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Magnetic Behavior of Spin-Crossover Iron(III) Complexes Adsorbed on the Surface of Silicon Dioxide and Metal Dilution Effects on Magnetism

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The effects of metal dilution and adsorption on the surface of silicon dioxide on the spin-crossover behavior of $[Fe(acpa)_2]PF_6$, $[Fe(acpa)_2]BPh_4$, and $[Fe(bzpa)_2]PF_6$, which undergo fast spin-state interexchange on the ^{57}Fe Mössbauer timescale have been studied by using ^{57}Fe Mössbauer and EPR spectroscopies, powder X-ray diffraction and magnetic susceptibility, where Hacpa is *N*-(1-acetyl-2-propylidene)-2-pyridylmethylamine and Hbzpa *N*-(1-benzoyl-2-propylidene)-2-pyridylmethylamine. Solid solution compounds, $[Fe_xCo_{1-x}(acpa)_2]BPh_4(x=0.035$ and $0.074)$ and $[Fe_{0.05}Co_{0.95}(bzpa)_2]PF_6$ exhibit spin-crossover phenomena. No difference in the spin-state interexchange rate is observed between the diluted compound and the corresponding undiluted one as far as the rates are evaluated by Mössbauer spectroscopy. Mössbauer spectra for $[Fe_{0.074}Co_{0.926}(acpa)_2]PF_6$ exhibit only a pair of quadrupole doublets assigned to the low-spin state in the temperature range from 78 to 298 K. The spin-state interexchange rates for $[Fe(acpa)_2]BPh_4$ and $[Fe(bzpa)_2]PF_6$ adsorbed on the surface of silicon dioxide become slow compared to those for the corresponding pure complexes and the narrowing of the spin-state transition temperature range is observed. On the contrary no detectable differences in the spin-state interexchange rates are observed between the Mössbauer spectra for $[Fe(acpa)_2]PF_6$ adsorbed on the surface of silicon dioxide and that for the pure complexes. These observations are interpreted in terms of a spin-state transition behavior in these complexes which is affected by the packing state in the solid state, which is dependent on the characteristic structure of the respective complex.

The study of thermally induced spin-state transition-(SST) phenomena has recently become an interesting research field.[1,2] Dynamical behavior in spin-state interexchange is caused by a cooperative solid state effect[3] and/or an intramolecular reorganization. It is important to gain some understanding about the mechanisms by which intermolecular interactions inhibit or enhance the rate of intramolecular spin-state interexchanges and to separate the intermolecular interaction from the intramolecular interaction. To solve the above problem, it is most effective to study the SST behavior in a system free from intermolecular interaction.

To study the nature of the interaction responsible for the spin-crossover behavior in "gradual transition type" complexes where SST takes place across a broad temperature range, the complexes $[Fe_xCo_{1-x}(acpa)_2]BPh_4(x=0.035$ and $0.074)$, $[Fe_{0.074}Co_{0.926}(acpa)_2]PF_6$, $[Fe_{0.05}Co_{0.95}(bzpa)_2]PF_6$, and the complexes adsorbed on the surface of silicon dioxide(SD) were prepared.

Mössbauer spectroscopy is a useful tool for observing spin-state interexchange rates because the lifetime of the excited state of ^{57}Fe is critical. For a system of a very rapid interexchange rate ($>10^7$ s^{-1}) iron nuclei "see" an average of the properties of the low-spin and the high-spin states in the Mössbauer spectrum which depends on the proportion of each state. For a slow system ($<10^7$ s^{-1}) the Mössbauer spectrum shows a superposition of the two electronic states. The magnetic, ^{57}Fe Mössbauer and EPR spectroscopic properties of the complexes have been examined by Maeda et al.[4–6] The spin-state interexchange rates of $[Fe(acpa)_2]PF_6$ are comparable to the reciprocal of the ^{57}Fe Mössbauer timescale (0.98×10^{-7}s) and those of $[Fe(acpa)_2]BPh_4$ and $[Fe(bzpa)_2]PF_6$ are fast on the ^{57}Fe Mössbauer timescale.

Gütlich et al. and Seki and Sorai studied the spin-crossover propersies of diluted solid solutions $[Fe_xM_{1-x}(phen)_2(NCS)_2]$ ($x=0.01$—1 and M=Mn, Co, Ni, and Zn),[7] $[Fe_xZn_{1-x}(2\text{-pic})_3]Cl_2\cdot C_2H_5OH$,[8,9] $[Fe_{0.01}Co_{0.99}(2\text{-}CH_3phen)_3](ClO_4)_2$[10] and $[Fe_xZn_{1-x}(ptz)_6](BF_4)_2$,[11] and suggested that for some systems the sizes of the low-spin domains decreased as the concentration of the host complexes increased.

Effects of counter ion sizes, solvation, grinding, and metal dilution on SST for $[Fe_xM_{1-x}(3\text{-}OCH_3\text{-SalEen})_2]PF_6$(M=Co, Cr)[12] and $[Fe_xCo_{1-x}(SalAPA)_2]ClO_4$[13] were studied by Hendrickson et al. They explained the various observations in terms of the nucleation and growth mechanism of phase.

All of these complexes except for $[Fe_xCo_{1-x}(SalAPA)_2]ClO_4$ are spin-crossover complexes of "abrupt transition type" (SST which takes place in narrow temperature range, i.e., 2 K) with large cooperativity. The metal dilution sometimes influences the spin-state interexchange rate (*R*), transition temperature range (ΔT) and the transition temperature (T_c) defined as the temperature at which equal amounts of the high-spin and low-spin states coexist.

Experimental

Iron complexes were prepared using enriched ^{57}Fe by the same method as described elsewhere.[15]

$[Co(acpa)_2]BPh_4$: An ethanol solution of $Co(CH_3COO)_2\cdot 4H_2O$ is added to a solution containing a Schiff base prepared by mixing acetylacetone and 2-(aminomethyl)-pyridine in ethanol. Oxidation to give Co(III) complexes was carried out by adding 30% H_2O_2 solution. After the oxidant was added, the solution was boiled for 5 min and an ethanol solution of K[BPh_4] was added to the solution. The precipitation was separated, washed with ethanol and recrystallized twice from CH_2Cl_2-methanol.

Other cobalt complexes were prepared with the same procedure as described above except that the [Co(bzpa)$_2$]BPh_4 was recrystallized from acetone.

The ^{57}Fe-doped cobalt complexes were prepared by dissolving the corresponding cobalt complexes together with the appropriate weight of ^{57}Fe enriched iron(III) complexes in the solvent used for recrystallization and then by evaporation to dryness. X-Ray powder diffraction patterns for [Fe(acpa)$_2$]BPh_4 and [Fe(bzpa)$_2$]PF_6 were similar to that for the corresponding cobalt complexes, respectively. The diffraction positions for the solid solutions [Fe_xCo_{1-x}(acpa)$_2$]BPh_4 and [$Fe_{0.05}Co_{0.95}$(bzpa)$_2$]PF_6 were situated near those for the corresponding cobalt complexes, respectively. The diffraction pattern for [Fe(acpa)$_2$]PF_6 did not agree with that of the corresponding cobalt complex. The diffraction pattern for [$Fe_{0.074}Co_{0.926}$(acpa)$_2$]PF_6 was the same as that for the corresponding cobalt complex.

Two types of silicon dioxide(SD) were used; SD(A) and SD(AB)(Fuji Davison Co.). They are characterized by pores of average diameter 2.2 and 4 nm and of specific surface 650 and 590 m^2 g^{-1}, respectively. Finely powdered SD was dried in vacuo at 120 °C before use. The iron complexes were adsorbed on the surface of the SD at room temperature.

SD(A) of 200 mg was introduced into a CH_2Cl_2 solution containing [Fe(acpa)$_2$]PF_6 of 15 mg. The solution was shaken for a few minutes. It turned pale in color and the SD was separated by using a glass filter. The iron content adsorbed on the SD was determined by an atomic absorption technique. The SD adsorbing the complexes was coated with cellulose adhesive (alcohol-free collodion solution diluted with ether) to avoid decomposition of the complexes. The saturated amounts of the complexes adsorbed on the SD were $(10.9\pm3.3)\times10^{-4}$ mol g^{-1}.

[Fe(acpa)$_2$]PF_6 of 7.7 mg was adsorbed on the surface of SD of 200 mg. This volume corresponds to the area occupation of 1.6×10^{-13} cm^2 (a spuare of 4 nm) per one molecule. The size of the molecule is about 0.85 nm in diameter, which is calculated from the data of the crystal structure.[5]

[Fe(acpa)$_2$]BPh_4 and [Fe(bzpa)$_2$]PF_6 adsorbed on SD were prepared with the same procedure as that for [Fe(acpa)$_2$]PF_6, except that SD(AB) was used for the former complex because the former complexes were adsorbed much more on SD(AB) than on SD(A). The saturated amounts of the complexes adsorbed on SD were $(1.1\pm0.1)\times10^{-4}$ mol g^{-1} for the tetraphenylborate and $(3.0\pm0.4)\times10^{-4}$ mol g^{-1} for the hexafluorophosphate.

Mössbauer spectra and magnetic susceptibilities were measured by using an apparatus described elsewhere.[6] EPR spectra were obtained with a FES-FEX(JEOL, Ltd.) X-band spectrometer. The Mössbauer spectra were fitted to Lorentzian lines by using a least squares method. The isomer shift, δ was calibrated relative to the center of a spectrum of iron foil enriched with ^{57}Fe at 296 K, which was also used as a standard material for the velocity calibration.

Results and Discussion

The purities of the iron and cobalt complexes were checked by elemental analysis for C, H, and N, and the magnetic behavior vs. temperature for the enriched iron complexes was similar to that reported before.[4,5]

Spin-Crossover Properties of the Iron Complexes Diluted with Cobalt Complexes. Figure 1 illustrates the temperature dependence of the Mössbauer spectra for [$Fe_{0.074}Co_{0.926}$(acpa)$_2$]BPh_4. The temperature dependences of the isomer shift and quadrupole splitting QS for [Fe_xCo_{1-x}(acpa)$_2$]BPh_4 are shown in Fig. 2. The decrease of the quadrupole splitting and the increase in the isomer shift for the diluted complexes

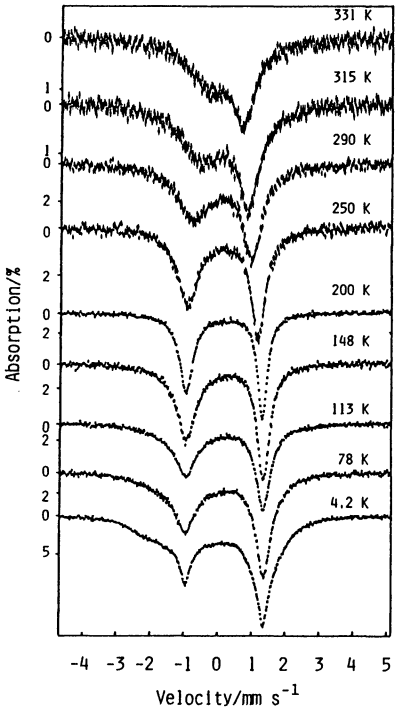

Fig. 1. Temperature dependence of Mössbauer spectra for [$Fe_{0.074}Co_{0.926}$(acpa)$_2$]BPh_4.

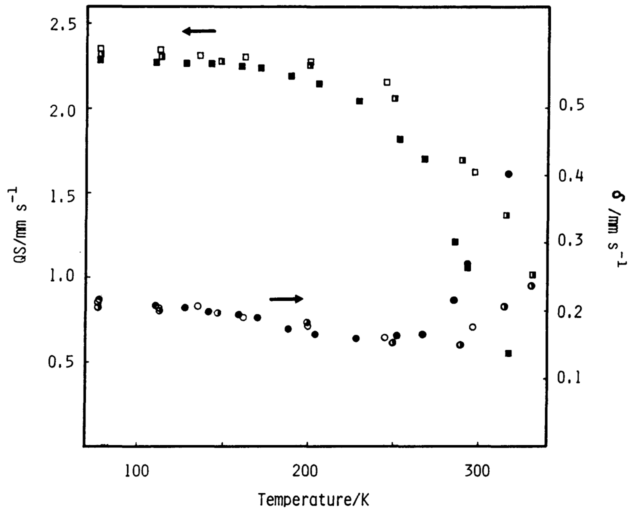

Fig. 2. Temperature dependences of the isomer shift and quadrupole splitting for [Fe_xCo_{1-x}(acpa)$_2$]BPh_4. QS; (■) for x=1, (◨) for x=0.074, (□) for x=0.035. δ; (●) for x=1, (◑) for x=0.074, (○) for x=0.035.

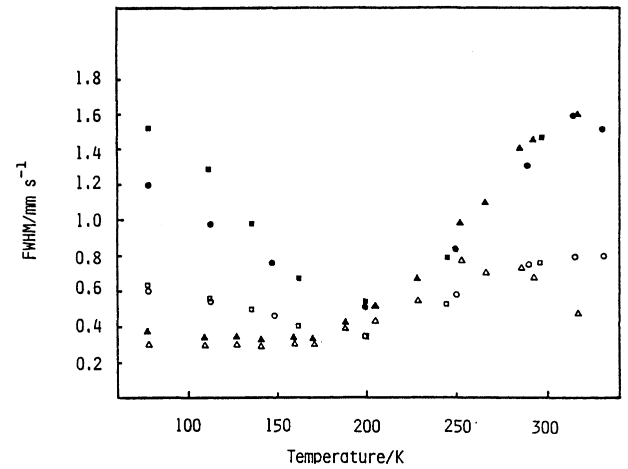

Fig. 3. Temperature dependences of fwhm for $[Fe_xCo_{1-x}(acpa)_2]BPh_4$. (△, ▲) for $x=1$, (○, ●) for $x=0.074$, (□, ■) for $x=0.035$. Open signs are for low energy line, closed ones for high energy line.

begin at higher temperature (about 20 K) than those for the undiluted complexes; the temperature range of SST for the diluted complexes shifts to higher temperature than that for the undiluted ones. Iron ions doped in cobalt complexes feel "positive pressure" by the lattice of the cobalt complexes because the radius of a cobalt(III) ion(0.075 nm in the high-spin state) is 0.004 nm smaller than that of an iron(III) ion(0.079 nm in the high-spin state). Therefore the ligand field at the position of an iron(III) ion becomes slightly stronger and thus the low-spin state is more stable. This "pressure effect/size effect" has been observed for some spin-crossover complexes.[7] The large shifts of T_c have been reported for $[(Fe_x, M_{1-x})(phen)_2(NCS)_2](M=Co, Cr, Zn)$ and $[Fe_xCo_{1-x}(3\text{-}OCH_3\text{-}SalEen)_2]PF_6$, which undergo "abrupt transition type" spin-crossover behavior. The complex $[Fe(acpa)_2]BPh_4$ belongs to the "gradual transition type" complexes, in which the coupling between SST and the lattice is supposed to be weak, and thus the small shift of T_c is reasonable. No difference in the spin-state interexchange rate between the diluted compound and the undiluted one is observed as far as the rates are evaluated by a Mössbauer spectroscopy.

The iron complexes doped in the cobalt complexes show broad spectra above or below 200 K. Figure 3 shows the temperature variation of full width at half maximum (fwhm) for $[Fe_xCo_{1-x}(acpa)_2]BPh_4$. The observation that the line broadening increases with rising temperature above 200 K shows that the decrease in mixing of the ^2T state with increase in temperature weakens the spin-spin interaction, because the interaction is significant in the high-spin iron(III) complexes ($^6A_{1g}$). The fraction of the low-spin isomers to the total isomers is estimated to be 0.77 at 200 K on the basis of the magnetic susceptibility data. The line broadening at temperatures below 200 K may result from the spin-lattice relaxation dependent on temperature and spin-spin relaxation. The reasons for the line broadening below 200 K are complex due to the magnetic effects and the spectral shape at 4.2 K is not similar to that for $K_3[Fe(CN)_6]$ doping $K_3[Co(CN)_6]$[14] This problem was not examined further, but the observation of the line broadening supports the view that the iron complexes are isolated.

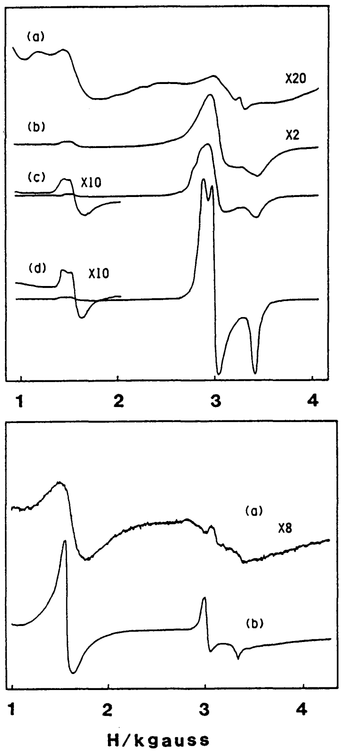

Fig. 4. Temperature dependences of EPR spectra for $[Fe_{0.035}Co_{0.965}(acpa)_2]BPh_4$ (in upper figure, a: 295 K, b: 193 K, c: 173 K, d: 130 K) and $[Fe_{0.05}Co_{0.95}(bzpa)_2]PF_6$ (in lower figure, a: 293 K, b: 78 K).

EPR spectra for the complexes were measured at various temperatures. The representative spectra are illustrated in Fig. 4 and the low-spin signals were observed at $g=1.965$, 2.219, and 2.291 for the diluted complexes. This observation suggests that an iron atom in the diluted complex is situated in a more distorted environment than that in the pure complex. The $g=4$ signal is characteristic of a high-spin ferric ion in a rhombically distorted environment.

The Mössbauer spectra for $[Fe_{0.05}Co_{0.95}(bzpa)_2]PF_6$ were measured at various temperatures and the temperature variations of the Mössbauer parameters are plotted in Figs. 5 and 6. In this case the effect of metal dilution on the magnetism is not clear except that slight line broadenings are observed. No observation of "pressure effect/size effect" for this complex shows that this effect does not have a dominant role in the stabilization of a low-spin state and that the effect of intermolecular interaction on spin-state transition may be weak for these complexes. SST properties T_c

and ΔT may be influenced by the lattice energy or elastic property of the complexes. The Mössbauer spectrum at 4.2 K is similar in the shape to that for $[Fe_{0.074}Co_{0.926}(acpa)_2]BPh_4$ except for the smaller quadrupole splitting observed. EPR signals for pure $[Fe(bzpa)_2]PF_6$ were very broad at 78 K,[4] but that for the diluted complexes are observed at $g_{//}=1.961$ and $g_{\perp}=2.166$ and the values are similar to that observed for pure $[Fe(acpa)_2]PF_6$. The observation of EPR spectra for the diluted complexes supports the view that the iron species are isolated satisfactorily in accordance with the results of the Mössbauer spectra measurements.

The Mössbauer spectra for $[Fe_{0.074}Co_{0.926}(acpa)_2]PF_6$ are shown in Fig. 7. From the Mössbauer spectrum for $[Fe_{0.074}Co_{0.926}(acpa)_2]PF_6$ at 298 K the ground state of the complexes is in a low-spin state. The iron complexes are not isomorphous with the cobalt complexes as seen from the powder X-ray diffraction patterns. The local geometric structure around an iron atom in $[Fe_{0.074}Co_{0.926}(acpa)_2]PF_6$ is assumed to be different from that in $[Fe(acpa)_2]PF_6$. This is reflected in the value of the quadrupole splitting; the diluted and pure complexes show QS=2.506 and QS=2.235 mm s^{-1} at 78 K, respectively. At 298 K the Mössbauer parameters for the former complex are QS=1.960 mm s^{-1} and δ=0.169 mm s^{-1}, and the decrease in the QS value for the diluted complexes is due to the increase in the population of the high-spin isomer or the temperature dependence of the quadrupole splitting. But the latter reason can be excluded because EPR analysis indicates that the first excited electronic state($^4T_2$) is at least 3000 cm^{-1} higher in energy than the ground state. The EPR signals for the low-spin isomer in the diluted com-

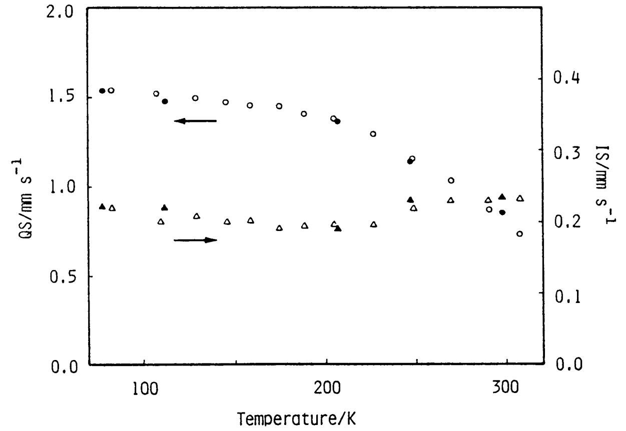

Fig. 5. Temperature dependences of the isomer shift and quadrupole splitting for $[Fe_{0.05}Co_{0.95}(bzpa)_2]PF_6$ (closed signs) and $[Fe(bzpa)_2]PF_6$ (open signs).

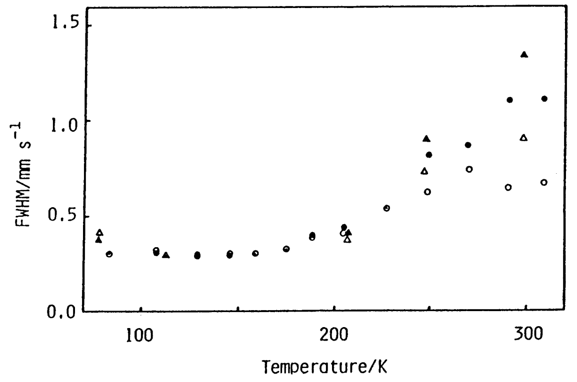

Fig. 6. Temperature dependences of fwhm for $[Fe_{0.05}Co_{0.95}(bzpa)_2]PF_6$ (○, ●) and $[Fe(bzpa)_2]PF_6$ (△, ▲). Open signs are for low energy peaks and closed ones for high energy peaks.

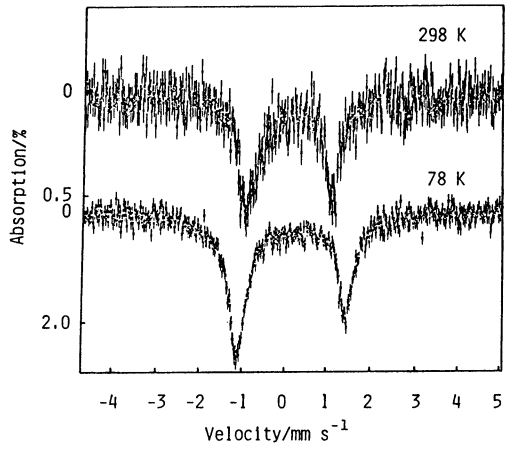

Fig. 7. Mössbauer spectra for $[Fe_{0.074}Co_{0.926}(acpa)_2]PF_6$ at 78 and 298 K.

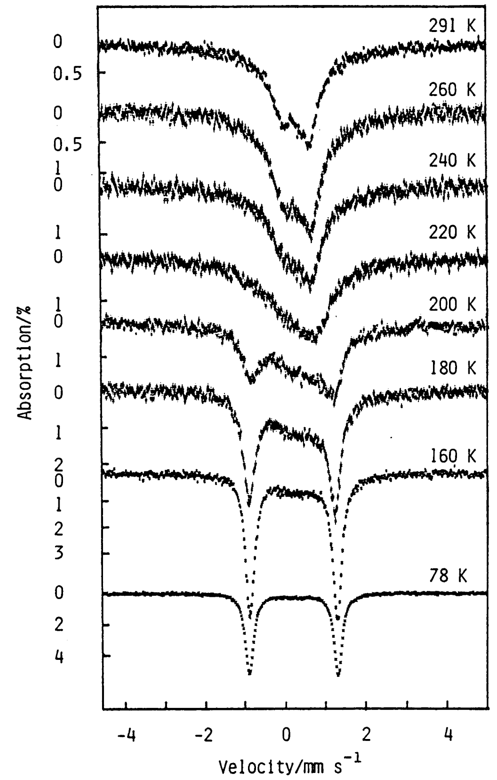

Fig. 8. Temperature dependence of the Mössbauer spectra for $[Fe(acpa)_2]PF_6$ absorbed on SD(A).

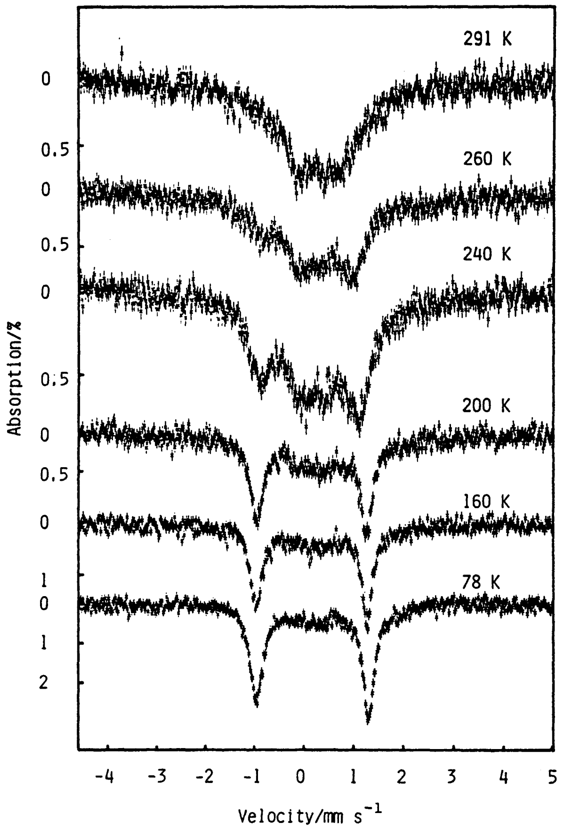

Fig. 9. Temperature dependence of the Mössbauer spectra for $[Fe(acpa)_2]BPh_4$ adsorbed on SD(AB).

plexes are observed at g=1.948, 2.207, and 2.287 at 130 K.

Spin-Crossover Properties of the Complexes Adsorbed on the Surface of SD. Figure 8 shows the temperature dependence of the Mössbauer spectra for $[Fe(acpa)_2]PF_6$ adsorbed on SD(A). These spectra apparently exhibit two pairs of quadrupole doublets; the inner doublet is assigned to the high-spin isomer and the outer doublet to the low-spin isomer. However it is assumed from the spectral shapes that the spin-state interexchange rate is comparable to the inverse of the Mössbauer lifetime. The apparent SST behavior—R, ΔT, and T_c— is estimated to be similar to that for the undiluted complexes. From the Mössbauer parameters for the low-spin isomers at 78 K, QS=2.187 mm s^{-1} and δ=0.198 mm s^{-1}, the geometric structure of the molecule on SD(A) is estimated not to be influenced by physical adsorption on SD in contrast to that of the diluted complexes.

It is curious that no line broadening is observed for the Mössbauer spectra of the complexes supported on SD and as one of the reasons it may be that the complexes are not isolated satisfactorily but adsorbed linearly in the pores. The EPR spectra for the complexes supported on SD are in accord with that for the pure complexes except that the former material shows a signal at g=4.

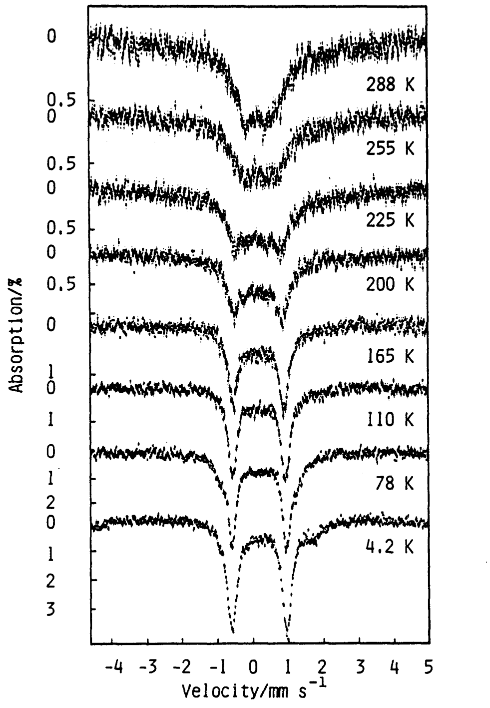

Fig. 10. Temperature dependence of the Mössbauer spectra for $[Fe(bzpa)_2]PF_6$ adsorbed on SD(A).

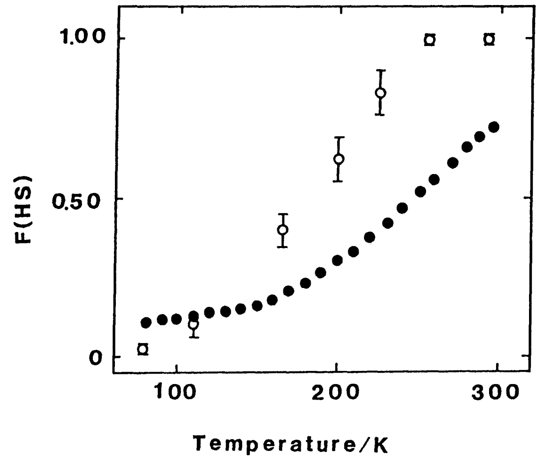

Fig. 11. Temperature dependences of the high-spin population F(HS) for $[Fe(bzpa)_2]PF_6$ adsorbed on SD(A) (○) and the pure complexes (●).

The Mössbauer spectra for $[Fe(acpa)_2]BPh_4$ and $[Fe(bzpa)_2]PF_6$ adsorbed on SD are illustrated in Figs. 9 and 10, respectively, in which the spectra show a superposition of the quadrupole doublets for the high-spin and low-spin isomers; The Mössbauer spectra at 78 K for both of the complexes show the existence of some impurity due to decomposed paramagnetic products and/or remaining high-spin species. In the spectra at 78 K (Fig. 9) the paramagnetic species and/or the high-spin isomers are observed in 0.4% absorption. They are observed in 0.7% absorption at 240 and 260 K. This illustrates that the absorptions in the center of the spectra are composed of that of the paramagnetic species and the high-spin isomers. That is, the spectra have a superposition of the spectra for the high-spin isomers and that for the low-spin isomers. This supports a fact that the packing effect enhances the spin-state interexchange rate because it is likely that the complexes feel "free" in the adsorbed state than in the solid state.

At 78 K the quadrupole splitting for the outer doublet(QS=2.254 mm s^{-1}) of the adsorbed $[Fe(acpa)_2]BPh_4$ is almost equal to that(QS=2.288 mm s^{-1}) of the pure complexes, and the quadrupole splitting(QS=1.539 mm s^{-1}) for the adsorbed $[Fe(bzpa)_2]PF_6$ is equal to that (QS=1.542 mm s^{-1}) for the pure complexes. This supports the view that the geometric structures of the adsorbed complexes are consistent with that of the corresponding pure complexes, respectively.

As a representative example the temperature dependence of population of the high-spin isomers F(HS) for $[Fe(bzpa)_2]PF_6$ is plotted in Fig. 11, where the values for the adsorbed complexes were estimated from the Mössbauer spectra and that for the pure complexes from the effective magnetic moments. For the adsorbed complexes corrected values were used because the paramagnetic species are observed in the Mössbauer spectrum at 78 K. The T_c for the adsorbed complexes is estimated to be about 60 K lower than that for the pure complexes, but this large shift is unreliable because the temperature dependence of recoilless fraction of the paramagnetic species is not taken into account. It is unfortunate not to be able to prepare pure samples free from the paramagnetic species. However it is likely that T_c for the adsorbed complexes shifts to lower temperature and that the complexes are essentially in a high-spin state at 300 K. Similar transition behavior is observed for the adsorbed $[Fe(acpa)_2]$-BPh_4.

The EPR spectra of $[Fe(bzpa)_2]PF_6$ adsorbed on SD were measured at 293 and 78 K. The EPR signals for the low-spin isomer are observed at $g_{/\!/}=1.960$ and $g_{\perp}=2.166$. These values are in accordance with that reported by Hendrickson et al. for the complexes dissolved in toluene and with that for the diluted complexes. This fact shows that the adsorbed complexes are satisfactorily isolated.

Finally the Mössbauer spectrum at 4.2 K for $[Fe(bzpa)_2]PF_6$ adsorbed on SD was measured. The high-spin species are not observed in the spectrum, but a shoulder which occurs at the Doppler velocity of 1.5 mm s^{-1} could have originated from decomposition products. The Mössbauer spectrum for $[Fe(bzpa)_2]PF_6$ decomposed by being kept in air on the surface of SD was measured. The relaxation spectrum of the magnetic hyperfine splitting observed will prove that the complexes are isolated from each other on the surface of SD.

The packing effects observed here are weaker than that for "spin transition type" complexes. The values of V and ΔV(V: volume per single molecule for the high-spin isomer, ΔV:volume difference between high-spin and low-spin isomers for single molecule) for $[Fe(acpa)_2]PF_6$ are $V=655.7$ Å^3, $\Delta V=23$ Å^3 and $\Delta V/V=3.5\%$. On the other hand for $[Fe(acpa)_2]BPh_4$ $V=1003.1$ Å^3. $\Delta V=34$ Å^3 and $\Delta V/V=3.4\%$ are observed.[15] Generally the ΔV values of from 23 to 98 Å^3, and $\Delta V/V$ values of from 3.4 to 6.2% are reported. These values for the complexes examined here seem to be in the same range as that reported for the abrupt transition type complexes. Hendrickson et al. have reported an example that the spin-state interexchange rate of diluted complexes is slower than that for the pure complexes.[13] Threfore, it is positive at the present time that spin-state interexchange rates are effected by crystal packing and that intramolecular SST takes place more or less under the co-oparativities with intermolecular interaction.

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