

# Mössbauer study of peroxynitrito complex formation with Fe<sup>III</sup>-chelates

Zoltan Homonnay · Peter Buszlai · Judit Nádor ·  
Virender K. Sharma · Erno Kuzmann · Attila Vértes

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**Abstract** The reaction of the  $\mu$ -oxo-diiron(III)-L complex (L = EDTA, ethylene diamine tetraacetate, HEDTA, hydroxyethyl ethylene diamine triacetate, and CyDTA, cyclohexane diamine tetraacetate) with peroxynitrite in alkaline solution was studied by Mössbauer spectroscopy using rapid-freezing technique. These complexes yield an (L)Fe<sup>III</sup>( $\eta^2$ -O<sub>2</sub>)<sup>3-</sup> complex ion when they react with hydrogen peroxide and the formation of the peroxide adduct results in a deep purple coloration of the solution. The same color appears when the reaction occurs with peroxynitrite. Although spectrophotometry indicated some difference between the molar extinction coefficients of the peroxo and the peroxynitrito adducts, the Mössbauer parameters proved to be the same within experimental error. It is concluded that the peroxynitrite ion decomposes when reacting with Fe<sup>III</sup>(L) and the peroxo adduct forms.

**Keywords** Mössbauer spectroscopy · Iron chelates · Peroxo adduct · Frozen solution

## 1 Introduction

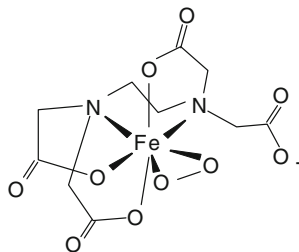
The reaction of the  $\mu$ -oxo-diiron(III)-EDTA complex (EDTA = ethylene diamine tetraacetate) with H<sub>2</sub>O<sub>2</sub> in alkaline solution has been studied earlier [1] by Mössbauer spectroscopy through rapid-freezing of the reaction medium in order to identify possible intermediate species during the formation and decomposition of the purple (EDTA)Fe<sup>III</sup>( $\eta^2$ -O<sub>2</sub>)<sup>3-</sup> complex ion (Fig. 1).

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Z. Homonnay (✉) · P. Buszlai · J. Nádor · E. Kuzmann · A. Vértes  
Institute of Chemistry, Eötvös University, Budapest, Hungary  
e-mail: homonnay@ludens.elte.hu

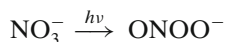
V. K. Sharma  
Florida Institute of Technology, Melbourne, FL, USA

**Fig. 1** Schematic structure of the  $(\text{EDTA})\text{Fe}^{\text{III}}(\eta^2\text{-O}_2)^{3-}$  complex ion.



This reaction has significance in environmental chemistry because photochemically formed peroxide in natural waters may be activated by this process and this facilitates decomposition of organic pollutants.

Nitrate is also an important industrial pollutant, and can interfere this reaction by forming peroxyxynitrite:



It is observed that when the dimer

$[(\text{EDTA})\text{Fe}^{\text{III}}\text{-O-Fe}^{\text{III}}(\text{EDTA})]^{4-}$  (which is stable at high pH) is reacted with peroxyxynitrite, the same color appears as that found in the reaction with hydrogen peroxide. It was observed that the UV-visible spectrum of this reaction product is the same as that of the *dihapto*-peroxo complex  $[(\text{EDTA})\text{Fe}^{\text{III}}(\eta^2\text{-O}_2)]^{3-}$ , while the molar extinction coefficients significantly differ [2].

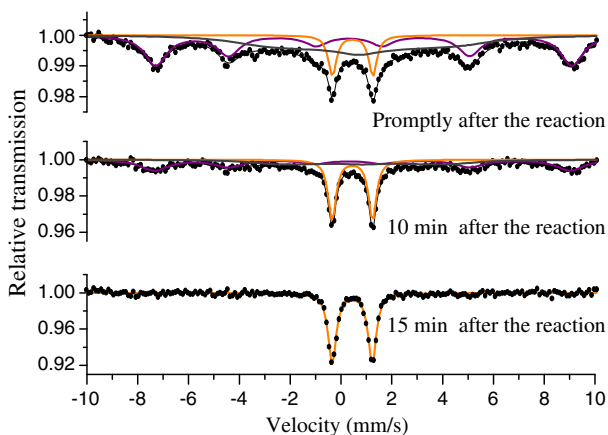
We have measured the Mössbauer spectra of the assumed peroxyxynitrito complexes in order to characterize them and to get information on their structure. In addition to EDTA, HEDTA, hydroxyethyl ethylene diamine triacetate, and CyDTA, cyclohexane diamine tetraacetate were also studied.

## 2 Experimental

Mössbauer Spectroscopy experiments were carried out in frozen solutions after mixing the solution of the  $\text{Fe}^{\text{III}}(\text{L})$  complex with peroxyxynitrite. The cooling rate was higher than 50 K/s which preserves the structure of the complexes [3]. The stock solution of peroxyxynitrite was purchased from Cayman Chemicals, and delivered in 0.3 M NaOH solution (required for its stability) with proper cooling. The maximum available concentration was 0.042 M and this set a limit of the maximum iron concentration (in the form of  $^{57}\text{Fe}$ ) used in the Mössbauer measurements. Peroxyxynitrite was applied in 3-fold excess relative to  $\text{Fe}^{\text{III}}$ . The final pH was set by the initial pH of the  $\text{Fe}^{\text{III}}(\text{L})$  solution.

The Mössbauer spectra were recorded in constant acceleration mode using a Ranger spectrometer with a  $^{57}\text{Co}(\text{Rh})$  source of about  $10^9$  Bq activity. The samples were kept frozen at 80 K in a tank type liquid nitrogen cryostat. The spectrum analyses were performed with help of the Moss Winn code. All isomer shifts are given relative to alpha iron at room temperature.

**Fig. 2** Mössbauer spectra of the Fe<sup>III</sup>-EDTA-peroxynitrite system at pH = 11



### 3 Results and discussion

As an example, selected Mössbauer spectra of the Fe—EDTA—peroxynitrite system can be seen in Fig. 2. The first spectrum was recorded right after mixing the Fe<sup>III</sup>(L) solution with peroxynitrite, and then the frozen sample was let melt and, depending on how fast the purple color began to fade away, it was rapidly frozen again. The aim of this process was to identify intermediate iron species as many as possible during the decomposition of the purple species. These details will be published elsewhere.

Here we concentrate on the first major sextet observed in the spectra, which is a signature of the peroxo adduct. This assignment was also proved by the parallel disappearance of the color of the reaction mixture and the sextet from the Mössbauer spectra. The final stage of the reactions is always the formation of the [(L)Fe<sup>III</sup>-O-Fe<sup>III</sup>(L)] type dimer with very characteristic Mössbauer parameters (a doublet with  $\delta = 0.45$  mm/s,  $\Delta = 1.59$  mm/s).

Let us note that magnetic splitting of the monomeric [(L)Fe<sup>III</sup>( $\eta^2$ -O<sub>2</sub>)] species is of paramagnetic spin relaxation origin and therefore it always appears with rather broad lines. In addition to this sextet, a relaxational component also shows up in most of the spectra which may be assigned to a so far unidentified intermediate species or simply due to random distance of the paramagnetic Fe<sup>III</sup> species in the frozen solution resulting in variable relaxation distortion of the sextets. However, at least a significant part of the Fe<sup>III</sup> species has relaxation slow enough to give rise to a well developed sextet, and this gives chance to determine the key parameters of this species. It is also noteworthy that monomeric species other than the peroxo adduct shows up only in the CyDTA system.

The well reproduced doublet of [(L)Fe<sup>III</sup>-O-Fe<sup>III</sup>(L)] is a result of fast relaxation due to the close proximity of the Fe<sup>III</sup> centers in the dimeric structure.

Table 1 shows the Mössbauer parameters of the purple species formed with peroxynitrite in comparison with those obtained in reaction with hydrogen peroxide.

It can be seen that the isomer shifts are very close to each other disregarding the type of the chelating ligand or the choice of hydrogen peroxide *vs.* peroxynitrite. The value is somewhat lower in the case of CyDTA with peroxynitrite but it is still within experimental error. The same is true for the quadrupole shifts even if here the differences are larger.

**Table 1** Mössbauer parameters of the assumed  $[(L)Fe^{III}(ONO_2)]$  species in comparison with those of  $[(L)Fe^{III}(\eta^2-O_2)]$ , L = EDTA, HEDTA and CyDTA

	Peroxynitrite experiment			Hydrogen peroxide experiment		
	$\delta$ (mm/s) $\pm 0.02$	$\varepsilon Q$ (mm/s) $\pm 0.15$	$B$ (T) $\pm 0.5$	$\delta$ (mm/s) $\pm 0.03$	$\varepsilon Q$ (mm/s) $\pm 0.18$	$B$ (T) $\pm 0.5$
EDTA	0.60	+0.54	51.0	0.62[1]	+0.53[1]	51.5[1]
HEDTA	0.63	+0.55	50.8	0.54[5]	+0.87[5]	50.5[5]
CyDTA	0.60	+0.71	50.7	0.61[4]	+0.80[4]	50.2[4]

The hyperfine magnetic fields can also be considered identical.

There are two possible scenarios to explain this. Peroxynitrite has a peroxo moiety which may behave like peroxide and gets bound to the iron center via side-on configuration (dihapto binding). In this case it is difficult to judge to what extent the presence of NO group on the OO unit would change the isomer shift and the quadrupole shift compared to the peroxo adduct but, very likely, the effect would be larger than the experimental error.

On the other hand, it is also possible that peroxynitrite decomposes into NO and  $H_2O_2$  as follows:  $2HONOO+2H_2O \rightarrow 3H_2O_2+2NO$ . This can provide conditions to the regular reaction between hydrogen peroxide and  $Fe^{III}(L)$ . Here the question arises whether the limited amount of hydrogen peroxide that forms from decomposing peroxynitrite is enough to form the purple species? As can be seen from the equation of the chemical reaction, the applied 3-fold excess peroxynitrite provides 4.5-fold excess  $H_2O_2$  if the decomposition is complete. Since in the hydrogen peroxide experiments we used 30-fold excess or even more, we ran an experiment with an amount of  $H_2O_2$  stoichiometrically just equivalent with peroxynitrite. The purple species readily formed and the Mössbauer parameters were well reproduced.

#### 4 Conclusion

We can now conclude that when peroxynitrite reacts with  $Fe^{III}(L)$  where L = EDTA, HEDTA or CyDTA, at high pH, the dihapto peroxo complex  $[(L)Fe^{III}(\eta^2-O_2)]$  readily forms. This assumes that peroxynitrite decomposes just before the reaction. This pre-decomposition may be initiated by the sudden drop of the pH from over 13 to about 10.5 to 11.

It is also possible that peroxynitrite gets bound to the iron center through its OO moiety which is followed by fast release of NO by a possibly multistep mechanism.

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