Spin-crossover of Tris[2-(aminomethyl)pyridine]iron(II) Ion in Y-Zeolite

Yasushi Umemura, Yoshitaka Minai, Noboru Koga and Takeshi Tominaga

Department of Chemistry, School of Science, University of Tokyo, Hongo, Tokyo 113, Japan

Mössbauer spectra and magnetic susceptibility measurement of *mer*-$[Fe(amp)_3]^{2+}$ and *fac*-$[Fe(amp)_3]^{2+}$ [amp = 2-(aminomethyl)pyridine] in supercages of Y-zeolite reveal that *mer*-$[Fe(amp)_3]^{2+}$ is high-spin even at 78 K whereas the spin-state of *fac*-$[Fe(amp)_3]^{2+}$ changes gradually from high- to low-spin as the temperature is decreased from 293 to 78 K, suggesting structural restrictions on the complexes in the supercage.

Spin-crossover of tris[2-(aminomethyl)pyridine]iron(II) $[Fe(amp)_3]^{2+}$ complexes has been extensively studied and reported in numerous papers.[1] It is well known that the spin state of the complex changes from low- to high-spin depending on temperature, in accordance with such structural changes as lengthening of the Fe–N bond from 2.0 to 2.2 Å,[2] decreases in the bite angle[3] and twisting around a threefold axis toward a trigonal prism.[4] Spin-crossover of $[Fe(amp)_3]^{2+}$ complex encapsulated in a small space, which is comparable to the size of the complex, would be expected to differ from that of the polycrystalline complex salt because structural change is restricted to the space. We report here spin-crossover of $[Fe(amp)_3]^{2+}$ in a Y-zeolite supercage with change in temperature.

$Fe^{II}Y$ zeolite prepared by ion exchange of NaY zeolite in aqueous $FeSO_4$ was suspended in aqueous amp (0.4 mol l^{-1}) at pH 1–2 for a day to form the complex in the zeolite supercage. After separation from the solution by decantation and washing with water several times, the zeolite was suspended in aqueous NaCl (0.4 mol l^{-1}) at pH 1–2 with an amount of amp for a day to replace ligand-free Fe^{2+} ion with Na^+ ion. After separation and repeated washing with water, greenish-brown zeolite encapsulating $[Fe(amp)_3]^{2+}$ was obtained. All manipulations were carried out under nitrogen atmosphere to minimize formation of Fe^{3+} species. The zeolite encapsulating $[Fe(amp)_3]^{2+}$ was dried *in vacuo* just prior to measurement since $[Fe(amp)_3]^{2+}$ in Y-zeolite can oxidize easily in air when it is dry.

Formation of $[Fe(amp)_3]^{2+}$ in the zeolite was verified by UV–VIS spectroscopy and XRD.[5] Magnetic susceptibility of $[Fe(amp)_3]^{2+}$ in the zeolite was recorded by SQUID, and the χT–T plot is shown in Fig. 1. The χT value was constant around room temp. and decreased gradually below 220 K.

Fig. 2 shows the Mössbauer spectra recorded at 293 and 78 K of $[Fe(amp)_3]^{2+}$ in the zeolite and $[Fe(amp)_3](ClO_4)_2$ polycrystalline powder. An asymmetric doublet (IS = 0.85, QS = 1.50 mm s^{-1}) attributed to high-spin Fe^{II} [Fig. 2(*a*)] and a singlet (IS = 0.52 mm s^{-1}) attributed to low-spin Fe^{II} [Fig. 2(*c*)] were seen in the spectra of $[Fe(amp)_3](ClO_4)_2$ recorded at 293 and 78 K, respectively. The spectrum of $[Fe(amp)_3]^{2+}$ in the zeolite at 293 K [Fig. 2(*b*)] was composed of two symmetric doublets (doublet A: IS = 0.40, QS = 0.76 mm s^{-1}; doublet B: IS = 1.02, QS = 2.35 mm s^{-1}) and an asymmetric doublet (doublet C: IS = 0.81, QS = 1.40 mm s^{-1}).

The IS and QS values of doublet A were similar to those for $Fe^{III}Y$ zeolite (IS = 0.38, QS = 0.71 mm s^{-1} at 293 K), and the

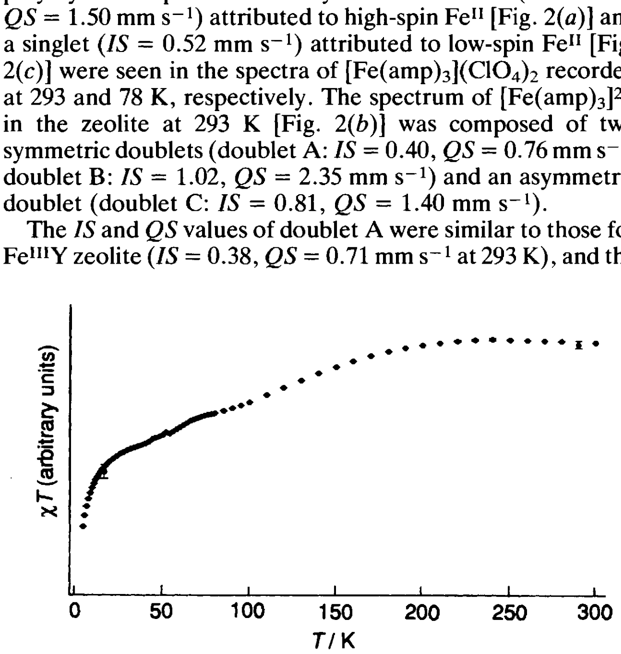

Fig. 1 χT–T plot for $[Fe(amp)_3]^{2+}$ in Y-zeolite

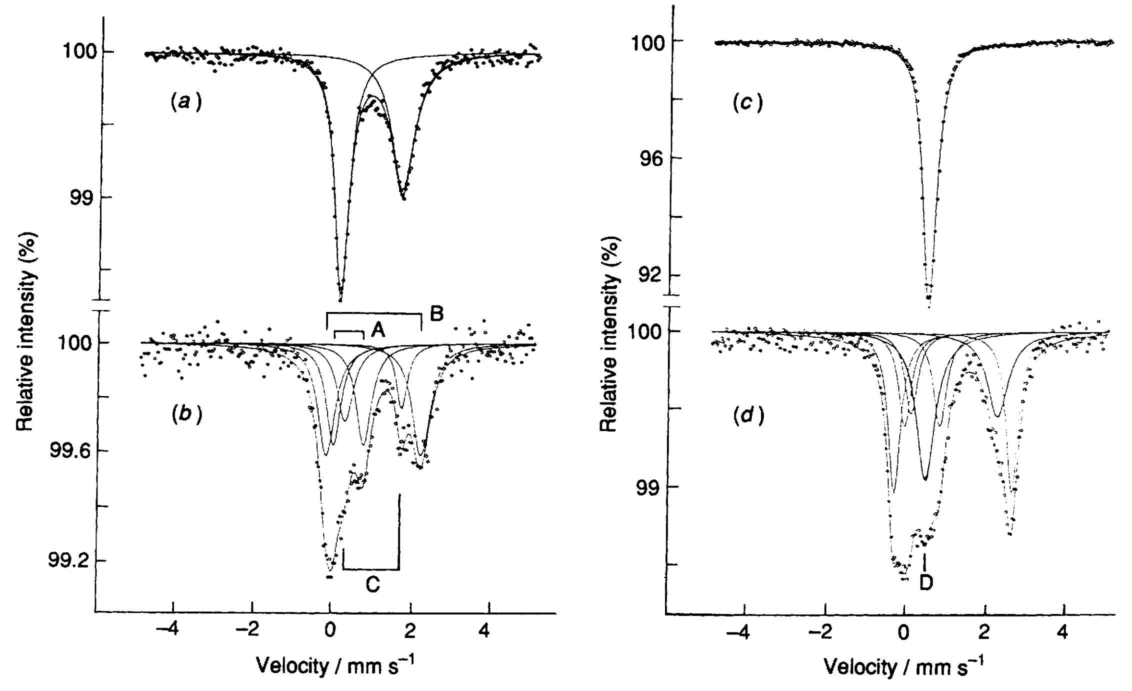

Fig. 2 Mössbauer spectra of $[Fe(amp)_3](ClO_4)_2$ (*a*) at 293 and (*c*) at 78 K, and $[Fe(amp)_3]^{2+}$ in Y-zeolite (*b*) at 293 and (*d*) at 78 K

doublet remained after exposure to air. Therefore, doublet A can be assigned to free Fe^{III} ion oxidized at the ion-exchange site of Y-zeolite. Since doublets B and C appeared after contact with the ligand solution, they can be ascribed to amp complexes in Y-zeolite. The Mössbauer parameters and asymmetry of doublet C were very similar to those of $[Fe(amp)_3](ClO_4)_2$. An IR study indicated that $[Fe(amp)_3](ClO_4)_2$ has facial configuration.[6] The Mössbauer spectrum at 293 K of $[Fe(6\text{-}mpy)_3tren](PF_6)_2$ [$(6\text{-}mpy)_3tren$ = tris{4-[(6-methyl)-2-pyridyl]-3-aza-3-butenyl}amine], which has facial configuration, also indicated an asymmetric doublet (*IS* = 0.98, *QS* = 1.43 mm s^{-1} at 294 K)[7] identical to those doublets. Accordingly, doublet C can be assigned to *fac*-$[Fe(amp)_3]^{2+}$ in Y-zeolite.

$[Fe(amp)_3]^{2+}$ in Y-zeolite was also prepared almost in the same way except using MeOH as solvent and methanolic $FeCl_2$. The Mössbauer spectrum (293 K) of $[Fe(amp)_3]^{2+}$ in the zeolite was composed of two doublets; *IS* = 0.37, *QS* = 0.84 mm s^{-1} and *IS* = 0.95, *QS* = 2.51 mm s^{-1}. The doublets correspond to, respectively, doublet A and doublet B in Fig. 2(*b*). However, no absorption corresponding to doublet C appeared in the spectrum. The UV–VIS spectrum of this sample suspended in methanol was similar to those of methanolic or aqueous $[Fe(amp)_3]^{2+}$. This implies that the doublet B can be ascribed to $[Fe(amp)_3]^{2+}$ formed in the zeolite.

The quadrupole splitting of doublet B was larger than that of doublet C ascribed to *fac*-$[Fe(amp)_3]^{2+}$ in the zeolite. Doublet B might be assigned to *mer*-$[Fe(amp)_3]^{2+}$ in the zeolite, because the *QS* value of the meridional complex, in general, tends to be larger than that of the facial isomer complex. For instance, the *QS* value of mer-$[Fe(amp)_3]Cl_2{\cdot}MeOH$ (*IS* = 0.95, *QS* = 2.03 mm s^{-1}), which is known as a spin-crossover complex,[4,8] is larger than that of *fac*-$[Fe(amp)_3](ClO_4)_2$.

The larger *QS* value of doublet B than that of *mer*-$[Fe(amp)_3]Cl_2{\cdot}MeOH$ may be related to distortion of $[Fe(amp)_3]^{2+}$ in the zeolite. If the (pseudo) threefold axis of $[Fe(amp)_3]^{2+}$ in the zeolite was parallel to that of the supercage, *fac*-$[Fe(amp)_3]^{2+}$ would be free from distortion (as will be discussed later), but *mer*-$[Fe(amp)_3]^{2+}$ would be distorted. This distortion would cause the *QS* value of the doublet B to be larger than that of *mer*-$[Fe(amp)_3]Cl_2{\cdot}MeOH$.

In the spectrum of $[Fe(amp)_3]^{2+}$ in the zeolite (78 K) prepared in aqueous solutions [Fig. 2(*d*)], a new singlet (singlet D: *IS* = 0.49 mm s^{-1}) developed. The isomer shift of singlet D is almost equal to that of the low-spin Fe^{II} peak in the spectrum of $[Fe(amp)_3](ClO_4)_2$ at 78 K (Fig. 2(*c*)], suggesting that singlet D is attributed to low-spin *fac*-$[Fe(amp)_3]^{2+}$ in the zeolite. Considering the decrease of magnetic susceptibility of $[Fe(amp)_3]^{2+}$ in the zeolite from 220 K (Fig. 1), it can be seen that the spin state of *fac*-$[Fe(amp)_3]^{2+}$ changed gradually from high- to low-spin with decreasing temperature.

In many spin-crossover complexes, including $[Fe(amp)_3](ClO_4)_2$, spin state becomes completely low spin at temperatures higher than 78 K, and the spin-state changes in a narrow range of temperature.[1,9] Gradual changes over a wide temperature range were reported for mixed crystals such as $[Fe_xZn_{1-x}(amp)_3]Cl_2{\cdot}MeOH$,[7,10] in which the interaction between the iron complexes is weaker than in the neat complex. Isolation of complex ions by a zeolite lattice will result in weakening of the interaction between the complexes and in the peculiar temperature dependence of populations in high- and low-spin states.

No change in spin state was seen in the Mössbauer spectra for *mer*-$[Fe(amp)_3]^{2+}$ in the zeolite over the temperature range from 293 to 78 K [Figs. 2(*b*) and 2(*d*)]. It was reported that the twist angle around a threefold axis from an ideal octahedron toward a trigonal prism was greater in a high-spin state than in a low-spin state.[4] Since it is expected that the octahedron of *mer*-$[Fe(amp)_3]^{2+}$ in the supercage is distorted by the zeolite lattice toward a trigonal prism around the threefold axis, *mer*-$[Fe(amp)_3]^{2+}$ in the zeolite maintained a high-spin state over a wide temperature range. On the other hand, *fac*-$[Fe(amp)_3]^{2+}$ will not be distorted because the pyridine rings of the ligands can protrude into the twelve-membered rings of the supercage. It is easy for *fac*-$[Fe(amp)_3]^{2+}$ to alter the molecular structure around the threefold axis even in the zeolite, accompanied by a change in the spin state.

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References

1 For example, P. Adler, H. Spiering and P. Gütlich, *J. Phys. Chem. Solids.*, 1989, **50**, 587; S. Decurtins, P. Gütlich, K. M. Hasselbach, A. Hauser and H. Spiering, *Inorg. Chem.*, 1985, **24**, 2174; G. A. Renovitch and W. A. Baker, Jr., *J. Am. Chem. Soc.*, 1967, **89**, 6377; H. L. Chum, J. A. Vain and M. I. D. Holanda, *Inorg. Chem.*, 1982, **21**, 1146.

2 J. K. Beattie, *Adv. Inorg. Chem.*, 1988, **32**, 1.

3 B. A. Katz and C. E. Strouse, *Inorg. Chem.* 1980, **19**, 658.

4 A. M. Greenaway and E. Sinn, *J. Am. Chem. Soc.*, 1978, **100**, 8080.

5 W. H. Quayle and J. H. Lunsford, *Inorg. Chem.*, 1982, **21**, 97.

6 M. L. Niven, G. C. Percy and D. A. Thornton, *J. Mol. Struct.*, 1980, **68**, 73.

7 M. A. Hoselton, L. J. Wilson and R. S. Drago, *J. Am. Chem. Soc.*, 1975, **97**, 1722.

8 M. Sorai, J. Ensling, K. M. Hasselbach and P. Gütlich, *Chem. Phys.*, 1977, **20**, 197.

9 A. M. Greenaway, C. J. O'Connor, A. Schrock and E. Sinn, *Inorg. Chem.*, 1979, **18**, 2692.

10 R. Jakobi, H. Spiering, L. Wiehl, E. Gmelin and P. Gütlich, *Inorg. Chem.*, 1988, **27**, 1823.