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Mössbauer Study of the Electronic Structure and Relaxation Rate of Iron(II) in Some Substituted Acetylacetonato Complexes[1]

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Mössbauer spectra of the structurally related compounds bis(trifluoroacetylacetonato)iron(II) dihydrate and bis(hexafluoroacetylacetonato)iron(II) dihydrate have been recorded for powder samples between 1.6 and 300 K in the absence of an applied magnetic field and at 4.2 K in external longitudinal magnetic fields up to 52 kG. The values of the isomer shift and quadrupole splitting parameters for both complexes are typical of the Fe(II) high-spin state. At low temperature a relaxation effect is apparent for the first compound, while none is observed for the second. Also, spectra recorded in a magnetic field show that the sign of the principal component of the electric field gradient, V_{zz}, is different for the two complexes. For the bis(trifluoroacetylacetonato)iron(II) dihydrate complex, V_{zz} is positive and the iron magnetic moment is aligned parallel to the z axis in an applied magnetic field, while for the bis(hexafluoroacetylacetonato)iron(II) dihydrate complex, V_{zz} is negative and the iron moment is oriented perpendicular to V_{zz}. These results are interpreted using a ligand field model. The ground states are a spin–orbit doublet ($D < 0$) and a spin–orbit singlet ($D > 0$) for the trifluoro and hexafluoro complexes, respectively.

Introduction

Electronic relaxation has a considerable effect on the observation of magnetic hyperfine structure in Mössbauer spectra of paramagnetic compounds.[3] The two main relaxation processes of paramagnetic ions in insulators are those due to electronic spin–spin interactions with neighboring ions and electronic spin–lattice interactions. Spin–spin relaxation processes involve energy transfer betweeen interacting spins via dipole and exchange spin relaxation. Spin–lattice relaxation involves the transfer of energy from the electronic spin system to the phonons of the lattice via spin–orbit coupling. For S state ions such as high-spin Fe^{3+}, the orbital angular momentum, $\langle L \rangle$, is zero; thus, the spin–orbit interaction can have no first-order effect and consequently relatively long spin–lattice relaxation times are observed. On the other hand, for high-spin Fe^{2+} (^5D state), the spin–lattice relaxation times in the absence of cooperative effects, such as ferro- or antiferromagnetism, are characteristically very rapid, on the order of 10^{-9}–10^{-11} s. This is much shorter than the ^{57}Fe nuclear precession time, thus preventing the observation of hyperfine interactions. However, a few cases have been reported where, at low temperature, there is an increase in the spin–lattice relaxation time of the Fe^{2+} ion, leading to the onset of paramagnetic hyperfine structure in the Mössbauer spectrum.[4,5] Also, relaxation effects in the presence of applied magnetic fields have been recently reported.[5-9]

In order to investigate the possible structural factors which are involved in this phenomenon in some high-spin Fe^{2+} systems and to relate them to the electronic structure of the Fe^{2+} ions, it is necessary to make a systematic investigation of structurally related complexes. In a previous paper,[5] we reported the observation of slow relaxation in a Mössbauer study of iron(II) bis(acetylacetonate) dihydrate (subsequently referred to as $Fe(acac)_2 \cdot 2H_2O$). Here we present a Mössbauer investigation of the parent complexes $Fe(F_3A)_2 \cdot 2H_2O$ and $Fe(F_6A)_2 \cdot 2H_2O$ where F_3A and F_6A represent the monoanions of trifluoro- and hexafluoroacetylacetone, respectively. The hyperfine interactions have been measured as a function of temperature between 300 and 1.6 K and of applied magnetic fields up to 52 kG. As shown here, very different behaviors are observed in these two complexes and allow us to derive information on the electronic structure of the Fe^{2+} ion.

Experimental Section

The complexes were prepared using reagents obtained from commercial sources as described elsewhere.[10,11] All operations were performed under a nitrogen atmosphere. ^{57}Fe Mössbauer spectra were recorded on a multichannel analyzer using a constant-acceleration drive calibrated with metallic iron foil absorbers. Spectra were taken for polycrystalline samples at 295, 77, 4.2, and 1.6 K in zero applied magnetic field and at 4.2 K in external magnetic fields with longitudinal configuration up to 52 kG using a superconducting magnet.[12] The $^{57}Co(Rh)$ source was maintained at ambient temperature. During the high-field Mössbauer experiments a simultaneous calibration of the velocity scale was performed with a second source attached to the end of the transducer opposite to the high-field region. An electronic interface allowed the memory of the multichannel analyzer to be shared between the two data-acquisition units.[13]

Results

Zero-Field Experiments. The Mössbauer spectra for the $Fe(F_3A)_2 \cdot 2H_2O$ complex at zero applied magnetic field and different temperatures are shown in Figure 1. At 77 K the Mössbauer spectrum for this chelate consists of a slightly asymmetrical quadrupole doublet. As for $Fe(acac)_2 \cdot 2H_2O$ the asymmetry of the doublet can be attributed to a texture effect resulting from the shape of the microcrystals.[5] At 4.2 and 1.6 K a significant broadening of the right-hand line is observed, while the left-hand line remains narrow. The lines can still be fitted very well by a Lorentzian shape. A similar but much less pronounced phenomenon was observed for the $Fe(acac)_2 \cdot 2H_2O$ complex. As has been discussed earlier,[5] the broadening of one component of the doublet at low temperatures arises as a result of interaction of the nucleus with fluctuating magnetic fields produced by the increase of the spin–lattice relaxation time of the paramagnetic Fe^{2+} ion. Blume[14] has shown theoretically that under slow relaxation conditions, the line which corresponds to the $|\pm^3/_2\rangle \rightarrow |\pm^1/_2\rangle$ nuclear spin transition of the ^{57}Fe Mössbauer nuclei will broaden first, and we conclude that the z component of the electric field gradient (EFG), V_{zz}, has a positive sign for the $Fe(F_3A)_2 \cdot 2H_2O$ complex. This conclusion is of interest since this compound is extremely sensitive to air oxidation, making it difficult to determine the sign of V_{zz} at room temperature from the magnetically perturbed spectrum. The positive sign of V_{zz} for this complex will be confirmed as shown below by the theoretical fit of magnetically perturbed spectra at 4.2 K.

Figure 2 shows Mössbauer spectra for the $Fe(F_6A)_2 \cdot 2H_2O$ compound as a function of temperature and at zero applied magnetic field. For this complex no broadening of the peaks occurs as happened in the case of the $Fe(F_3A)_2 \cdot 2H_2O$ chelate. This would indicate no relaxation effect for the Fe^{2+} ion at zero applied field. Table I shows the values of the Mössbauer parameters for the two complexes at different temperatures and zero applied magnetic field. The values of the isomer shift,

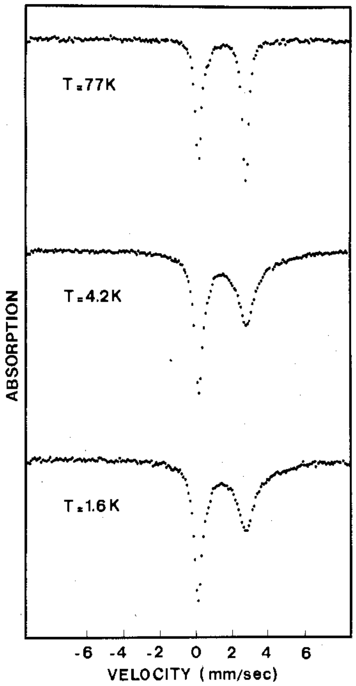

Figure 1. Mössbauer spectra of $Fe(F_3A)_2{\cdot}2H_2O$ taken in zero magnetic field at 77, 4.2, and 1.6 K.

Table I. Isomer Shift δ^a and Quadrupole Splitting ΔE_Q in Mössbauer Spectra of $Fe(F_3A)_2{\cdot}2H_2O$ and $Fe(F_6A)_2{\cdot}2H_2O$ Complexes as a Function of the Temperature^b

Compd	Temp, K	δ, mm s^{-1}	$\lvert\Delta E_Q\rvert$, mm s^{-1}
$Fe(F_3A)_2{\cdot}2H_2O$	77	1.26 (3)	2.63 (5)
	4.2	1.27 (3)	2.64 (5)
	1.6	1.27 (3)	2.64 (5)
$Fe(F_6A)_2{\cdot}2H_2O$	300	1.22 (3)	2.68 (5)
	77	1.24 (3)	2.68 (5)
	4.2	1.24 (3)	2.69 (5)
	1.6	1.24 (3)	2.71 (5)

^{a} Relative to metallic iron. ^{b} Errors in the last figures are indicated in parentheses.

δ, and quadrupole splitting, $|\Delta E_Q|$, for both complexes are typical of the Fe(II) high-spin state.

Magnetic Field Experiments. Typical Mössbauer spectra for $Fe(F_3A)_2{\cdot}2H_2O$ and $Fe(F_6A)_2{\cdot}2H_2O$ compounds at 4.2 K and at different applied longitudinal magnetic fields are shown in Figures 3 and 4, respectively. As can be observed, the behavior of the two complexes in applied magnetic fields is drastically different. For the $Fe(F_3A)_2{\cdot}2H_2O$ chelate, a hyperfine structure develops for relatively weak applied fields. The sign of the induced hyperfine field is negative since an increase of the applied field, H_{app}, produces a shrinking of the overall spectrum. The hyperfine field, H_{hf}, reaches saturation for applied fields of about 7 kG, with a saturation value, $H^s_{hf} = -178$ kG. H^s_{hf} was derived from comparison of the experimental spectrum for $H_{app} = 50$ kG and $T = 4.2$ K (Figure 3) with a spectrum calculated using a phenomenological model developed by Varret.[15] This model accounts for an anisotropic hyperfine field, H_{hf}, induced by the external magnetic field, H_{app}, applied along the γ-ray propagation direction. The hyperfine levels are calculated using the Hamiltonian

$$\mathcal{H} = \hbar g_n \vec{H}_{eff} \vec{I} + \frac{e^2 V_{zz} Q}{4I(2I-1)}\left[3I_z^2 - I(I+1) + \frac{\eta}{2}(I_+^2 + I_-^2)\right] \qquad (1)$$

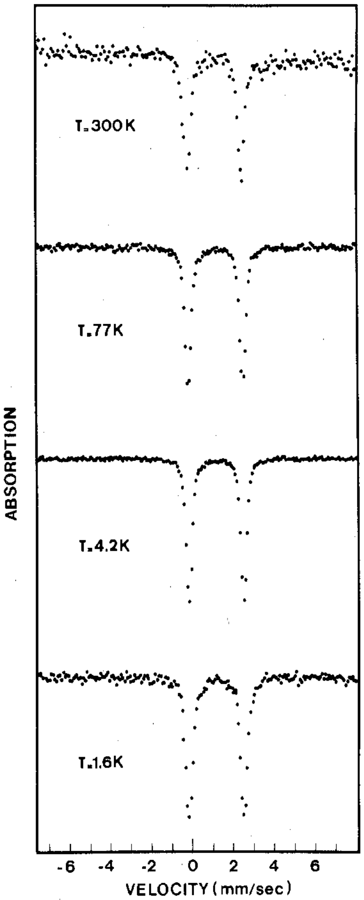

Figure 2. Mössbauer spectra of $Fe(F_6A)_2{\cdot}2H_2O$ taken in zero magnetic field between 300 and 1.6 K. Sample temperatures are indicated in the figure.

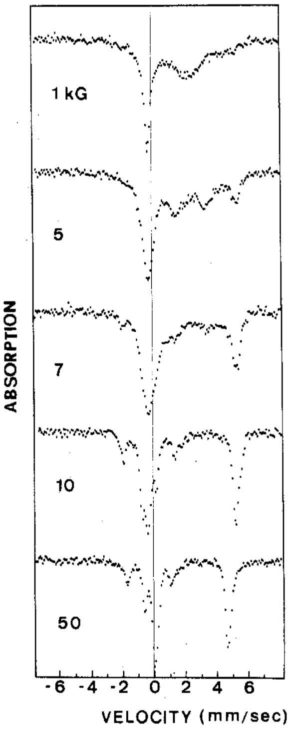

Figure 3. Mössbauer spectra of a powder sample of $Fe(F_3A)_2{\cdot}2H_2O$ at 4.2 K in longitudinal applied magnetic fields up to 50 kG.

where the first and second terms are the magnetic and quadrupole interactions, respectively. In eq 1, g_n is the nuclear g factor, $\vec{I}$ is the nuclear spin, and η is the EFG asymmetry

Table II. Mössbauer Parameters of the Computed Spectra of Figures 5 and 6 for Different Values of the Applied Field[a]

Compd	H_{app}, kG	ΔE_Q, mm s^{-1}	η	$H^x{}_{hf}$, kG	$H^y{}_{hf}$, kG	$H^z{}_{hf}$, kG
$Fe(F_3A)_2 \cdot 2H_2O$	50	+2.64	0.3 (1)	0 (5)	0 (5)	−178 (5)
$Fe(F_6A)_2 \cdot 2H_2O$	2	−2.69	0.0 (1)	−17 (5) +13 (5)	−17 (5) +13 (5)	0 (5) 0 (5)
	52	−2.69	0.0 (1)	−220 (5) +116 (5)	−220 (5) +116 (5)	0 (5) 0 (5)

[a] E_Q is taken from the zero-field experiments. Errors in the last figures are given in parentheses.

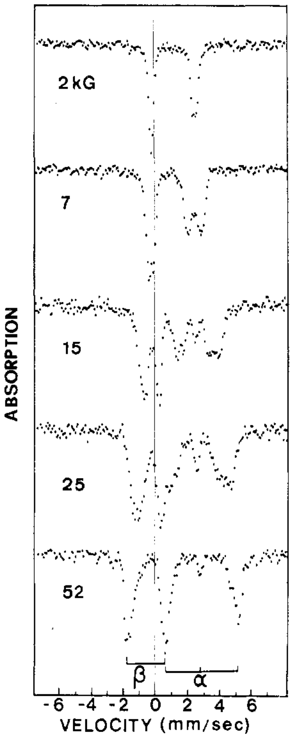

Figure 4. Mössbauer spectra of a powder sample of $Fe(F_6A)_2 \cdot 2H_2O$ at 4.2 K in longitudinal applied magnetic fields up to 52 kG.

parameter defined by $\eta = (V_{xx} - V_{yy})/V_{zz}$. The effective field experienced by the ^{57}Fe nucleus is

$$\vec{H}_{eff} = \vec{H}_{hf} + \vec{H}_{app} \quad (2)$$

For a given microcrystal, the three components of $\vec{H}_{eff}$ may be expressed as

$$\begin{aligned} H^x{}_{eff} &= (H^x{}_{hf} + H_{app}) \sin\theta \cos\phi \\ H^y{}_{eff} &= (H^y{}_{hf} + H_{app}) \sin\theta \sin\phi \\ H^z{}_{eff} &= (H^z{}_{hf} + H_{app}) \cos\theta \end{aligned} \quad (3)$$

where θ and ϕ are the polar angles of H_{app} relative to the EFG axes $0xyz$.[15] Since our samples are polycrystalline, one must average over all possible values of θ and ϕ. In the calculation we take for the quadrupole interaction the values observed in zero field (Table I) assuming that they are not significantly modified by the applied field. Equations 3 are valid for small values of H_{app} (low magnetization limit) when H_{hf} is proportional to H_{app}. For large values of H_{app}, H_{hf} becomes independent of H_{app} and eq 3 become

$$\begin{aligned} H^x{}_{eff} &= H^x{}_{hf} + H_{app} \sin\theta \cos\phi \\ H^y{}_{eff} &= H^y{}_{hf} + H_{app} \sin\theta \sin\phi \\ H^z{}_{eff} &+ H^z{}_{hf} + H_{app} \cos\theta \end{aligned} \quad (4)$$

In eq 3 and 4, $H^x{}_{hf}$, $H^y{}_{hf}$, and $H^z{}_{hf}$, which account for the anisotropic hyperfine field, are the values of H_{hf} when H_{app} lies along $0x$, $0y$, and $0z$ respectively. In a first approach we set $\eta = 0$ and determine the combination of these three components which fits best the experimental spectrum. Then the fit is improved by letting η vary. Figure 5 shows a spectrum calculated with eq 4 for $H_{app} = 50$ kG. The corresponding Mössbauer parameters are given in Table II. One sees that this spectrum is very similar to that obtained for $Fe(F_3A)_2 \cdot 2H_2O$ submitted to the same field (Figure 3, lowest spectrum). It is consistent with a *positive* sign for V_{zz} (reversing its sign would give a mirror pattern with respect to the center of gravity of the spectrum) and a *slow relaxation* rate. In addition it indicates that the hyperfine field is *parallel* to the V_{zz} component. The weak intensity of the $\Delta m = 0$ in the experimental spectrum compared to the calculated one is indicative of texture effects as mentioned above. It was not possible to fit the low-field spectra of Figure 3 with either eq 3 or 4, probably because it would require an intermediate relaxation scheme where the spin-relaxation rate and the nuclear Larmor frequency are comparable.

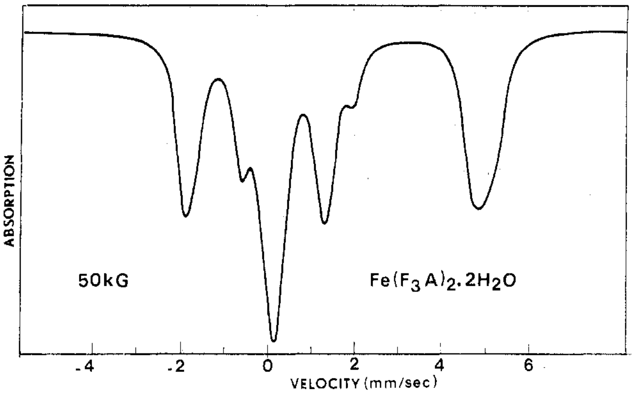

Figure 5. Calculated Mössbauer spectrum for $Fe(F_3A)_2 \cdot 2H_2O$ complex at 4.2 K using eq 4 for $H_{app} = 50$ kG. Lines have intensities and line widths different from those in the spectrum of Figure 3. This is due to texture in the sample. In that case the experimental spectrum is intermediate between that of a powder and of a single crystal while the calculated spectrum is an average over all possible orientations of H_{app} and the symmetry axis of the electric field gradient.

A similar analysis for the $Fe(F_6A)_2 \cdot 2H_2O$ compound shows that *no relaxation* takes place since the spectra are correctly fitted using eq 3. Saturation is not reached for the largest applied fields. The high-field Mössbauer spectra (Figure 4) are reminiscent of Collins and Travis calculated spectra of diamagnets submitted to an external magnetic field.[16] In particular they indicate that V_{zz} is *negative* in the hexafluoro compound. However here we are dealing with a paramagnet at low temperature, which means that the magnetic susceptibility may be different from zero and may be anisotropic. Then, the deviation from unity of the ratio of the "triplet" (α) and "doublet" (β) splittings constituting the Mössbauer spectrum may be used to obtain an estimate of the angle θ between V_{zz} and the hyperfine field.[12] The value of this ratio for the $Fe(F_6A)_2 \cdot 2H_2O$ complex, derived from the spectrum at 4.2 K and $H_{app} = 52$ kG is $\simeq 1.8$, indicating that θ is nearly 90°. The hyperfine field induced by the external field is therefore *perpendicular* to V_{zz}. Figure 6 shows spectra computed with eq 3 using the Mössbauer parameters of Table II. Since saturation is not reached, it is not possible to derive

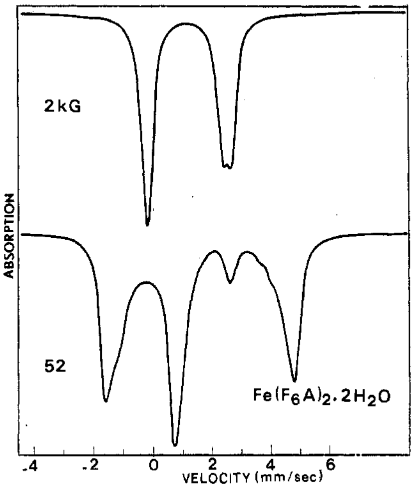

Figure 6. Calculated Mössbauer spectra for $Fe(F_6A)_2{\cdot}2H_2O$ complex at 4.2 K using eq 3 for H_{app} = 2 and 52 kG.

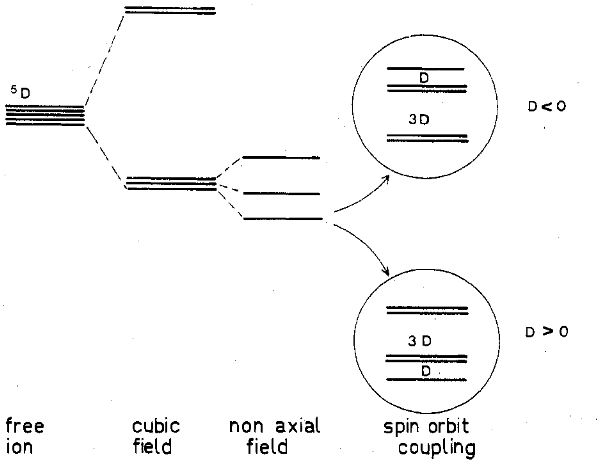

Figure 7. Energy level scheme for high-spin Fe(II) under the action of the crystalline field and spin–orbit coupling.

the sign of H_{hf}. Two values of opposite signs are therefore indicated in Table II which give an equally good fit. One sees that these spectra closely ressemble those of Figure 4 for the corresponding values of the applied field.

Discussion

The ground term of the ferrous ion is $3d^6$ ^5D, with $L = 2$ and $S = 2$, where L and S are the orbital and spin operators, respectively. Under the action of nonaxial ligand fields an orbital singlet is the lowest state (Figure 7). The relatively small magnitude of the quadrupole splittings (2.64 and 2.69 mm s^{-1} at 4.2 K for the trifluoro and hexafluoro complexes respectively) indicates some mixing of the excited orbital states with the ground state via spin–orbit coupling.[17] The effect of the ligand field and of the spin–orbit coupling can be expressed (in the principal axis system of the **g** tensor) by the spin Hamiltonian

$$\mathcal{H} = D[S_z^2 - {}^1/_3 S(S+1)] + E(S_x^2 - S_y^2) \qquad (5)$$

where D and E are the axial and nonaxial field splittings. When E is zero (small), the spin–orbit ground state is a doublet (pseudodoublet) or a singlet depending on the sign of D (negative or positive, respectively).

In $Fe(F_3A)_2{\cdot}2H_2O$ slow relaxation is observed at low temperature. In addition the hyperfine field reaches its saturation value for small applied fields ($H_{app} \simeq 7$ kG). Both observations indicate that the ground state is a *doublet*; i.e., D is negative (Figure 7). In fact, because of the rhombic term $E(S_x^2 - S_y^2)$ in eq 5, this doublet is somewhat split into two levels whose separation is probably of the order of 1 wavenumber.[5]

Table III. Summary of the Results Regarding the Relaxation Behavior and the Electronic Properties of the Fe^{2+} Ion in Acetylacetonato Complexes

	$Fe(acac)_2{\cdot}2H_2O$[a]	$Fe(F_3A)_2{\cdot}2H_2O$[b]	$Fe(F_6A)_2{\cdot}2H_2O$[b]
Sign of V_{zz}	Positive	Positive	Negative
Direction of the Fe^{2+} magnetic moment	Parallel V_{zz}	Parallel V_{zz}	Perpendicular V_{zz}
Relaxation rate	Slow	Slow	No relaxation
Sign of D	Negative	Negative	Positive
Spin-orbit state	Doublet	Doublet	Singlet

[a] From ref 5. [b] This work.

For $Fe(F_6A)_2{\cdot}2H_2O$, no relaxation effect is observed. Also saturation is not reached even in large magnetic fields. This results from the ground state being a *singlet*; i.e., D is positive (Figure 7). These conclusions are summarized in Table III.

Let us finally remark that x-ray studies of $Fe(acac)_2{\cdot}2H_2O$ indicate that the iron atom lying on a center of symmetry is surrounded by four oxygen atoms of the acetylacetone ligand and two water molecules, forming a tetragonally distorted octahedron.[10,18] Varret and Hartmann-Boutron have studied the effects of spin–orbit coupling on the ground state of transition-metal ions in different crystalline environments from a theoretical viewpoint.[19] According to their findings for the high-spin Fe^{2+} ion in tetragonal symmetry, the iron magnetic moment tends to align itself parallel to the tetragonal axis in the case of a ground-state doublet and perpendicular for a ground-state singlet. These conclusions agree with our experimental results.

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Registry No. $Fe(F_3A)_2{\cdot}2H_2O$, 64146-53-8; $Fe(F_6A)_2{\cdot}2H_2O$, 64146-52-7.

References and Notes

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(2) Visiting Scientist, Centre d'Etudes Nucléaires de Grenoble, 1975–1976.
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