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Mössbauer and EPR Spectroscopic Study of the Iron–EDTA System

A. MARTON

II Department of Biochemistry, Semmelweis University, Medical School, Budapest, Hungary

N. SÜKÖSD-ROZLOSNIK

Department of Atomic Physics, L. Eötvös University, Budapest, Hungary

A. VÉRTES, I. NAGY-CZAKÓ

Radiochemical Laboratory, L. Eötvös University, Budapest, Hungary

and K. BURGER*

Department of Inorganic and Analytical Chemistry, A. József University, Szeged, P.O. Box 440, 6701-Hungary

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Abstract

Mössbauer and EPR spectroscopic studies of the iron(III)–EDTA system have shown that primarily the mode of preparation (the reaction of iron(III) with the ligand, or oxidation of the iron(II) complex) determines the iron(III)–iron(III) spin–spin interaction (dimer formation) in the complexes. Increases in the concentration and the pH also promote the dimerization process.

The pH-dependence of the Mössbauer spectra of the iron(II)–EDTA complexes revealed the formation of a protonated complex, besides the parent complex, in acidic solution.

Introduction

X-ray structural analysis [1–3] and Mössbauer spectroscopy [4] of iron(III) complexes of EDTA have shown that species of different compositions are formed, depending on the iron concentration and the pH of the reaction mixture used in the preparation process. Recent biochemical investigations [5] have indicated that the complexes prepared by the interaction of iron(III) salts with EDTA and by oxidation of the iron(II)–EDTA complex, respectively, have different biological effects. The latter enhances lipid preoxidation in brain tissue but the former does not [5].

Since Mössbauer spectroscopy is probably the most specific method for studying the electronic structure of iron in its compounds [6], and EPR spectroscopy can give direct information on the interaction of paramagnetic iron(III) centres [7], these methods were used to study the iron(III)–EDTA system in the present work. Both preparation modes mentioned above were carried out in solutions with different iron concentrations and different pH values. The results are presented in this paper.

Experimental

Aqueous solutions of EDTA–iron complexes (molar ratio = 1:1) were prepared by the interaction of $FeCl_3$ with EDTA (preparation mode A) or by bubbling oxygen through a solution containing $FeSO_4$ and EDTA in a 1:1 molar ratio (preparation mode B). The concentrations and pH values of the resulting solutions are given in the Tables. For all samples the pH was adjusted with NH_4OH to the value given in the Tables.

For the Mössbauer study, the solutions were quenched by the quick-freezing technique of Vértes *et al.* [6], and the Mössbauer spectra were recorded at liquid nitrogen temperature. Three typical spectra of the iron(III)–EDTA system are shown in Fig. 1. The Mössbauer parameters are reported in Table I. The isomer shifts refer to α-iron. For comparison, Mössbauer spectra of the iron(II)–EDTA system were also recorded.

The EPR spectra were recorded with an X-band EPR spectrometer at 80 K. The aqueous solutions of the complexes prepared by procedures A and B, respectively, were quenched by rapid freezing in the EPR sample holder with liquid nitrogen.

Two typical EPR spectra are shown in Fig. 2. The EPR parameters are given in Table II.

*Author to whom correspondence should be addressed.

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TABLE I. Mössbauer Parameters[a] of 0.5 mol dm^{-3} Iron–EDTA Aqueous Solutions Quenched by Quick-freezing

Preparation[b] mode	Oxidation state of Fe	pH	Isomer shift (mm s^{-1})	Quadrupole splitting (mm s^{-1})	Line width (mm s^{-1})
	+2	2.5	1.14	2.96	0.78
			1.34	3.19	0.78
	+2	7.0	1.29	3.32	0.56
A	+3	7.0	0.49		2.69
B	+3	7.0	0.54		2.10
A	+3	8.5	0.47	1.65	0.38
			0.43	0.57	0.28
B	+3	8.5	0.46	1.64	0.32

[a]Uncertainty: ±0.03 mm s^{-1}. [b]A: preparation by reaction of iron(III) with EDTA; B: preparation by oxidation of the iron(II)–EDTA complex.

TABLE II. EPR Data on Iron(III)–EDTA Complexes in Aqueous Solution

Preparation mode	Iron concentration (mol dm^{-3})	pH	g = 2.0 line		g = 4.2 line		Isolated iron(III) (%)
			Line width (G)	Integral intensity[a]	Line width (G)	Integral intensity[a]	
A	0.00500	6.0			350	0.16	100
	0.0500	6.5			260	1.6	100
	0.500	6.5			550	9.2	100
	0.00500	7.0			250	0.32	100
	0.0500	7.0	900	0.97	150	0.93	50
	0.500	7.0	900	1.59	150	2.0	57
	0.0500	7.5	750	3.15	40	0.16	5
	0.0500	8.1	700	2.78	30	0.045	0.16
	0.500	8.5	520	30.0	60	0.33	1.0
B	0.500	6.5			340	7.76	100
	0.00500	7.0			350	0.35	100
	0.0500	7.0			370	2.4	100
	0.0500	8.1			100	0.24	100
	0.0500	8.5			50	0.35	100
	0.500	8.5	500	3.0	300	0.60	16

[a]Determinated by double integration of the first derivative spectra.

Results and Discussion

Mössbauer Studies

The iron(II)–EDTA system (metal:ligand ratio 1:1, iron(II) concentration 0.5 mol dm^{-3}) revealed the presence of two types of iron(II) species at pH 2.5. The Mössbauer parameters of both differed from those of $Fe(OH_2)_6^{2+}$ [6], indicating the formation of two different EDTA complexes of iron(II). The integral intensities of the two doublets suggested roughly equal concentrations of the two complexes in the solution. In the same system at pH 7, only one quadrupole-split line-pair appeared, with similar parameters to those for one of the species in the previous solution (Table I).

These results led us to assume that, besides the iron(II)–EDTA parent complex, a protonated iron(II)–EDTA complex is also present in the solution at pH 2.5. The smaller isomer shift and quadrupole splitting in the latter species indicate a higher electron density at the iron nucleus and a higher symmetry of the electronic shell of the iron in the protonated complex. Different coordination numbers and configurations for protonated and non-protonated EDTA complexes of iron(III) have been demonstrated in previous investigations [1, 2].

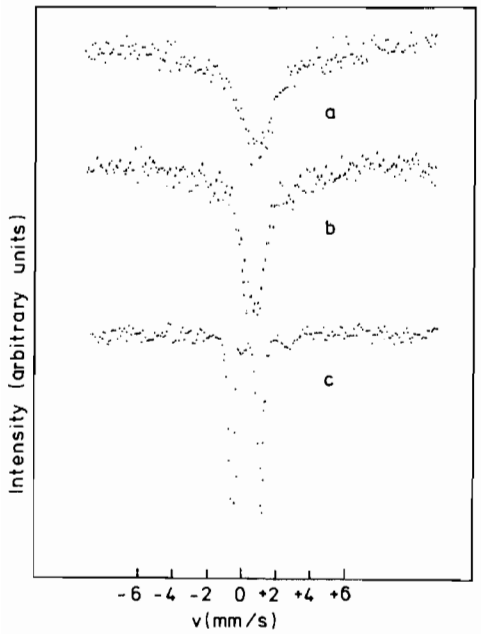


Fig. 1. Mössbauer spectra of frozen solutions of the iron(III)–EDTA complex (iron concentration, 0.500 mol dm^{-3}) prepared: (a) by the interaction of $FeCl_3$ with EDTA in aqueous solution at pH = 7; (b) by oxidation of the iron(II)–EDTA complex (the oxidation was performed by bubbling oxygen through the solution at pH = 7); (c) by oxidation of the iron(II)–EDTA complex at pH = 8.5.

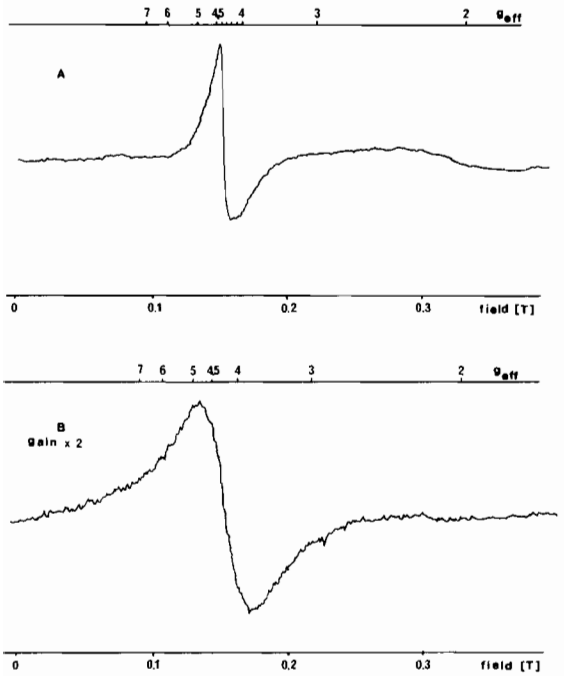
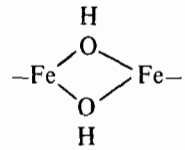


Fig. 2. The 80 K X-band EPR spectra of the iron(III)–EDTA complex in aqueous solutions (iron concentration 0.050 mol dm^{-3}) at pH = 7, prepared: (a) by the interaction of $FeCl_3$ with EDTA; (b) by oxidation of the iron(II)–EDTA complex.

A similar phenomenon can be assumed in the analogous iron(II) system.

The Mössbauer spectra of the iron(III)–EDTA system prepared by the direct reaction of iron(III) with the ligand and by oxidation of the iron(II) complex, respectively, proved to be different in solutions at pH 8.5. In aqueous solutions at such a high pH, iron(II) is spontaneously oxidized. The Mössbauer spectrum of its frozen solution shows a uniform pattern, with a doublet with a surprisingly high quadrupole splitting for iron(III) (*QS* 1.64 mm s^{-1}). The same doublet appears in the spectrum of the complex prepared by the reaction of iron(III) with the ligand, but a typical iron(III) doublet (*IS* 0.43 mm s^{-1}, *QS* 0.57 mm s^{-1}) is also present. The ratio of the integral intensities of these two patterns is 8.6:1.4.

The literature data [4, 6 and references in the latter] allow both patterns to be assigned to binuclear iron(III) complexes. The two central iron(III) atoms are connected by one oxygen bridge (>Fe–O–Fe< moiety) in the species with *QS* –1.6 mm s^{-1} [8], and by two hydroxide ligands



in the other one [9]. The narrow line width for both types of pattern (0.38 and 0.28 mm s^{-1}, respectively) reveals a fast paramagnetic spin relaxation due to the strong spin–spin interaction in the dimer in both species, preventing line broadening [10].

When the same preparation procedures were repeated in solutions at pH 7, both spectra (of samples prepared by direct reaction or by oxidation) exhibited very broad lines, demonstrating a relatively slow paramagnetic spin relaxation ($\tau^{-1} \sim 10^9$ s^{-1} [11]). This experimental result demonstrates that some of the iron(III) is in the mononuclear form at pH 7.

The Mössbauer studies had to be performed in rather concentration solution (0.5 mol dm^{-3}) in order for accurate data to be obtained. This favoured dimer formation in the system. In contrast, the earlier biochemical investigations [5] revealing the differences in behaviour of the iron(III) complexes prepared in different ways were performed in more dilute solutions. To acquire information on possible differences in dimerization in the latter solution, the concentration- and pH dependences of this process were studied by EPR spectroscopy.

EPR Studies

The EPR spectra of the complexes prepared by the reaction of iron(III) with EDTA (method A)

showed both a concentration- and a pH-dependence (between 0.005 and 0.5 mol dm^{-3} and in the pH interval 6–8.5). One narrow peak at $g = 4.2$ reflects the presence of non-interacting iron(III) centres in solutions with $pH < 7.0$. Besides this peak at $g = 4.2$, a much broader line appears at $g = 2.0$ for solutions with $pH > 7.0$, and for the solution with iron concentration 0.05 mol dm^{-3} and $pH = 7.0$, but not in that with iron concentration 0.005 mol dm^{-3} and $pH = 7.0$. The latter line at $g = 2.0$ indicates the presence of interacting iron(III) centres in the solution.

These data show that the intramolecular iron(III)–iron(III) magnetic interaction (*i.e.* dimer formation) is not only concentration-dependent but is also pH-dependent. At pH 6.5 no dimerization is observed even in solutions with iron concentration 0.5 mol dm^{-3}, in contrast to solutions with higher pH, in which dimer formation is also favoured at low iron concentrations. The dimer concentration in the latter solutions (constant iron concentration 0.05 mol dm^{-3}) increases with an increase in pH.

The EPR studies of the iron(III) complex prepared by oxidation of the iron(II)–EDTA complex (method B) did not reflect intramolecular iron(III)–iron(III) mgnetic interactions in the concentration range 0.005–0.05 mol dm^{-3} and the pH range 6.0–8.5. The spectra contained only the line at $g = 4.2$, typical of isolated iron(III) centres. However the widths of the line at $g = 4.2$ for solutions of analogous composition and pH, but prepared by the two different methods (direct interaction of iron(III) with EDTA or oxidation of the iron(II) complex) displayed significant differences, indicating different intermolecular interactions.

In the solution with iron concentration 0.500 mol dm^{-3} and $pH = 8.5$ prepared by method B, the EPR spectrum showed (in accordance with the Mössbauer studies) that 84% of the iron(III) content is present in the dimeric form. In a solution of identical composition but prepared by method A, 99% of the iron(III) content is in the dimeric form.

The results of all these investigations permit the conclusion that the differences in biochemical behaviour of the iron(III)–EDTA complexes prepared by the two methods discussed above are due to the different iron(III)–iron(III) interactions (different types of dimer formation) in the corresponding systems.

The EPR line widths in the spectra decreased with increasing pH of the solution, reflecting relaxation time increases, probably resulting from the decreased interaction of the paramagnetic centres with the chemical environment. This phenomenon may be due to the fact that the pH increase results in an increased coordination of hydroxide ligands by the central iron(III) atoms of the EDTA complexes. The EDTA–OH^- mixed complexes seem to be more isolated from their surroundings than the parent complex.

The pH-dependence of the line width relating to the spectral pattern at $g = 2.0$ is in accordance with the Mössbauer observation indicating the formation of a second dimer in the system at high pH, in which one oxide bridge connects the iron(III) centres instead of the two hydroxide bridges formed at lower pH values.

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References

1 M. D. Lind and J. L. Hoard, *Inorg. Chem. 3*, 34 (1964).
2 J. L. Hoard, C. H. L. Kennard and G. S. Smith, *Inorg. Chem., 2*, 1316 (1963).
3 H. G. Cohen and J. L. Hoard, *J. Am. Chem. Soc., 86*, 2749 (1964).
4 G. E. Stein and J. A. Marinsky, *J. Inorg. Nucl. Chem., 37*, 2421 (1975).
5 A. Marton, N. Sükösd-Rozlosnik, A. Vértes and I. Horváth, to be published.
6 A. Vértes, L. Korecz and K. Burger, 'Mössbauer Spectroscopy', Elsevier, Amsterdam/Oxford/New York, 1979, p. 230.
7 L. Nagy, J. Kürti, L. Korecz and K. Burger, *Inorg. Chim. Acta, 124*, 55 (1986).
8 F. T. de Aranjo, A. Du Fresne, C. G. de Lima and J. M. Knudsen, *Chem. Phys. Lett., 7*, 333 (1970).
9 J. Dézsi, A. Vértes and M. Komor, *Inorg. Nucl. Chem. Lett., 4*, 649 (1968).
10 A. Vértes and F. Parak, *J. Chem. Soc., Dalton Trans.*, 2062 (1972).
11 H. H. Wichman, in I. J. Gruverman (ed.), 'Mössbauer Effect Methodology', Vol. 2, Plenum Press, New York, 1966, p. 39.