An NMR and Mössbauer Spectroscopic Study of Mixed-valence Iron Fluoride Heptahydrate and Related Compounds

Takuhiko SAKAI and Takeshi TOMINAGA*

Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113

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The powder X-ray patterns of $Fe^{III}Fe^{II}F_5 \cdot 7H_2O$, $AlFe^{II}F_5 \cdot 7H_2O$, $Fe^{III}ZnF_5 \cdot 7H_2O$ and $AlZnF_5 \cdot 7H_2O$ indicate that they are all isomorphous. When the Mössbauer spectra of the fluorides containing iron were measured, Fe^{II} and/or Fe^{III} oxidation states were recognized distinctly. The ^{19}F NMR spectra reveal that all the fluorine atoms are bonded to the trivalent metal ion (Al or Fe^{III}) in these compounds. On the basis of these results, a possible structure is proposed for $Fe^{III}Fe^{II}F_5 \cdot 7H_2O$.

Although a few works have been reported on the Mössbauer spectrum[1,2] and the X-ray powder pattern[3] of the mixed-valence iron fluoride heptahydrate, $Fe^{III}Fe^{II}F_5 \cdot 7H_2O$, no previous study has elucidated the bonding of ligands to iron in this compound. While Mössbauer spectroscopy can be used to recognize different oxidation states of central iron atoms in such mixed-valence systems, the ^{19}F and proton NMR spectra may provide us with important information concerning the bonding of ligands to central atoms. Hence, we have recently investigated $Fe^{III}Fe^{II}F_5 \cdot 7H_2O$ and several related compounds, such as $Fe^{III}ZnF_5 \cdot 7H_2O$, $AlFe^{II}F_5 \cdot 7H_2O$ and $AlZnF_5 \cdot 7H_2O$ (containing **para**magnetic and/or non-magnetic metal ions), by means of Mössbauer and/or NMR spectroscopy, and have concluded that all the fluoride ions are bonded to the ferric iron.[4] The object of this article is to report the results of our recent work in further detail.

Experimental

Materials. *$Fe^{III}Fe^{II}F_5 \cdot 7H_2O$*: This compound was prepared as has been reported previously.[2] Found: Fe(III), 16.8; Fe(II), 16.8; F, 28.3%. Calcd for $Fe^{III}Fe^{II}F_5 \cdot 7H_2O$: Fe(III), 16.8; Fe(II), 16.8; F, 28.6%.

$AlFe^{II}F_5 \cdot 7H_2O$: A hot 20% HF solution containing iron powder was heated for several hours on a water bath under a reducing atmosphere. The resulting Fe^{2+}–HF solution was filtered, and more iron powder was added to the filtrate so as to ensure the complete reduction of Fe^{3+} to Fe^{2+} in the solution. The solution was then filtered and poured over iron wire, immediately mixed with an equivalent amount of $Al(OH)_3$, and heated for one hour on a water bath. After the solution had stood for several hours, pale green crystals of $AlFe^{II}F_5 \cdot 7H_2O$ were filtered, washed with water and dried in air. Found: Al, 9.1; Fe(II), 18.3; F, 31.7%. Calcd for $AlFe^{II}F_5 \cdot 7H_2O$: Al, 8.9; Fe(II), 18.4; F, 31.3%.

$Fe^{III}ZnF_5 \cdot 7H_2O$: This was prepared by modifying Weinland's method[5] as follows: $Fe(OH)_3$ was dissolved in a hot 20% HF solution, to which an equivalent amount of $ZnCO_3$ was then added. After the solution had been condensed by heating on a water bath, it was kept standing overnight at room temperature. Then, white crystals of $Fe^{III}ZnF_5 \cdot 7H_2O$ were filtered out, washed with water and dried in air. Found: Fe(III), 16.3; Zn, 19.1; F, 28.2%. Calcd for $Fe^{III}ZnF_5 \cdot 7H_2O$: Fe(III), 16.3; Zn, 19.1; F, 27.8%.

$AlZnF_5 \cdot 7H_2O$: The procedure of preparation was similar to that used for $Fe^{III}ZnF_5 \cdot 7H_2O$, except that $Al(OH)_3$ was used as the starting material instead of $Fe(OH)_3$. Found: F, 30.6%. Calcd for $AlZnF_5 \cdot 7H_2O$: F, 30.3%. The determination of the metal contents was interfered with by the presence of fluoride ions.

$Fe^{III}CoF_5 \cdot 7H_2O$ and $Fe^{III}NiF_5 \cdot 7H_2O$: They were prepared by procedures similar to that used for $Fe^{III}ZnF_5 \cdot 7H_2O$, except that basic cobalt carbonate or basic nickel carbonate was used instead of $ZnCO_3$.

Measurements. The powder X-ray patterns of $Fe^{III}Fe^{II}F_5 \cdot 7H_2O$, $Fe^{III}ZnF_5 \cdot 7H_2O$, $AlFe^{II}F_5 \cdot 7H_2O$ and $AlZnF_5 \cdot 7H_2O$ were obtained at room temperature by using Cu$K\alpha$ radiation. The observed data were calibrated by referring to the spectrum of the quartz added as an internal standard.

The Mössbauer spectra of $Fe^{III}Fe^{II}F_5 \cdot 7H_2O$, $Fe^{III}ZnF_5 \cdot 7H_2O$, and $AlFe^{II}F_5 \cdot 7H_2O$ at 80, 195, and 293 K, as well as those of $Fe^{III}CoF_5 \cdot 7H_2O$ and $Fe^{III}NiF_5 \cdot 7H_2O$ at 80 and 293 K, were measured by means of a Shimadzu MEG-2 Mössbauer Spectrometer with a ^{57}Co source diffused into copper foil.

The NMR measurements of the powder samples of these compounds were made at 298 and 113 K by a Varian VF-16 broad-line NMR Spectrometer operating at 7.994 MHz or at about 16 MHz.

Results and Discussion

Powder X-Ray Patterns. The powder X-ray patterns of the four fluorides shown in Fig. 1 appear to be generally alike except for an unimportant difference observed in the vicinity of the diffraction angle, $2\theta \sim 20°$. The lattice constants of these compounds were calculated for the tetragonal symmetry from the data calibrated by referring to the spectrum of the quartz used as the internal standard. The lattice constants obtained in the

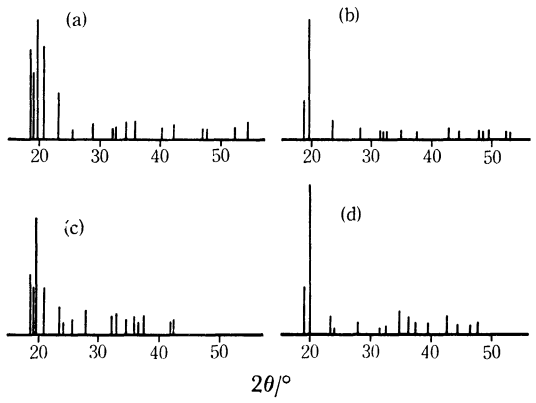

Fig. 1. Powder X-ray patterns of (a) $Fe^{III}Fe^{II}F_5 \cdot 7H_2O$, (b) $AlFe^{II}F_5 \cdot 7H_2O$, (c) $Fe^{III}ZnF_5 \cdot 7H_2O$, and (d) $AlZnF_5 \cdot 7H_2O$.

* To whom all correspondence should be addressed.

present work (±0.03 Å) are: $a=12.64$ and $b=7.05$ Å for $Fe^{III}Fe^{II}F_5\cdot 7H_2O$; $a=12.89$ and $b=6.94$ Å for $Fe^{III}ZnF_5\cdot 7H_2O$; $a=12.71$ and $b=6.99$ Å for $AlFe^{II}F_5\cdot 7H_2O$, and $a=12.75$ and $b=7.01$ Å for $AlZnF_5\cdot 7H_2O$. The results indicate that these four compounds ($M^{III}M'^{II}F_5\cdot 7H_2O$) are all isomorphous.

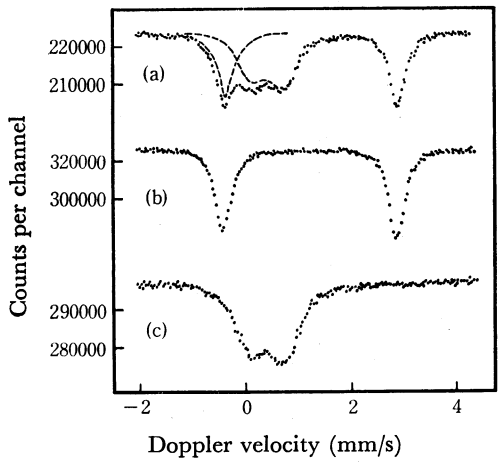

Fig. 2. Mössbauer spectra at 293 K of (a) $Fe^{III}Fe^{II}F_5\cdot 7H_2O$, (b) $AlFe^{II}F_5\cdot 7H_2O$, and (c) $Fe^{III}ZnF_5\cdot 7H_2O$.

Table 1. Mössbauer parameters of $M^{III}M'^{II}F_5\cdot 7H_2O$

Compound	Isomer shift[a] (mm/s)			Quadrupole splitting (mm/s)		
	293 K	195 K	80 K	293 K	195 K	80 K
	(±0.02)			(±0.02)		
$Fe^{III}Fe^{II}F_5\cdot 7H_2O$ Fe^{II}	1.26	1.34	1.39	3.28	3.52	3.55
Fe^{III}	0.45	0.52	0.54	0.51	0.52	0.59
$AlFe^{II}Fe_5\cdot 7H_2O$	1.24	1.30	1.38	3.27	3.51	3.63
$Fe^{III}ZnF_5\cdot 7H_2O$	0.41	0.48	0.53	0.47	0.47	0.52
$Fe^{III}CoF_5\cdot 7H_2O$	0.44		0.53	0.44		0.58
$Fe^{III}NiF_5\cdot 7H_2O$	0.42		0.53	0.52		0.53

a) With respect to the centroid of the spectrum of iron foil at 293 K.

Mössbauer Spectra. Some typical Mössbauer spectra of $Fe^{III}Fe^{II}F_5\cdot 7H_2O$, $AlFe^{II}F_5\cdot 7H_2O$, and $Fe^{III}ZnF_5\cdot 7H_2O$ obtained at 293 K are shown in Fig. 2. In Table 1 are summarized the Mössbauer parameters of these compounds at 80, 195, and 293 K, together with those of $Fe^{III}CoF_5\cdot 7H_2O$ and $Fe^{III}NiF_5\cdot 7H_2O$ at 80 and 293 K. The Mössbauer spectrum of $Fe^{III}Fe^{II}F_5\cdot 7H_2O$ appears to consist of two sets of doublets of nearly equal intensities. The outer doublet corresponds to Fe(II), while the inner doublet is ascribed to Fe(III). At 80, 195, and 293 K, the Mössbauer parameters of the Fe(II) doublet in $Fe^{III}Fe^{II}F_5\cdot 7H_2O$ are in good agreement with those of the doublet in $AlFe^{II}F_5\cdot 7H_2O$. The spectrum of $Fe^{III}Fe^{II}F_5\cdot 7H_2O$ can be resolved to reveal the Fe(III) peaks distinctly by subtracting the superposed Fe(II) doublet (the broken lines in Fig. 2a). The shape of the Fe(III) peaks thus obtained is similar to the spectra of $Fe^{III}ZnF_5\cdot 7H_2O$, $Fe^{III}CoF_5\cdot 7H_2O$, and $Fe^{III}NiF_5\cdot 7H_2O$. Accordingly, the Mössbauer results are compatible with the conclusion based on the X-ray data, indicating that these compounds are all isomorphous. Furthermore, it is worth mentioning that the shape of the Fe(III) peaks in either $Fe^{III}Fe^{II}F_5\cdot 7H_2O$ or $Fe^{III}ZnF_5\cdot 7H_2O$ (Fig. 2) appears to be a composite of at least two sets of unresolved doublets. Accordingly, the spectra of $Fe^{III}Fe^{II}F_5\cdot 7H_2O$ and $Fe^{III}ZnF_5\cdot 7H_2O$ were analyzed by means of a computer fitting based on the assumption that the Fe(III) peaks were composed of two sets of doublets. The best-fit curves obtained imply the presence of at least two different Fe(III) sites (Fig. 3).

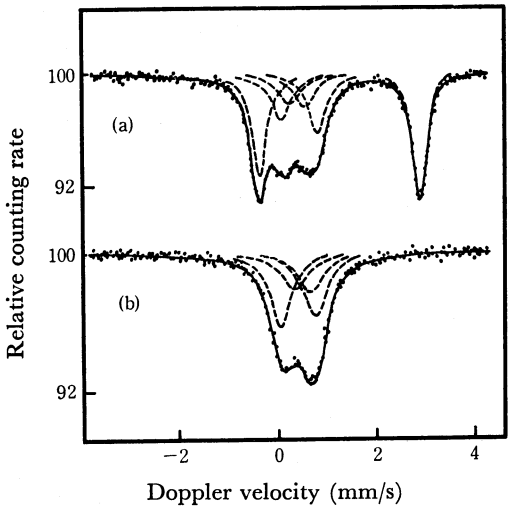

Fig. 3. Computer-fitting analysis of Mössbauer spectra (293 K) of (a) $Fe^{III}Fe^{II}F_5\cdot 7H_2O$, and (b) $Fe^{III}ZnF_5\cdot 7H_2O$.

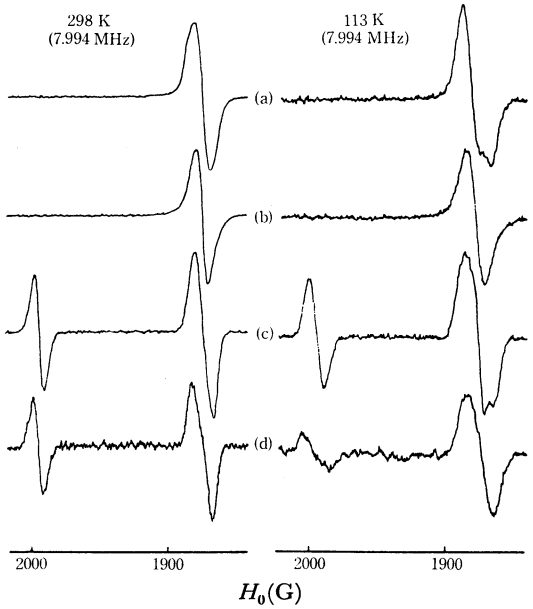

Fig. 4. NMR spectra at 298 K (left) and 113 K (right) of (a) $Fe^{III}Fe^{II}F_5\cdot 7H_2O$, (b) $Fe^{III}ZnF_5\cdot 7H_2O$, (c) $AlFe^{II}F_5\cdot 7H_2O$, and (d) $AlZnF_5\cdot 7H_2O$.

^{19}F NMR Spectra. Figure 4 represents the nuclear magnetic resonances of ^{19}F and protons in these fluorides observed at 113 and 298 K. The signals at about 2000 G and 1880 G indicate the NMR lines of ^{19}F and the protons respectively. As is shown in Fig. 4, the ^{19}F nuclear magnetic resonances are observed only in $AlFe^{II}F_5\cdot 7H_2O$ and $AlZnF_5\cdot 7H_2O$, not in $Fe^{III}ZnF_5\cdot 7H_2O$ and $Fe^{III}Fe^{II}F_5\cdot 7H_2O$. Since the comparison of

the area under the ^{19}F and proton signals in the NMR spectra of $AlFe^{II}F_5 \cdot 7H_2O$ and $AlZnF_5 \cdot 7H_2O$ indicates the $^{19}F/^{1}H$ ratio of 5/14, it may be presumed that all the ^{19}F and ^{1}H nuclear spins are detected in these compounds.

While the ^{19}F resonance signals in paramagnetic compounds would, in general, be unobservable because of the large internal dipole or hyperfine field arising from the electronic spins,[6] the resonance signals of the ^{19}F atoms bonded to such diamagnetic ions as Al^{3+} and Zn^{2+} should be observable because of the weak influence on ^{19}F of the magnetic field due to the diamagnetic ions. The absence of the ^{19}F resonance signals in $Fe^{III}ZnF_5 \cdot 7H_2O$ reveals that all the ^{19}F atoms are bonded to Fe^{3+}, but not to Zn^{2+}, and that these ^{19}F atoms are possibly influenced by the very strong internal magnetic field due to the paramagnetic spins of the Fe^{3+} ions. The ^{19}F NMR spectra thus indicate that all the fluorine atoms are bonded to M^{III} (Al^{3+} or Fe^{3+}) in these fluorides. Since the X-ray and Mössbauer data have shown that they all isomorphous, the structures of the four fluorides, $M^{III}M'^{II}F_5 \cdot 7H_2O$ ($M^{III}=Fe^{III}$ or Al, and $M'^{II}=Fe^{II}$ or Zn), may be generally represented as $[M^{III}F_5OH_2] \cdot [M'^{II}(OH_2)_6]$, and we may presume the structure of $Fe^{III}Fe^{II}F_5 \cdot 7H_2O$ to be $[Fe^{III}F_5OH_2] \cdot [Fe^{II}(OH_2)_6]$.

Proton NMR Spectra. In the proton NMR spectra at 7.994 MHz, the proton signals of $Fe^{III}Fe^{II}F_5 \cdot 7H_2O$ and $AlFe^{II}F_5 \cdot 7H_2O$ at 113 K appear to be asymmetric (Fig. 4). In order to make a more detailed analysis convenient, the proton NMR spectra of these fluorides, together with those of $Fe^{III}CoF_5 \cdot 7H_2O$ and $Fe^{III}NiF_5 \cdot 7H_2O$ were also measured during operation at 16 MHz; asymmetric signals were obtained at 113 K in all the compounds except $Fe^{III}ZnF_5 \cdot 7H_2O$ (Fig. 5). In accordance with the proposed structures, these results may be generally explained as follows. The asymmetric proton NMR signals reflect the influence of the magnetic anisotropy of the paramagnetic ion with a short spin-relaxation time (*i.e.*, Fe(II), Co(II), or Ni (II)), to which the water molecules are bonded. If a water molecule is bonded to a ferric ion with a long spin-relaxation time, however, the local magnetic field changes slowly and the proton experiences various magnetic fields. Hence, the proton NMR line-width is so broadened that the resonance can hardly be detected. Since all proton signals can be observed in $AlFe^{II}F_5 \cdot 7H_2O$, its spectrum is composed of asymmetric signals reflecting the magnetic anisotropy of Fe(II) and the superimposed, unperturbed signals from protons of the water bonded to Al. In $Fe^{III}ZnF_5 \cdot 7H_2O$ we observed only the symmetrical signals of protons of water bonded to Zn(II), which are not perturbed magnetically.

The proton NMR spectra of these compounds observed at 298 K are all symmetrical (Figs. 4 and 5). This may be attributable to the disappearance of the magnetic anisotropy because of the accelerated motion of protons around the oxygen atom at elevated temperatures.

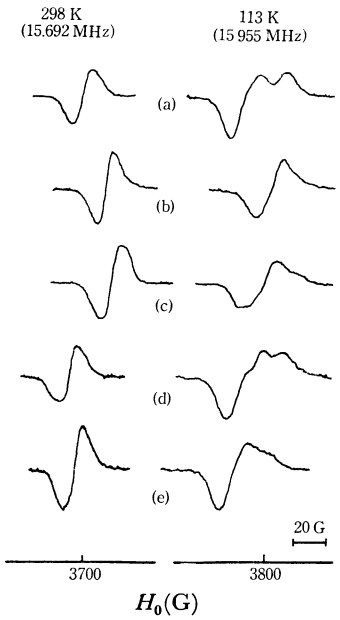

Fig. 5. Proton NMR spectra at 298 K (left) and 113 K (right) of (a) $Fe^{III}Fe^{II}F_5 \cdot 7H_2O$, (b) $Fe^{III}ZnF_5 \cdot 7H_2O$, (c) $AlFe^{II}F_5 \cdot 7H_2O$, (d) $Fe^{III}CoF_5 \cdot 7H_2O$, and (e) $Fe^{III}NiF_5 \cdot 7H_2O$.

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