ESRF	**Experiment title:** **X- RAY ABSORPTION STUDIES USING XAFS OF HIGH VALENT PORPHYRINATO METAL COMPLEXES WITH OZONE**	**Experiment number:** **CH -62**
Beamline: BL6 / ID12A	**Date of experiment:** from: December 13th 1995 to: December 15th 1995	**Date of report:** March lrst 1996
shifts: **9**	Local contact(s): **J. GOULON and A. ROGALEV**	***Received at ESRF:***

Names and affiliations of applicants (* indicates experimentalists):

Vincent GOTTE[1] *, Andrej ROGALEV[1]*, Chantal GOULON-GINET[1,2]*, José GOULON[1]*
Jean-Michel BARBE[3]*, Roger GUILARD[3], Panayotis COCOLIOS[4]
[1] ESRF - XAS group, [2] Faculté de Pharmacie, Université Joseph Fourier - GRENOBLE, France
[3] LIMSAG, Laboratoire mixte du CNRS et AIR-LIQUIDE, Faculté des Sciences Gabriel,
6 Bd Gabriel -21100 DIJON
[4] Centre de Recherche Claude Delorme - AIR LIQUIDE - Les Loges-en-Josas
78350 JOUY-EN-JOSAS France

I. Motivations

Very little is known regarding the activation of ozone by metalloporphyrins. B. Meunier ***et al.* [1]** have described the epoxidation of olefins by ozone in the presence of a Manganese (III) porphyrin and suggested that the reactive species was a high valent Mn(V) oxo complex. It is the aim of the present project to try to clarify the catalytic schemes and to characterize the structure of the active species.

Samples: Ozone is known to be a very powerful oxidising agent and common metalloporphyrins are simply destroyed during the reaction with ozone. Meunier has shown, however, that such a destruction can be avoided by using porphyrins with β-substituted pyrrol rings. Thus, a wide variety of porphyrins with protective groups have been synthesized in Dijon (LIMSAG) where the catalytic reaction with ozone is studied. For the sake of efficiency, we decided to concentrate our investigations only on a new family of Manganese dodecaphenylporphyrins with perfluorinated protective groups on the meso bridging carbons: [DPP-F_{20} : Mn (X)(Y)]. Here, X and Y denote various axial ligands, e.g. X= F, Cl, Br ; Y = Pyridine . The active complexes with ozone can be isolated in the solid state and this is simplifying a lot the XAFS studies. We checked systematically that the samples were still active after the measurements carried out at the ESRF.

Method: EXAFS and XANES spectra have been recorded in the fluorescence mode at both the Mn K-edge and whenever relevant, at the chlorine K-edge. Fluorescence is preferable because the samples are heavily absorbing, especially at the chlorine K-edge. A good way to exploit the high sensitivity of EXAFS to small structural changes is to carry out difference analyses using reference spectra that have been slightly "perturbed" in order to take into account small structural changes.

References : [1] B. Meunier, ***Chem. Rev. (1992), 92, 1411-1456***
[2] J.Goulon ***et al,, Springer series in Biophysics, (1987),2, 191-199***

2. Results and preliminary conclusions

We have shown that excellent data can be recorded with an undulator source in spite of the narrow bandwith of the undulator peaks. At the Chlorine K-edge, the experience is time-consumming because one has to move the gap of the undulator every 10 eV. We have to admit that we wasted part of our beamtime due to the unexpected contamination of the first few Mn EXAFS spectra by a parasitic iron fluorescence signal. Once this problem was solved, EXAFS oscillations have been detected at room temperature (... for low Z scatterers!) up to 19 Å^{-1}. At this stage, we can already draw the following conclusions:

(i) There is no evidence in any FT spectrum of the complexes activated with ozone of a signature supporting the presence of a high valent Mn(V) oxo complex with a short Mn=O bond length. This is obvious from the Fig. 1 which reproduces as a reference the spectrum of the true Mn(V) nitrido complex which has a short Mn $\equiv$ N distance at 1.51Å.

(ii) In the FT spectra of [DPP-F$_{20}$: Mn -X +·O$_3$] species, there is a strong additional signal that indicates that the Mn coordination is modified (Fig.2). It is only weakly dependent on the nature of X. This signal does not show up in the FT spectrum of [DPP-F$_{20}$: Mn (X)(Y)+ 03] which has different catalytic properties.

(iii) The metal atoms (Mn) are lying in the basal plane of the 4 Nitrogen atoms of the porphyrin.

(iv) The Cl ligand is itself most probably oxidized by ozone into C1O or ClO$_2$. This is immediately apparent from the chlorine K-edge XANES spectra (Fig.3 and Fig.4)

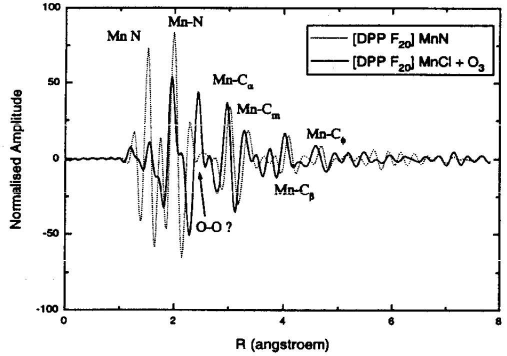

Fig1 FT spectra of [DPP-F$_{20}$: Mn-Cl+O$_3$] and [DPP-F$_{20}$: Mn $\equiv$N]

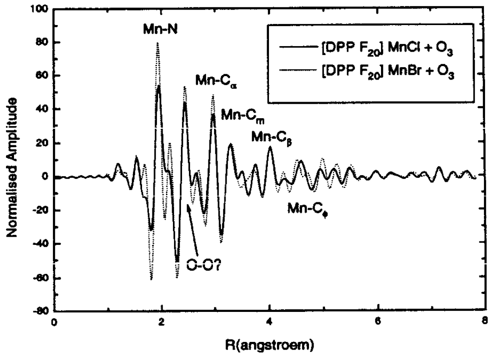

Fig2 FT spectra of [DPP-F$_{20}$: Mn-Cl+O$_3$] and [DPP-F$_{20}$: Mn-Br+O$_3$]

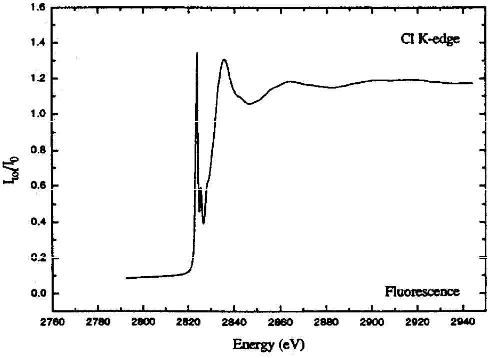

Fig3 XANES of [DPP-F$_{20}$: Mn-Cl*+O$_3$]

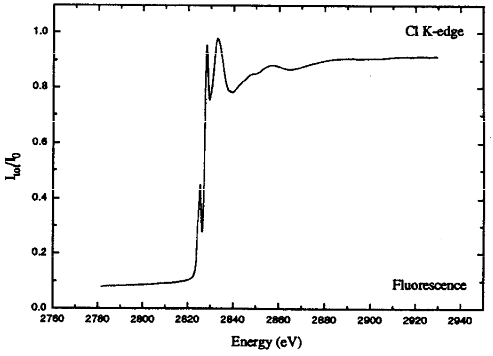

Fig4 XANES of [DPP-F$_{20}$: Mn-Cl*]