secondly the broadening at 78 K results in spin–spin relaxation because the volume of a molecule of the complex is so big that the intermolecular Fe–Fe distance is long. The existence of two iron sites is denied by the observation of a single low-spin species in EPR spectra shown in Fig. 4.

The EPR spectra of Li- and Na-complexes were measured at 78 and 298 K. Absorptions observed at $g = 2.80, 2.08$, and 1.81 for Li-complexes at 78 K are characteristic of a low-spin iron(III) in rhombic octahedral and that at $g = 4.39$ is assigned to a high-spin iron(III). An absorption due to a low-

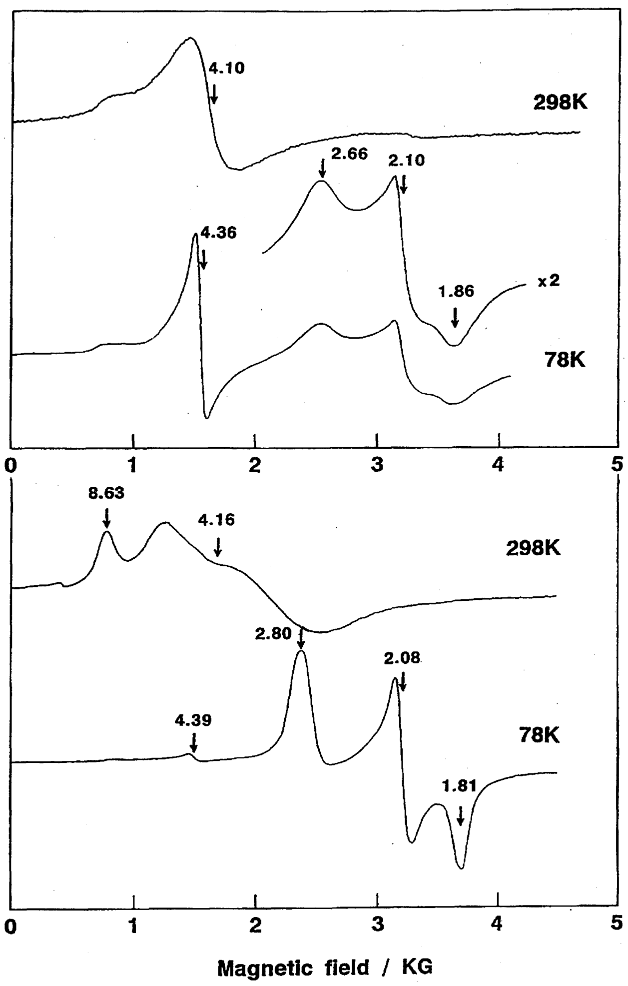


Fig. 4. EPR spectra for Li- and Na-complexes. Lower two spectra for Li-complexes and upper two spectra for Na-complexes.

Table 2. Mössbauer Parameters for the Complexes

Complexes	Temp	Low-spin species				High-spin species				FR$_{\mathrm{hs}}$ d)
		Δ	δ	Γ_{l} a)	Γ_{h} b	Δ	δ	Γ_{l} a)	Γ_{h} b)	%
1	78	2.92	0.20	1.67	1.57	0.50	0.25	0.78 c)	0.78 c)	3 e)
2	78	2.73	0.27	1.12	0.37	1.12	0.40	1.11 c)	1.11 c)	42
3	78	2.19	0.36	1.42	1.51	0.97	0.45	0.56	0.45	66
4	78	2.68	0.28	1.21	1.05	0.91	0.45	0.71	0.57	53
5	95	2.68	0.28	0.60 c)	0.60 c)	1.46	0.27	1.10 c)	1.10 c)	50

The parameters listed below were obtained by analyzed the spectra as a doublet.

		Δ	δ	Γ_{l} a)	Γ_{h} b)
1	110	2.76	0.22	1.57	1.88
	150	2.66	0.22	0.77	1.07
	200	2.56	0.21	0.54	0.66
	250	2.36	0.18	0.50	0.58
	298	1.96	0.23	0.82	0.57
2	298	1.38	0.33	1.20	1.20
3	298	1.12	0.36	0.81	0.72
4	298	0.93	0.35	0.71	0.71
5	298	1.20	0.28	0.96	1.06

a) Full width at half maximum for a low energy line. b) Full width at half maximum for a high energy line. c) This absorption is analyzed with some constraints. d) Absorption area of high-spin species vs. the total absorption area. e) maybe impurities.

spin iron(III) is not observed at 293 K and these observations are in accordance with the results reported for other spin-crossover complexes.[36)]

Infrared Spectra. The variation of IR spectra of crown ethers with cation-encapsulation has been discussed by Pedersen.[37)] Figure 5 shows IR spectra for the complexes in the range from 900 to 1200 cm^{-1}, the stretching vibration of C-O bands is usually observed at about 1100 cm^{-1} and that of =C–O vibration at about 1250 cm^{-1}. An antisymmetric stretching band of C–O–C band of a crown ether is observed at 1150—1070 cm^{-1}. Complex **5** shows a broad peak at 1150—1070 cm^{-1}: a crown ring is flexible because there is no cation in a cavity and therefore the overlapped C–O bands in the 1150—1070 cm^{-1} are observed. On the other hand the spectrum for the Li-complex shows sharp bands in the 1150—1070 cm^{-1} region, which shows that lithium ions are symmetrically located in the plane of L. The spectra for Na- and K-complexes are broader than that for Li-complexes, showing the distortion of the aza-crown.

Electronic Spectra. Figure 6 shows reflection spectra for the complexes. The charge transfer (CT) bands for the high-spin species of [Fe(salten)py]X have been reported to be observed at about 430 nm and that for the low-spin species to be observed at about 530 nm.[34)] The CT bands for the high-spin species are observed in higher energy than that for the low-spin one. The CT bands observed for the complexes are the superposition of the CT bands of high-spin and low-spin species from the consideration of the values of magnetic moments for the complexes. Li-complexes are in a mixed state with a low-spin state of 62% and of a high-spin state of 38% (under an assumption that the values of magnetic moment of high-spin and low-spin states are 6.00 and 2.00 B.M., respectively) and K- and Rb-complexes are rich in a high-spin state. Na-complexes are in the middle between Li- and Rb(or K)-complexes. The observed reflection spectra are consistent with these considerations because Li-complex shows a broad band at about 600 nm, K- and Rb-complexes at about 530 nm, and the Na-complexes at about 560 nm.

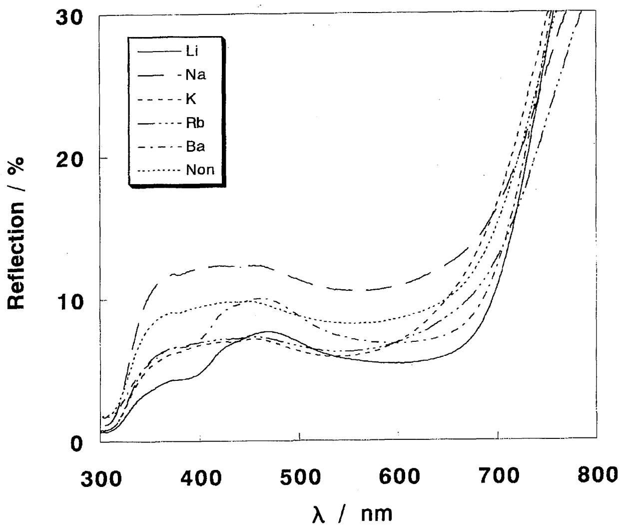


Fig. 6. Reflection spectra for the complexes at 293 K. Li; Li-complexes, Na; Na-complexes, K; K-complexes, Rb; Rb-complexes Non; complexes **5**.

The absorption spectra of the complexes in acetonitrile were measured in the temperature range from 273 to 333 K. The complexes show thermochromic behavior in acetonitrile solvent. The temperature dependence of the absorption spectra of Li-complexes is shown in Fig. 7. At 293 K the

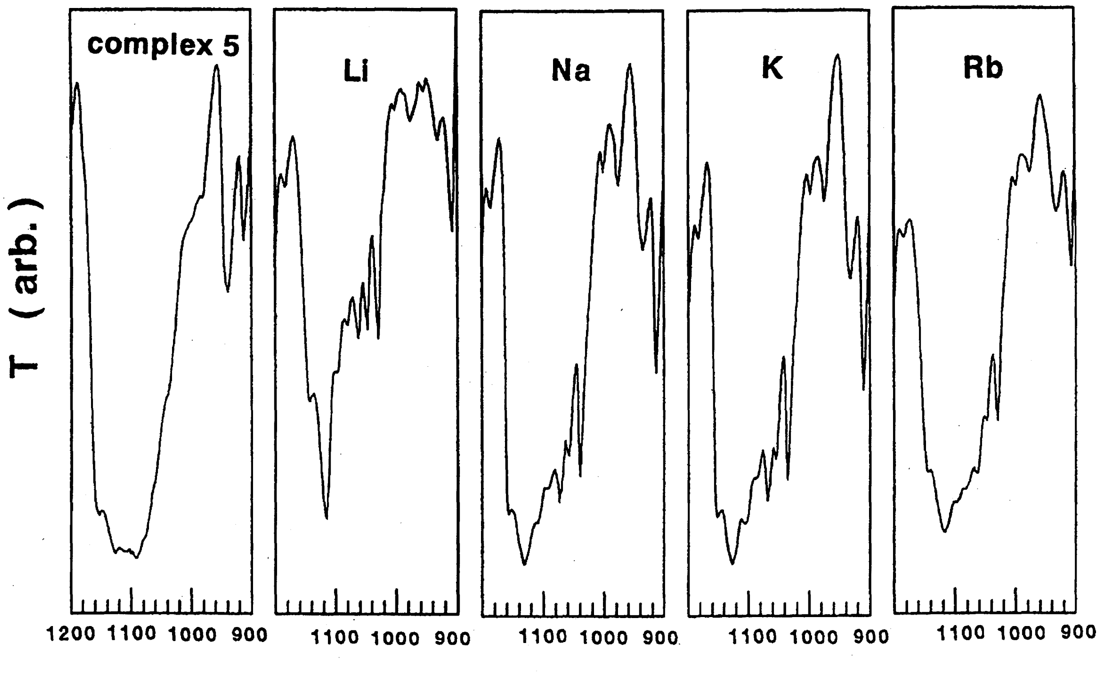


Fig. 5. IR spectra for the complexes. Li; Li-complexes, Na; Na-complexes, K; K-complexes, Rb; Rb-complexes.

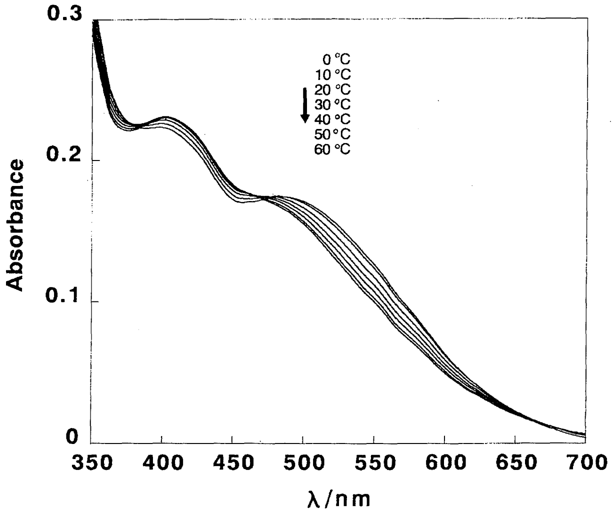


Fig. 7. Temperature dependence of the absorption spectra for the acetonitrile solution containing 5×10^{-5} mol dm^{-3} Li-complexes.

spectrum has two absorptions at 405 and 475 nm with absorption coefficient of 4.5×10^3 and 3.5×10^3 dm^3 mol^{-1} cm^{-1}, respectively. The CT bands observed at 475 nm in the absorption spectrum shift to low-energy side in the reflection. This observation suggests that the molecular structure of the complexes in acetonitrile is different from that in the solid state or the electronic state of iron atoms is influenced by the solvent. Absorption bands at 405 nm increase in intensity with rising temperature and the absorption bands at 475 nm have a significant blue shift with an decrease in intensity. The pseudo-isosbestic points are observed at about 375 and 470 nm but they are shifted. The color of the solution is blue-purple at room temperature and green at liquid nitrogen temperature. It should be pointed out that pseudo-isosbestic points are observed for these salten complexes although the spectra are reversible. The reason for the shift of the isosbestic point is not clear at this time because the time resolution of electronic spectra is short that 10^{-7} s, even if the complexes show rapid interexchange between high-spin and low-spin states. This observation, however, supports the idea that the complexes show spin-crossover behavior between the high- and low-spin states in acetonitrile. The spectroscopic behaviors of the other complexes were similar to that of Li-complexes.

Effects of Addition of Alkali Ions on Magnetic Properties. Addition of Na$^+$ (or Li$^+$) to an acetonitrile solution of complex **5** was tried to trigger the change in the spin-state of the complexes by the encapsulation of an alkali metal ion in aza-crown. The absorption at 400 nm is decreased in intensity and the absorption at around 500 nm shifts to a longer wavelength upon addition of NaClO$_4$. An isosbestic point is observed at 380 nm, although those in Fig. 7 are observed at 380 and 470 nm. The change in absorption spectra with addition of Na$^+$ ions suggests that the spin-state transition from high-spin to low-spin states may occur by addition of Na$^+$ although the spectral change is not similar to that observed in the temperature dependence. The complexes in solution with the addition of a stoichiometric volume of NaClO$_4$ was measured to be 4.5 B.M. The result from the absorption spectra was not consistent with the result obtained from the magnetic data. One of the reason may be the interaction of Na$^+$ with O (or N) atoms on an equatorial position resulted from the bending of L on the methylene carbon.

Addition of excess Na$^+$ (or Li$^+$) ions than stoichiometric ratio Li$^+$ (or Na$^+$)/Fe^{3+} = 1 does not bring about spectral change, which observation supports the idea that almost all of the Li$^+$ (or Na$^+$) cations added are included in the aza-crown of the complex for the strong interaction of Li$^+$ (or Na$^+$) ions with aza-crown of the complexes.

Conclusion. Spin-crossover behaviors of the iron(III) complexes dependent on temperature in the solid are observed in the Mössbauer spectra, EPR, and magnetic susceptibilities, and those in acetonitrile are confirmed by the electronic spectra. The magnetic properties of the complexes in the solid are changed with the species of alkali metal ions included in a macrocycle, and the Li complex is more rich in low-spin state than other complexes. The absorption spectra of acetonitrile solutions of the complexes are changed with temperature due to spin-crossover phenomena, and by addition of alkali ions.

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