FROM IRON(II) TO IRON(III) BASKET HANDLE PORPHYRINS : STATIC AND KINETICS X-RAY ABSORPTION STUDIES

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RESUME

Les porphyrines de fer à anses de panier présentent des gênes stériques sur les deux faces du cycle porphyrinique et une grande stabilité par rapport à l'oxydation par le dioxygène. Nous présentons une étude d'absorption X d'une série de ces composés [Fe(II), plan carré; Im-Fe(II)-O₂, octaédrique; Fe(III)-OH, pyramide à base carrée], en solution ou à l'état solide, pour mieux connaître structure moléculaire et fonction de ces analogues d'hèmes fixant l'oxygène. Nous présentons également les résultats préliminaires de l'étude cinétique par EXAFS résolu dans le temps, de l'oxydation par l'oxygène moléculaire d'une porphyrine de Fe(II) à anse de panier (B H P), en dérivé BHP-Fe(III)-OH.

ABSTRACTS

The so-called iron basket handle porphyrins present steric hindrance on both faces on the porphyrin ring and a large stability towards oxidation by dioxygen. We are investigating a series of such compounds [Square planar Fe(II), octahedral Im-Fe(II)-O₂, and square pyramidal Fe(III)-OH], in solution or in solid state, to get new insights into the molecular structure and function of these analogs of O₂ binding heme proteins. Finally, we present preliminary results using dispersive mode EXAFS, about the reaction of oxidation of Fe(II) basket handle porphyrins (B H P) by dioxygen, towards the formation of BHP-Fe(III)-OH compound.

In solution, autoxidation of flat-open porphyrin-iron (II) complexes which involves an extremely rapid bimolecular reaction gives finally a μ -oxodimer when they are exposed to dioxygen(1,2). This reaction does not occur in hemoproteins (hemoglobin, myoglobin) because the protein chain surrounding the heme prevents the close approach of the two hemes and the subsequent oxidation.

To inhibit such an undesirable reaction several superstructured porphyrins have been proposed(3). With the so-called "Basket-handle" porphyrins-iron(II) in which steric hindrance on both faces is obtained by polymethylene chains attached at the orthoposition of the phenyl rings of 5,10,15,20 tetraphenylporphyrin by ether or secondary amide linkages, total dimerisation is prevented(4). The slow oxidation of these four coordinated compounds (S=1) in toluene gives pure hematin derivatives [Fe(III)-OH] (S=5/2)

which have been characterized by U.V.-visible, EPR and NMR spectroscopies(5) and by electrochemistry(6). On the other hand, the presence of an appended nitrogen donor ligand (pyridine, imidazole) in one of the two handles allowed to obtain pure five coordinated - iron(II) complexes ($S=2$), as in the deoxyform of dioxygen carrier hemoproteins. They reversibly bind dioxygen at room temperature and provide synthetic model systems to analyse the factors controlling the dioxygen affinity and the exact electronic nature of stable dioxygen adduct ($S=0$) in natural compounds(7). Such complexes can be also obtained from single face hindered compounds bearing one handle and two pivalamido pickets in the presence of free nitrogenous base in solution(6).

We present in this communication the investigation of EXAFS and XANES data of BHP Fe(II), Fe(II)-O₂ and Fe(III)-OH complexes of basket-handle porphyrins (Figure 1). The assignment of structural data for the hematine derivate are compared to those of analogous chlorohemin [Fe(III)-Cl] determined by X-Ray diffraction (9). The XANES spectra of the different species is sufficiently different to allow kinetics results about the reaction of oxidation of four-coordinated Fe(II) complexes by dioxygen, towards the formation of Fe(III)-OH species, using dispersive mode EXAFS (10).

Figure 1: 1 BHP-Fe(II), 2 BHP-Fe(II)-O₂,Im , 3 BHP-Fe(III)-OH.

EXPERIMENTAL CONDITIONS

Classical XANES and EXAFS data were recorded at LURE on EXAFS I spectrometer using a channel cut Si 400 monochromator, and EXAFS III (double crystal Si 311). The ring storage energy was 1.72 GeV. A 8 μ m Fe metallic foil spectrum was recorded just before each XANES experimental spectrum.

Time resolved XANES data were recorded on the dispersive X-Ray absorption facility (10), using a BHP-Fe(II) solution in toluene (0.05 M), in a 1 cm cell with kapton windows, under gaseous oxygen flow and stirring. Accumulation time was 10s per spectrum.

XANES

XANES spectra for BHP-Fe(II) 1, BHP-Fe(II)-O₂,Im 2, and BHP-Fe(III)-OH 3, are given in Fig.2 .

Fe(II) compounds : The intense well defined transition observed at 7112.6 eV is characteristic of the square planar Fe(II)($S=1$) in porphyrinic surroundings. For compounds 1 and 2, there is no shoulder in the edge. Preedge features (weak intensity even in the octahedral Fe(II)-O₂,Im) lies at low energy (7108.0 eV for Fe(II), 7108.2 eV for Fe(II)-O₂,Im). This favours the Fe(II)-O₂ formulation rather than the Fe(III)-O₂⁻ one, to characterize the electronic state of iron in BHP.

Fe(III)-X square pyramidal complexes : For all the compounds, we observe an unresolved shoulder in the edge, the energy of which is X dependent. A possible attribution should be an allowed charge transfert $X \rightarrow Fe$. As expected, preedge features lies at higher energy than in iron(II) and the [square pyramidal] intensity of the dipolar allowed transitions increases with distortion from square planar to square pyramidal [larger participation of 4p(Fe) atomic orbitals in the molecular orbital containing the 3d(Fe)] . Preedge structures show trend to higher energy from Fe(II) to Fe(III) but the energy of the edge inflexion point has no unique correlation with oxidation state : square pyramidal BHP-Fe(III)-X soulders can coincide with square planar BHP-Fe(II) inflexion point. Multiple scattering interpretation of postedge remains to be done.

Figure 2: XANES spectra for 1, 2, 3.

EXAFS

We use the classical plane wave EXAFS analysis described elsewhere (11). We study two compounds : the BHP-Fe(III)-Cl species with a known crystallographic structure (9) and the rare BHP-Fe(III)-OH where no structural data are available. For the two first shells, results are obtained by a two shells fitting procedure, with Teo and Lee phase shifts and amplitudes. Distances Fe-C and Fe-C_{meso} are obtained using Beni and Lee criterion, with a phase correction on the first neighbour shell. The results are in Table I. The proposed structure for the hydroxo species is schematized in Fig.3. The axial Fe-O distance (1.94 Å) is to be compared to the only one known from X-Ray diffraction (1.89 Å) in a porphyrinoid ligand (12).

TABLE I

COMPOUND	BOND	DISTANCES R/Å		DEBYE WALLER $2\sigma^2/\text{Å}^2$	χ^2_p
		X.R.D.	E.X.A.F.S.		
MODEL BHP Fe(III)-Cl	Fe-N	2.06	2.06	0.0032	1.5
	Fe-Cl	2.21	2.24	0.0008	
	Fe-C	3.09			
	Fe-C _{meso}	3.48			
HYDROXO SPECIES BHP Fe(III)-OH	Fe-N		2.08	0.005	3.4
	Fe-O		1.94	0.0018	
	Fe-C		3.10		
	Fe-C _{meso}		3.49

Figure 3: proposed structure for BHP-Fe(III)-OH.

TIME RESOLVED XANES : Kinetics of oxidation.

Fig.4 shows experimental spectra of the Fe(II) square planar complex 1, before the oxidation. During the reaction, we observe the disappearance of the Fe(II) square planar characteristic feature at 7112,6 eV. The evolution of the relative intensity of this peak is given in Fig.5 . At the present stage, quantitative conclusions about kinetics would be imprudent given the low signal/noise ratio due to the photon statistics (work in too dilute solution and too short time of accumulation). A study of a slower oxidation reaction with more concentrated solutions (more soluble BHP) would be necessary to give quantitative conclusions. Nevertheless, these preliminary results confirm the power of time resolved X-Ray absorption in the emergence of a new tool for reactivity studies: structural kinetics.

Figure 4: XANES spectra for the Fe(II) square planar complex.

Figure 5: Evolution of the relative intensity of the peak at 7112.6 eV.

CONCLUSIONS

Besides the fundamental interpretation of XANES spectra of Fe(II) or Fe(III) BHP, which is difficult (mixing of states, multiplets ...), XANES allows to distinguish clearly between BHP-Fe(II) and BHP-Fe(III) in different stereochemistries. This allows to perform kinetics experiments as shown by our preliminary measurements in dispersive mode.

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