

Evidence for a μ -Oxi-diiron(III) Species from Mössbauer Spectroscopy

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Abstract

Mössbauer spectra of frozen aqueous solutions that were formed by dissolving pyridinium μ -oxo-bis(trichloroferrate(III))pyridine in water provide direct evidence for the existence of a μ -oxo-bis(ferrate(III)) species. Thus the μ -oxo-bis(ferrate(III)) bridge remains intact in aqueous solution. This species should be of use in modelling two iron proteins such as haemerythrin.

Introduction

Extensive studies of solutions containing iron(III) studies of solutions containing iron(III) salts at low pH have been carried out using Mössbauer spectroscopy [1, 2]. Paramagnetic and electric quadrupole hyperfine interactions of ferric ions in ice and in $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ established evidence for the presence of $[\text{Fe}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ ions at low pH [3]. The effect of anions on the hydrolysis of iron(III) salts has received much attention [4, 9]. The anions present in iron(III) salt solutions are capable of exerting a considerable influence on the course and mechanism of the hydrolysis; this is mainly due to the presence of anions capable of coordinating iron(III) such as Cl^- [4–8] and SO_4^{2-} [9].

Recently the anion $[\text{Cl}_3\text{Fe}-\text{O}-\text{FeCl}_3]^{2-}$ has received much attention [10–17]. This anion is prepared from non-aqueous media. We have been interested in the chemistry of this species when it is redissolved into aqueous media, as it has potential as a model for dimers in the initiation of hydrolysis and also as a model complex for non-haem two-iron proteins [15].

Mössbauer spectra of iron(III) nitrate frozen solutions have been studied by several research groups [2, 18–22]. Though the measured Mössbauer parameters agree (within experimental error) there are differences in the interpretation of the results. The quadrupole splitting of about 1.6 mm s^{-1} which appears at $\text{pH} \approx 1$ is ascribed to oxygen-bridged

binuclear iron ions $[\text{Fe}-\text{O}-\text{Fe}]^{4+}$ by Du Fresne and others [20–22], whereas Vertes *et al.* [2] have assumed the presence of the dihydroxy ion as in perchlorate solutions [23].

Chaves and Garg [21] studied iron(III) perchlorate and nitrate solutions; they considered that the quadrupole doublet of *ca.* 0.6 mm s^{-1} that appears at $\text{pH} > 2$ is caused by the $[(\text{H}_2\text{O})_5\text{Fe}-\text{O}-\text{Fe}(\text{H}_2\text{O})_5]^{4+}$ complex ion, and at lower pH (0.2–2) the two quadrupole doublets that appear at *ca.* 1.6 and 0.4 mm s^{-1} are related to the complex ion with an iron–hydroxide bridge and to the hydrate $[\text{Fe}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}]$. A number of studies on FeCl_3 frozen solutions at various pH values have been reported [1], most of these have been low temperature studies attempting to utilize hyperfine splitting to characterise species present, but no definite spectra have been assigned to dimer formation.

With the above literature in mind, we have studied frozen solutions prepared either from anhydrous FeCl_3 or from pyridinium salt of $[\text{Cl}_3\text{Fe}-\text{O}-\text{FeCl}_3]^{2-}$; we now report our findings.

Results and Discussion

The Mössbauer data are presented in Table I. Typical spectra are seen in Figs. 1 and 2.

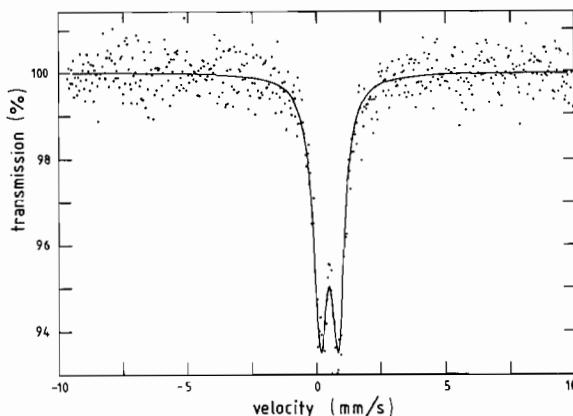


Fig. 1. 80 K Mössbauer spectrum of a frozen aqueous solution of FeCl_3 (2 M) (frozen at pH 2.0).

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TABLE I. ^{57}Fe Mössbauer Parameters for Frozen Solutions Containing Iron(III) and Chloride at 80 K

Compound	pH Solution frozen at	δ (mm s $^{-1}$)	Δ (mm s $^{-1}$)	Γ (mm s $^{-1}$)
(1) FeCl_3 (solid anhydrous)		0.525(5)	—	0.294(8)
(2) FeCl_3^{b}	1.0	0.461(7)	0.70(1)	0.31(1)
(3) FeCl_3^{b}	1.6	0.452(4)	0.70(7)	0.304(6)
(4) FeCl_3^{b}	2.0	0.463(8)	0.693(13)	0.310(12)
(5) FeCl_3^{b}	3.55	0.444(3)	0.756(4)	0.304(4)
(6) $[\text{Hpy}]_2[\text{Fe}_2\text{OCl}_6] \cdot \text{py}^{\text{d}}$ (solid)		0.335(4)	1.272(8)	0.199(6)
(7) $\text{A}^{\text{b,c}}$	2.0	0.461(7)	0.695(11)	0.233(9)
(8) $\text{A}^{\text{b,c}}$	2.1	0.487(6)	0.667(10)	0.215(8)
(9) $\text{A}^{\text{b,c}}$	4.0	0.467(5)	0.711(8)	0.234(7)
(10) $\text{A}^{\text{b,c}}$	4.5	0.478(3)	0.716(5)	0.248(5)
(11) $\text{A}^{\text{b,c}}$	5.91	0.459(4)	0.732(6)	0.270(5)
(12) $\text{FeCl}_3 + \text{py}^{\text{d}} + \text{H}_2\text{O}$	1.8	0.452(11)	0.722(17)	0.324(16)
(13) $\text{FeCl}_3 + \text{py}^{\text{d}} + \text{ethanol}$	e	0.370(4)	1.329(7)	0.258(6)

$^{\text{a}}$ Half width at half height. $^{\text{b}}$ Frozen solution. $^{\text{c}}\text{A} = [\text{Hpy}]_2[\text{Fe}_2\text{OCl}_6] \cdot \text{py}$ dissolved in water. $^{\text{d}}\text{py}^{\text{d}} = \text{pyridine}$. $^{\text{e}}$ pH unknown.

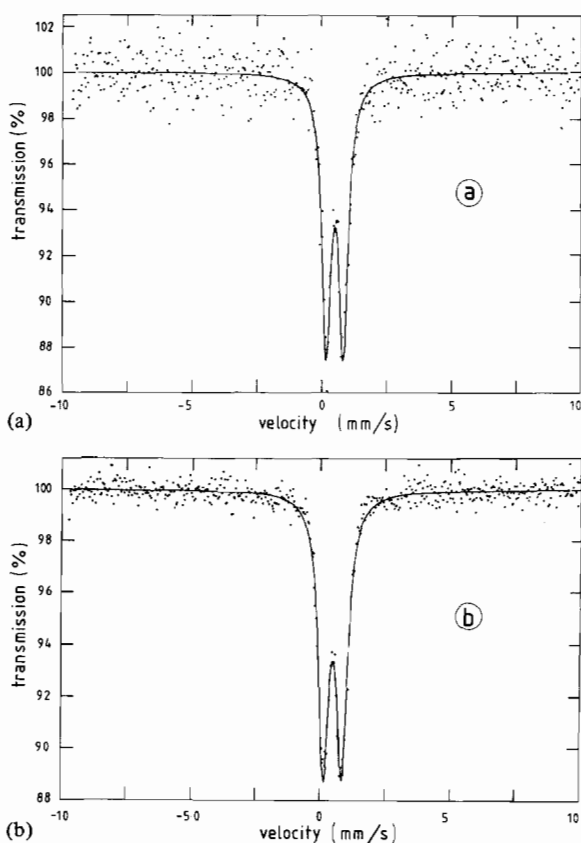
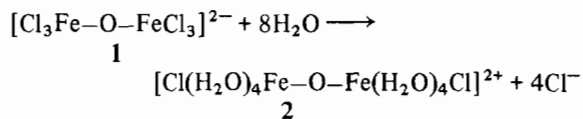


Fig. 2. 80 K Mössbauer spectrum of a frozen aqueous solution of pyridinium μ -oxo-bis(trichloroferrate(III))pyridine (0.3 M) (frozen at pH 2.0 (a) and pH 4.5 (b)).

On examination of this data several points of significance emerge. Perhaps the most important is that although the isomer shifts and quadrupole splitting

for the FeCl_3 frozen solutions spectra 2–5 (Table I) are very similar to those for the pyridinium μ -oxo-bis(trichloroferrate(III)) solutions spectra 7–11 (Table I) the linewidths of the latter are about one-third less. This can only be interpreted in that the latter solutions contain fewer or perhaps only one iron(III) species whereas the former contain at least two. The logical conclusion for the similarity of the Mössbauer data in the two systems is that one species is in common to both. We believe the most likely candidate is a μ -oxo-oligomer of the following type $(\text{H}_2\text{O})_4\text{ClFe}-\text{O}-\text{Fe}(\text{H}_2\text{O})_4\text{Cl}$. It can be derived from the anion of the pyridinium salt as follows:



Evidence for this reaction comes from conductometric studies (see Experimental section) which show the presence of 7 ions; (of these, two originate from the two pyridinium cations and 5 from the anion).

The decomposition of **1** in aqueous systems to replace two Cl^- ions by four water molecules is highly likely as **1** has not yet been isolated from aqueous media. The evidence for the μ -oxo-bridge remaining intact is the small linewidth when compared to FeCl_3 solutions, suggesting that a complete breakdown of the anion **1** does not occur. In support of this, a 10^{-1} M aqueous solution of pyridinium μ -oxo-bis(trichloroferrate(III))–pyridine is red brown in colour until a pH of 5.3 at which point as the pH is raised the colour fades and a pale yellow orange

precipitate forms. This must indicate that the solubility of this μ -oxo-bis(chlorotetraaquaferrate(III)) cation is higher than that of most iron(III) species that form in the FeCl_3 solutions (the latter are known to start precipitating below pH 4). Indeed from the Mössbauer spectrum 10 at pH 4.5 there is still a predominance of the μ -oxo complex, and only at pH 5.9 spectrum 11, does definite evidence appear for the precipitate being similar in nature to that of the FeCl_3 frozen solution spectrum 5, which also contains a precipitate. In spectrum 11 the quadrupole splitting and linewidths are closer to those of spectrum 5 than those of spectra 7–10. The fact that the Mössbauer parameters for the μ -oxo species in these systems have a quadrupole splitting of about 0.7 mm s^{-1} which is different to that reported in iron(III) nitrate frozen solutions we take as evidence for some Cl^- still binding to the Fe(III) in our systems. The work of Nozik and Kaplan [3] which found Cl^- bound to Fe(III) and that reported by Vertes for $[\text{FeCl}_2(\text{H}_2\text{O})_4]^+$ and $[\text{FeCl}(\text{H}_2\text{O})_5]^{2+}$ we feel also supports our prognosis.

An obvious point that must be noted here is that this μ -oxo species 2 cannot be a main intermediate in FeCl_3 solutions or they would not begin precipitating below pH 4. This observation is in keeping with a similar finding for iron(III) perchlorate [22], and also with a study of the rate of precipitation made by Knight and Sylva [24] who found that the 4+ dimer represents a 'trap' for iron(III) when Fe^{3+} is hydrolysed. They also deduced that acidified 'iron hydroxide' does not form from the 4+ dimer directly but only via a monomeric iron(III).

The Mössbauer data spectrum 12 of the aqueous solution of pyridine and FeCl_3 are similar to those of the FeCl_3 solutions (spectra 2–5) even the line widths are similar. Thus this spectrum provides evidence that the pyridinium (and pyridine) in the solutions does not account for the narrow lines found in spectra 7–10.

The parameters from the frozen solutions of pyridine and FeCl_3 in ethanol are not very different to those for the solid pyridinium μ -oxo-bis(trichloroferrate(III)) pyridine. It is thus likely that the latter solid forms quickly when high concentrations of the starting products are used, (compare slow formation previously reported).

Conclusions

It is apparent from this work that the solutions prepared from pyridinium μ -oxo-bis(trichloroferrate(III))-pyridine contain a μ -oxo-bis(ferrate(III)) species which may have potential use as a model for two-iron proteins such as haemerythrin. This μ -oxo species will be of use in the pH range 2–5 in aqueous solution.

Experimental

Materials

Pyridinium μ -oxo-bis(trichloroferrate(III))pyridine was prepared by the method of Drew *et al.* [10]. FeCl_3 anhydrous (Aldrich) pyridine (Fisons) were all used without further purification.

Frozen solutions for Mössbauer studies were prepared using Fe concentrations of around 2 M for the FeCl_3 experiments, and 0.6 M for the pyridinium μ -oxo-bis(trichloroferrate(III)) pyridine solutions. The aqueous solutions were all adjusted to the required pH using 2 M sodium hydroxide solution. The solutions used for the $\text{FeCl}_3 + \text{py}^1$ in water and in ethanol solutions (refs. 12 and 13 and Table I) contained 2 M FeCl_3 and 6 M pyridine. The solutions once prepared were frozen in a polythene cell for the Mössbauer experiments.

The Mössbauer spectrometer and experimental details have been described previously [25].

Conductometric Studies

A solution was prepared by dissolving pyridinium- μ -oxo-bis[trichloroferrate(III)] in water to give a concentration of 0.01 M. This stock solution was then diluted to 0.005, 0.004, 0.003, 0.002 and 0.001 M and conductivities were measured. (The natural pH of the stock solution was 2.6). The molar conductivity at infinite dilution was then determined and the number of ions in solution established as 7. This indicates that the most likely species resulting from the $[\text{Cl}_3\text{Fe}-\text{O}-\text{FeCl}_3]^{2-}$ anions are 4Cl^- anions and a $[\text{Cl}(\text{H}_2\text{O})_4\text{Fe}-\text{O}-\text{Fe}(\text{H}_2\text{O})_4\text{Cl}]^{2+}$ cation.

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