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Characterization of Decaaqua-μ-oxodi-iron(III) by Mössbauer and Vibrational Spectroscopy

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Iron(III) nitrate and perchlorate solutions to which 0.5 – 2.0 equivalents of base were added have been investigated by Mössbauer, Raman and IR spectrometry. These methods establish conclusively the existence of the decaaqua-μ-oxodi-iron(III) ion.

The hydrolysis of iron(III) has been studied extensively over many years. Recently, the subject has been reviewed by Sylva[1] and to some degree by Murray.[2] The first systematic investigation of the equilibria involved in the hydrolysis was made by Hedström using electrometric titrations of dilute solutions.[3] The system was described by the following three equilibria involving mono- and binuclear iron(III) species:

$$Fe^{3+} + H_2O \rightleftharpoons Fe(OH)^{2+} + H^+,$$
$$K_{11} = 9.0 \times 10^{-4}\ M$$
$$Fe^{3+} + 2H_2O \rightleftharpoons Fe(OH)_2^+ + 2H^+,$$
$$K_{12} = 4.9 \times 10^{-7}\ M^2$$
$$2Fe^{3+} + 2H_2O \rightleftharpoons Fe_2(OH)_2^{4+} + 2H^+,$$
$$K_{22} = 1.2 \times 10^{-3}\ M$$

Since the work of Hedström the hydrolysis products of iron(III) at relatively low pH values have usually been considered to be at least the three species $Fe(OH)^{2+}$(1:1), $Fe(OH)_2^+$(1:2), $Fe_2(OH)_2^{4+}$ (2:2). Arnek and Schlyter[4] included also the trinuclear $Fe_3(OH)_4^{5+}$ (3:4). However, the reported equilibrium constants show that the 1:2 and 3:4 species are present in concentrations usually several orders of magnitudes lower than the concentrations of the other species.

Hedström formulated the 2:2 complex as $[(H_2O)_4Fe(OH)_2Fe(H_2O)_4]^{4+}$ but potentiometric measurements cannot distinguish between this and $[(H_2O)_5Fe-O-Fe(H_2O)_5]^{4+}$. However, Mulay and Selwood[5] performed magnetic susceptibility measurements on partly hydrolyzed solutions of iron(III) perchlorate and their results were interpreted by Schäffer[6] in favour of the μ-oxo dimer. These observations and contemplations were not appreciated and instead Schugar *et al.*[7] suggested that the dimer was a di-μ-hydroxodi-iron(III) complex. This point of view was also taken by Murray[2] in spite of the preliminary information then available from the application of the Mössbauer effect to the study of frozen solutions of partly hydrolyzed iron(III).[8]

The present paper is focussing on this controversy and several techniques are used to demonstrate beyond reasonable doubts that the binuclear complex is a nearlinear oxo-bridged species.

EXPERIMENTAL

Mössbauer spectra. Solutions of iron(III) nitrate and perchlorate were made from reagent-grade salts. Weighed amounts of the iron salt and of sodium hydrogen carbonate were dissolved in distilled water in separate flasks and the bicarbonate solution was mixed dropwise to the iron solution while stirring to prevent high local concentration of base. Distilled water was then added to reach the desired volume and the solution was stirred for some minutes to free it

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from carbon dioxide. All reported spectra were taken using freshly prepared frozen solutions. However, it was ascertained that even aged solutions (over weeks) gave identical spectra.

The Mössbauer samples consisted of approximately 2 ml of solution in a plastic cell of 2.0 cm diameter. The cell with the sample was quickly dipped into liquid nitrogen thus freezing with a cooling rate of about 400 K per minute. This cooling rate seems to be high enough to secure the formation of a glass when iron(III) perchlorate is used. With iron(III) nitrate segregation effects appear when the above procedure is followed. The segregation effects may be avoided either by increasing the cooling rate or by the addition of small amounts of a glass former such as ethanol.[9] Apart from differences due to glassforming properties of the nitrate and perchlorate ions there are no differences between the Mössbauer spectra of frozen solutions of $Fe(NO_3)_3$ and $Fe(ClO_4)_3$. Therefore, most of the computational work concerning the Mössbauer spectra was done for solutions made from iron(III) perchlorate.

The Mössbauer spectra were taken with a conventional constant acceleration set-up incorporating a Nuclear Data multichannel analyzer. The source used was ^{57}Co on Pd. The velocity scale was calibrated periodically with metallic iron as a standard. Isomer shifts quoted here are relative to Co on Pd. The source was always at room temperature. The temperature of the absorbers was held constant at 100 K for most runs but results are not very sensitive to temperature from liquid nitrogen temperature to around 160 K for rapidly quenched samples. We have observed that for higher temperatures segregation effects can again be a disturbing factor.

Mössbauer parameters were obtained by an iterative curve fitting procedure in a RC 4000 computer. Estimates of the concentration of the various species based on Mössbauer spectra were made from areas in the fitted spectra.

Vibrational spectra. Raman spectra of solutions in H_2O and D_2O prepared as above in the concentration range 0.4 – 2 M were obtained at room temperature using a Coderg PH1 spectrometer with a cooled PM-tube (EMI 9558) and a photon counting system. The 514.5 nm line of a Spectra-Physics 165 Ar^+-laser ($\sim$350 mW) was used as light source. A cylindrical 4 mm i.d. glass tube was used as cell. A 90° scattering was used and the polarization of the laser beam was kept fixed. The depolarization measurements were made by the conventional method of two different analyzer orientations in the scattered beam. Due to sample absorption of the exciting line a rather poor signal-to-noise ratio was obatined making the depolarization measurements less accurate than usual. Raman shifts from 200 to 600 cm^{-1} are reported. The observed lines are rather broad and weak and the Raman shifts are only considered accurate to ± 5 cm^{-1}.

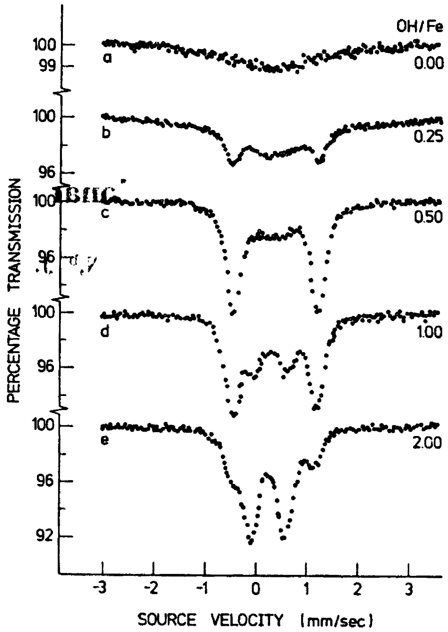

Fig. 1. Mössbauer spectra of rapidly frozen aqueous solutions of $Fe(ClO_4)_3$ for different ratios between the concentration of added base and the total concentration of iron(III). The solutions were 0.67 M in Fe(III). All spectra were recorded at the temperature $T = 100$ K.

Infrared spectra were obtained from D_2O solutions in the concentration range 0.7 – 1.2 M. An RIIC GC-1 silver chloride microcell with 0.025 mm path length was used in a Perkin-Elmer 125 spectrometer. Only the region 700 – 1000 cm^{-1} was studied in detail. The observed line frequencies are considered accurate to ± 3 cm^{-1}.

RESULTS

Mössbauer spectra. In Fig. 1 are shown the Mössbauer spectra of rapidly frozen 0.67 M aqueous solutions of $Fe(ClO_4)_3$ recorded at $T = 100$ K, for different ratios between the concentration of added base, and the total concentration of iron(III) (OH/Fe). Solutions of $Fe(NO_3)_3$ frozen by quenching and at the same concentrations show Mössbauer spectra similar to those seen in Fig. 1 (see Ref. 9, Fig. 1).

Spectrum 1a shows a broad line characteristic of magnetic relaxation effects in the high-spin ferric ion.[10] This spectrum corresponds to a perchlorate solution without any base added. At room temperature, this solution has pH ~ 0.8 and its colour is light yellow.

Addition of base to the iron(III) solution up to about 0.5 equivalent of base per mol of iron results in the appearing of a quadrupole doublet in the Mössbauer spectra of the frozen solutions.

Fig. 1c shows the Mössbauer spectrum obtained for a 0.67 M iron perchlorate solution with 0.5 equivalent of base added per mol of total iron(III). For this orange solution pH at room temperature is 1.5. In the spectrum in Fig. 1c the broad line dominant in Fig. 1a and b is still visible but now a quadrupole doublet with an isomer shift of 0.31 ± 0.06 mm/s and a quadrupole splitting of 1.67 ± 0.06 mm/s is dominating.

Further addition of base results in a new component with isomer shift 0.25 ± 0.06 mm/s and quadrupole splitting 0.66 ± 0.06 mm/s (Spectra 1d and 1e), while the intensity of the lines for the other components decreases.

The component with quadrupole splitting 0.66 mm/s is practically the only component present when the ratio OH/Fe exceeds 2.0 until no more base can be added without immediate precipitation.

In Fig. 2 are shown the Mössbauer spectra of three binuclear iron(III) species at 100 K and the Mössbauer parameters are collected in Table 1.

Vibrational spectra. In Table 2 are listed the observed infrared absorption frequencies and Raman shifts for hydrolyzed iron(III) complexes of $Fe(NO_3)_3$ and $Fe(ClO_4)_3$ solutions in H_2O and D_2O.

DISCUSSION

In the following we shall discuss the results of the different kinds of spectroscopy to prove that the binuclear iron(III) hydrolysis product is a μ-oxo rather than a di-μ-hydroxo complex.

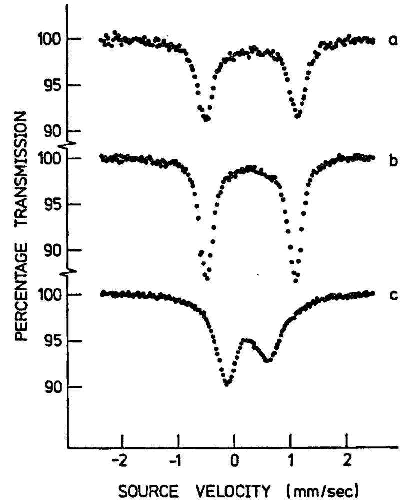

Fig. 2. Mössbauer spectra of: (a) a frozen aqueous solution of $Fe(ClO_4)_3$ with OH/Fe = 0.5; (b) a powder of $Na_3[(Fe\ heedta)_2O]$; (c) a powder of $[Fe(pic)_2OH]_2$. All spectra were recorded at the temperature $T = 100$ K.

Nozik and Kaplan [11] discussed the significance of the Mössbauer spectra of frozen acid solutions of $FeCl_3$ and $Fe(NO_3)_3$. They considered that for the $FeCl_3$ solution, 80 % of the ferric ion was in the form $Fe(H_2O)_5Cl^{2+}$ and that for the $Fe(NO_3)_3$ solution the only species present was the hexahydrated ion $Fe(H_2O)_6^{3+}$. The $Fe(NO_3)_3$ solution showed a Mössbauer spectrum similar to the spectrum seen in Fig. 1a.

Using the hydrolysis equilibrium constants measured by Milburn and Vosburgh,[12] calculations suggest that for the iron(III) perchlorate solution without any addition of base (OH/Fe = 0) most of the iron is present in the form

Table 1. Mössbauer parameters of some iron(III) dimers at 100 K.

δ: isomer shift in mm/s relative to ^{57}Co on Pd. Uncertainty ± 0.06 mm/s.

ΔE_q: quadrupole splitting in mm/s. Uncertainty ± 0.06 mm/s. Γ_1 and Γ_2: linewidth in mm/s at half intensity. Uncertainty ± 0.06 mm/s.

A_1/A_2: Ratio between area of lines in the quadrupole doublets.

Compound	δ	ΔE_q	Γ_1	Γ_2	Γ_1/Γ_2	A_1/A_2
Aqua dimer	0.31	1.67	0.37	0.38	0.97	1.03
(Fe heedta)$_2$O	0.26	1.66	0.30	0.29	1.03	1.01
(Fe pic$_2$OH)$_2$	0.23	0.78	0.48	0.67	0.72	0.95

Table 2. Infrared spectra (700 – 1000 cm^{-1}) and Raman spectra (200 – 600 cm^{-1}) of hydrolyzed iron(III) complexes in H_2O and D_2O solutions (0.4 – 2 M) of $Fe(ClO_4)_3$ and $Fe(NO_3)_3$.

$Fe(ClO_4)_3$ in H_2O			$Fe(ClO_4)_3$ in D_2O				$Fe(NO_3)_3$ in H_2O			$Fe(NO_3)_3$ in D_2O				Assignment
Raman			Raman			IR	Raman			Raman			IR	
ν	I_{rel}	pol.	ν	I_{rel}	pol.	ν	ν	I_{rel}	pol.	ν	I_{rel}	pol.	ν	
						870							870	Fe – O – Fe antisym. stretch
	[a]						~501	vw	p					Fe – O stretch in $Fe(H_2O)_6{}^{3+}$
				[a]						488	vw	p		Fe – O stretch in $Fe(D_2O)_6{}^{3+}$
388	s	p					388	s	p					Fe – O stretch in $-Fe(H_2O)_5$
			377	s	p					378	s	p		Fe – O stretch in $-Fe(D_2O)_5$
335sh	w	p?					337sh	w	p?					Fe – O stretch in $-Fe(H_2O)_5$
			324sh	w	p?					325sh	w	p		Fe – O stretch in $-Fe(D_2O)_5$
246?	vw	p	248?	vw	p		250?	vw	p	247?	vw	p		Fe – O – Fe sym. stretch

[a] A weak, broad band may be hidden by the $ClO_4{}^-$ band at 460 cm^{-1}. s, strong; w, weak; vw, very weak; p, polarized; sh, shoulder.

of the hexahydrated monomer $[Fe(H_2O)_6]^{3+}$.

We shall assume that monomeric species $[Fe(H_2O)_6]^{3+}$ are the species that give rise to the large relaxation broadened line seen in Fig. 1a. The other monomeric and dimeric species are only present in a small proportion and their contribution to the Mössbauer spectrum at this pH can be neglected.

Addition of base to the iron(III) solution up to about 0.5 equivalent OH^- per Fe^{3+} results in the appearing of a quadrupole doublet in the Mössbauer spectra of the respective frozen solutions. This feature is seen in spectra 1b and 1c. In spectrum 1c (OH/Fe = 0.5) the most prominent lines come from a quadrupole doublet with isomer shift of 0.31 mm/s and quadrupole splitting of 1.67 mm/s. The value of this isomer shift is characteristic of a high spin iron(III) state.[13] The quadrupole splitting of 1.67 mm/s is large for a high spin iron(III) species. Mössbauer spectra of high spin iron(III) compounds which show quadrupole splitting in this range (~1.5 mm/s) have been reported by several investigators [14–16] and assigned to iron(III) μ-oxo bridges of the type LFe – O – FeL where L can be different ligands.

Using the equilibrium constants of Milburn and Vosburgh [12] for $Fe(NO_3)_3$ or $Fe(ClO_4)_3$ 0.67 M aqueous solutions with OH/Fe = 0.5 we estimate that *ca.* 50 % of the total iron is in the form of the aqua dimer. Spectrum 1c was by computer fitted to three lorentzians, one lorentzian corresponding to the relaxation broadened spectrum of the ion $Fe(H_2O)_6{}^{3+}$ and the other two lorentzians corresponding to the quadrupole splitting. Measuring the areas of the lines we may get a rough estimate of the relative amount of each species present in the sample. The ratio between the areas in the Mössbauer spectrum of Fig. 1c corresponding to the monomeric species (broad line) and wide split species (quadrupole doublet) gives a proportion of 60 % of the total area for the species corresponding to the quadrupole splitting of 1.67 mm/s. The χ^2 tests for the computer fitting were excellent. This fact may be taken as a support of the assumption of only two species being present in the sample.

We assign the quadrupole split spectrum ($\Delta E_q = 1.67$ mm/s) to the dimeric species which is one of the hydrolysis products.

The Mössbauer technique is one way of

studying the magnetic interaction between the two high spin (${}^6A,t_{2g}{}^3e_g{}^2$) iron(III) ions of the dimer. In this connection it is noteworthy that the lines of the quadrupole doublet are comparatively narrow. This may be explained by assuming a zero magnetic field on the site of the absorbing nucleus and since we know the iron(III) to be in the high spin state this fact is indicative of a strong antiferromagnetic coupling producing a diamagnetic dimer ground state.

The Mössbauer spectrum of $[(\text{Fe heedta})_2\text{O}]^{2-}$ (where heedta^{3-} is the anion of *N*-(2-hydroxyethyl)-ethylene diamine-*N*,*N′*,*N′*-triacetic acid) is shown on Fig. 2 spectrum b. From an X-ray investigation[17] this species is known to be an oxo-bridged dimer. Spectrum 1a is the spectrum of the aqua dimer.

For the purpose of comparison we have in Fig. 2c included the Mössbauer spectrum of the picolinate (pic complex $[(\text{pic})_2\text{Fe(OH)}_2\text{Fe(pic)}_2]$). This complex is reported[18] to be a di-μ-hydroxo complex. While the lines for $[(\text{Fe heedta})_2\text{O}]^{-2}$ and the aqua dimer have line widths less than twice the natural line width and are approximately symmetric, the lines for $[(\text{pic})_2\text{Fe(OH)}_2\text{-Fe(pic)}_2]$ are much broader and asymmetric. In Table 1 the relevant parameters obtained at 100 K are given, allowing a quantitative comparison.

Buckley *et al.* studied the relation between the antiferromagnetic coupling and asymmetry of Mössbauer spectra for symmetrical, binuclear iron(III) complexes.[19] For complexes having strong antiferromagnetic coupling with $J \sim -100$ cm^{-1} (J is the constant of the Heisenberg-Dirac-Van Vleck operator $2J\ \mathbf{S}_a \times \mathbf{S}_b$ of the spin-Hamiltonian[20]) the population of the lowest lying, diamagnetic state is close to 100 % even at elevated (*i.e.* room) temperatures, and symmetric quadrupole split lines are observed. For binuclear complexes with weak antiferromagnetic coupling such as $[(\text{Fe salen Cl})_2]$ (salen = ethylenebis(salicylaldimine)) with $J = -7.5$ cm^{-1} the diamagnetic ground state is populated close to 100 % only at very low temperatures (≈liquid He temperatures). At higher temperatures the paramagnetic states are populated and this fact is observed in the Mössbauer spectrum as an asymmetric broadening increasing with increasing temperature.[19]

The observations of Buckely *et al.* are quite similar to our findings for $[(\text{Fe heedta})_2\text{O}]$ (strong coupling) and $[(\text{Fe pic}_2\text{OH})_2]$ (weak coupling) as is evident from Fig. 2. We furthermore conclude that the aqua dimer (spectrum 2a) is an oxobridged dimer with such a value of the antiferromagnetic coupling constant, J, that mainly the ground state is populated at $T = 100$ K.

The Mössbauer spectra in Fig. 1d and e are obtained on frozen solutions where the iron(III) is hydrolyzed beyond the stage of the binuclear species. The narrow-split quadrupole lines seen in Fig. 1d and 1e are similar to the Mössbauer spectrum of the polymer isolated from nitrate solutions by Spiro and co-workers.[21]

As far as they can be detected by the Mössbauer spectra, the polymeric species appear only in solutions containing more than 0.5 equivalent of base added per mol of iron, at the concentration used in this work (0.67 M). This is in concordance with the results obtained from ultracentrifuge experiments.[21]

The Mössbauer spectra of the polymeric species, at $T = 4$ K, as recorded by Spiro *et al.*[21] are six-line, hyperfine split spectra. This rules out the possibility that the spectrum of highly hydrolysed solutions (Spectrum 1e) can be due to an antiferromagnetically coupled dimeric species, for instance $(\text{Fe}-(\text{OH})_2-\text{Fe})^{4+}$, as suggested by Dezsi and co-workers.[22] The quadrupole doublet seen in the spectra of iron nitrate or perchlorate solutions, at moderate values of pH (Spectrum 1c) is not magnetically split at $T = 4$ K, as it can be seen in the spectra recorded by Dezsi *et al.*[22]

From the Mössbauer spectra it is very likely that the high-molecular species which gives rise to spectrum 1e is not formed by the condensation of oxo bridged dimers. This idea elucidates the study of rate of precipitation made by Knight and Sylva[23] who found that the 4+ dimer represents a "trap" for iron(III) when Fe^{3+} is hydrolyzed. They also found that acidified "iron hydroxide" does not form from the 4+ dimer directly but only *via* a monomeric iron(III).

Vibrational spectra

The vibrational spectra seem to corroborate the existence of $[(\text{H}_2\text{O})_5\text{Fe}-\text{O}-\text{Fe}(\text{H}_2\text{O})_5]^{4+}$ in the solutions investigated.

Raman spectra. Within experimental uncertainty the results for the dimer are independent of the anion. However, in the solutions made from iron(III) nitrate, mononitrato iron(III) is expected and Raman lines attributable to this complex are seen at 387 and 338 cm^{-1} in solutions without base added. No corresponding perchlorate complex has been observed. This may appear strange considering that NO_3^- and ClO_4^- carry the same charge but it may be rationalized in terms of the large difference in pK_a for HNO_3 and $HClO_4$. The nitrato iron(III) complex will not be discussed further in this paper. It was convenient to use both iron salts because the Raman lines from the anions overlap lines from the iron complex differently. Thus in the partly hydrolyzed H_2O solution from $Fe(NO_3)_3$ the FeO_6 symmetric stretching mode is observed at 501 cm^{-1},[24] whereas this band is partly covered by the 460 cm^{-1} band from perchlorate in the solutions made from $Fe(ClO_4)_3$. The corresponding FeO_6 stretching vibration for $Fe(NO_3)_3$ in D_2O is observed at 488 cm^{-1}.

The bands observed at 388 cm^{-1} and 335 cm^{-1} in H_2O solutions are found at 377 cm^{-1} and 325 cm^{-1} in D_2O. They are assigned to Fe−O stretching vibrations in $-FeO_5$ since frequency shifts with this order of magnitude between the hydrogen and deuterium compounds are expected for these stretching vibrations.[25]

The band found near 250 cm^{-1} is attributed to the symmetric Fe−O−Fe stretching vibration because it is nearly independent of hydrogen-deuterium exchange. Unfortunately, a very weak grating ghost may be seen at ~245 cm^{-1}, but instrumental conditions under these experiments have been chosen such that the ghost most probably should be considered excluded.

Infrared spectra. Partly hydrolyzed iron(III) nitrate in D_2O exhibits a band at 870 cm^{-1} and a weaker band at 830 cm^{-1} and the partly hydrolyzed perchlorate shows bands at 870 cm^{-1} and 933 cm^{-1}, the latter being weak.

The 830 cm^{-1} band can be assigned to the IR-active $\nu_2(A_2'')$-vibration of the nitrate ion, and the 933 cm^{-1} band can correspondingly be assigned to the $\nu_1(A_1)$-vibration of the perchlorate ion indicating a violation of selection rules for the free ion.[26] The 870 cm^{-1} band cannot be caused by librational modes of the coordinated D_2O molecules because these modes are found at lower frequencies in similar complexes.[25] Furthermore, we expect the corresponding HDO modes at lower frequencies and the H_2O modes, which might be expected at this frequency, should be excluded in D_2O solutions. In accordance with observations[27] on monooxo-bridged systems it seems reasonable to assign the band at 870 cm^{-1} to a Fe−O−Fe *anti*-symmetric stretching vibration.

The assignment of the vibrational spectra is given in Table 2. It is interesting to compare the frequencies for the symmetric (~250 cm^{-1}) and the *anti*-symmetric (~870 cm^{-1}) Fe−O−Fe stretching vibrations found in this work with corresponding frequencies[27] for oxo-bridged compounds with known structures. In dioxo-bridged systems all stretching vibrations are observed at frequencies below 760 cm^{-1} and this is certainly incompatible with the iron dimer. For bent mono oxo-bridged species an *anti*-symmetric stretching vibration is observed in the range 770−835 cm^{-1} and a symmetric vibration falls between 450 and 560 cm^{-1}. The linear μ-oxo dimers exhibit corresponding stretching vibrations between 820 and 950 cm^{-1} (*anti*-sym.) and between 215 and 230 cm^{-1} (symmetric). The observed stretching frequencies for the iron complex not only prove that it is a μ-oxo dimer but also point towards a linear structure. A linear structure is very sensible from a chemical consideration because this geometry maximizes the π-bonding of the system and in this way makes the oxide ion less basic than it would be with a lone pair available for proton attack.

Other measurements. Since the magnetic susceptibility measurements by Selwood[5] also Schugar *et al.*[7] have reported such measurements. The latter authors held the opinion that the 4+ dimer should have a rather low J value infering a di-μ-hydroxo bridge. Such result is not surprising considering the low precision of the technique for the study of solutions containing several paramagnetic species. Broersma[28] observed proton magnetic relaxation rates for iron(III) perchlorate solutions as a function of pH. The results were interpreted in terms of a diamagnetic dimer. A similar conclusion was obtained by Judkins[29] studying the ^{17}O NMR of hydrolyzed ferric perchlorate. These latter results are thus in accordance with the results presented in this paper.

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