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Short Communication

Iron and Terahydropterin Complex with 1,3,5-Triamino-2,4,6-trihydroxy-cyclohexane as Ligand

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Introduction

During our reaserch on the complexes of tetrahydropterin (THP) or tetrahydrobiopterin (THP) with molybdenum and iron, we used 2,4-dioxo-pentane (acetylacetonate, acacoH), whose chelate properties are well known, as second ligand [1-4]. During the formation of these complexes, THP or THB occupies two of the six coordination sites of the metal, while two acaco anions occupy the four other, so that an activation of O_2 by the nucleus Fe(II) seems rather difficult. On the contrary, a complex of THP Fe(II) with a tricoordinate ligand will have only five coordination sites occupied, leaving a sixth site free for a possible oxygen activation. With this argumentation in mind, we tried to obtain such a complex using 1,3,5-triamino-2,4,6-trihydroxy-cyclohexane (TAHC) as ligand, especially because the structure of $(TAHC)_2$ Fe(III). 3HCl has been resolved by X-ray [5]. Using the ESI- and FAB-MS technology, which gave excellent results in the study of (THP) Fe(II) or Fe(III) complexes [2], we measured the spectrum of **1** in solution (10^{-3}M, H_2O/CH_3OH, 4:1, spectrum A, Fig. 1) As in the case of THB or THP, we did not obtain the lone signal of a complex, but signals of a mixture of complexes whose constitution was resolved by the calculation of each singular signal.

M/Z signals: **178**: $[TAHC+H^+]^+$, theor.=178; **204.7** : [(TAHC) (TAHC-3H$^+$)Fe(III)]°, theor.=407°, $407+2H^+=[409]^+ : 2=204.5$; 231.4 : [(TAHC-3H$^+$) Fe (III)]°, theor.=[230]°, $230+H^+=[231]^+$; **267.5** : $[(TAHC-3H^+)Fe(III)]^\circ+[HCl+H^+]^+$, theor.=267.5; **303.3** : $[(TAHC-3H^+)Fe(III)]^\circ+[2HCl+H^+]^+$, theor. =303.5. Perhaps a similar complex with 3HCl exists but without an electrical charge and without a signal; such a complex cannot carry a 4th proton because it does not have a 4th basic group at disposition. **408** : [(TAHC) (TAHC-3H$^+$) FE(III)]° theor. =[407]°, $+[H^+]$ = 408 (**1**, Fig. 2); **444.4**: $[1^+ +$ HCl], theor. 444.5 (**2**, Fig. 2); **480,7**: $[1^+, 2HCL]^+$, theor. 481 (**3**, Fig. 2); **517** : $[\mathbf{1}^+ + 3HCl]^+$, theor. 517.5. The ESI-MS became more complicated as soon as an equivalent of THP was added to the solution of 1 (Fig. 1, spectrum B). The new spectrum possesses all the signals of the mixture **1+2+3** mentioned above. The difference between spectrum A and spectrum B gave the image of a new spectrum C (Fig. 1) where a mixture of new complexes with [(THP) Fe(III)] nucleus could be calculated :

M/Z: **167**: (radical-p-quinonoid-THP)$^+$, abr. (ra-p-q-THP)$^+$, theor.=167; **196** : $[TAHC+H_2O+H^+]^+$, theor.= 196; **289** : ?; **331** : ?; **396.9** : $[(TAHC-2^+)$ (ra-p-q-THP)Fe(II)]°(**4**), Fig. 2), theor.=[397]°, no signal; $(\mathbf{4}+H^+).Cl^-$, $=\mathbf{5}.Cl^-$, theor.=[398]$^+$; **434** : $[\mathbf{5} + HCl]^+=\mathbf{6}$, here Cl^- fills the free sixth coordination, theor.=$[434.5]^+$; **470** : $[6+HCl]^+$, here Cl^- fills a second coordination which was not free, while 4 protons are found to the 4 basic groups of the complex, theor.=471. A complex with a third Cl^- as ligand can not exist. **568** and **670** are signals of two complexes where, it seems so, two pterin molecules

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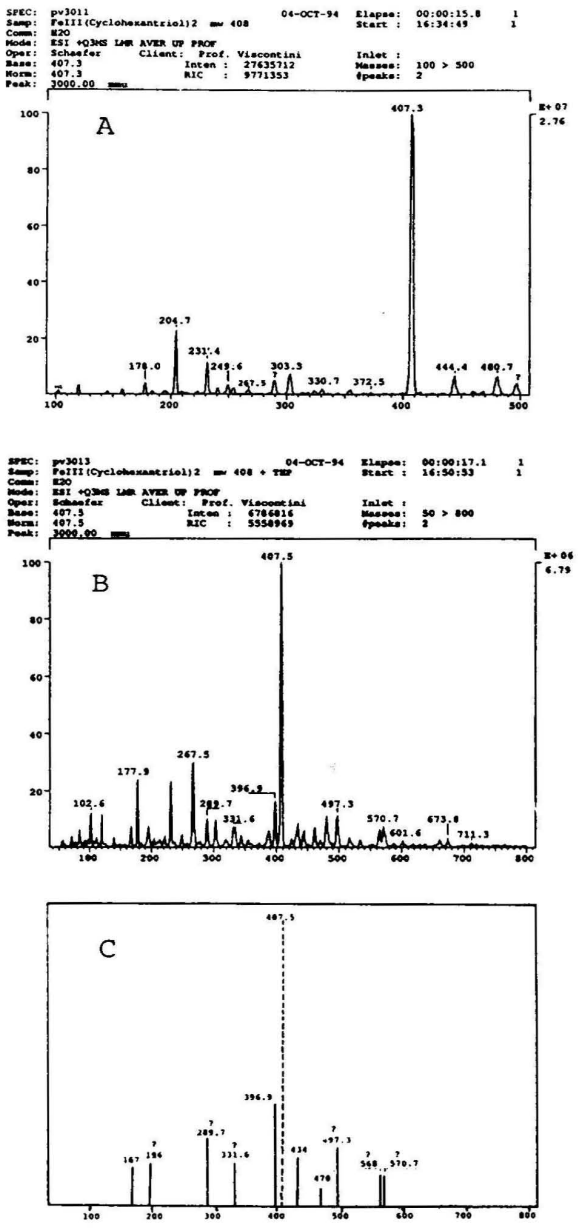


Figure 1.

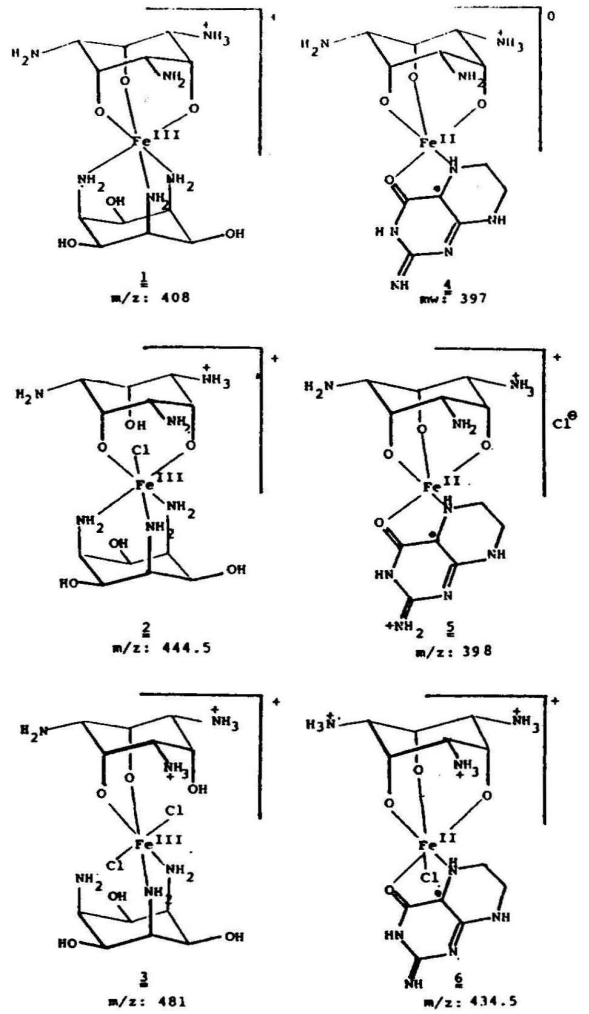
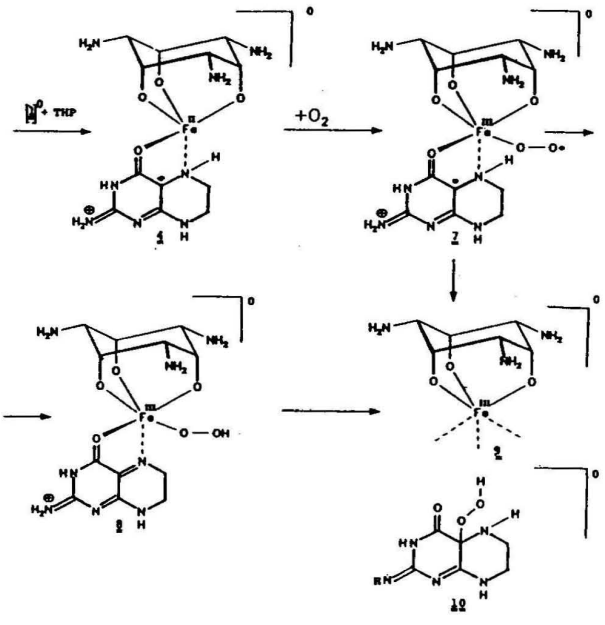


Figure 2.



are present together with TAHC and iron.

We propose, for example, that oxygen is activated by filling the sixth free coordintion of **4**, giving **7**, then **8**, which could divide into [(TAHC-3H$^+$) Fe (III)]° (**9**) and [(p-q-THP-peroxide)]° (**10**).

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