

## REPORT OF THE EXPERIMENT CH-1397

### Experiment title:

*Focussing on the XANES part of XAS spectrum to obtain structural information on metal cation environment in solutions: Study of some challenging cases.*

**Beamline:** BM29                      **Shifts :** 12

**Date of Experiment:** from: 30.1.2003            to: 3.2.2003

**Local contact:**            Dr. Gloria Subías

**Name and affiliations of applicants:** Prof. Enrique Sánchez Marcos<sup>1</sup>, Dr. Adela Muñoz Páez<sup>2</sup>, Dr. Patrick Merklings<sup>1</sup>, Dr. Sofía Díaz Moreno<sup>3</sup>, Ms. Flora Carrera López<sup>2</sup>, Mr. Francisco Torrico Perdomo<sup>1</sup>

<sup>1</sup>Departamento de Química Física. Universidad de Sevilla. 41012-Sevilla (Spain).

<sup>2</sup>Departamento de Química Inorgánica-ICMSE. Universidad de Sevilla-CSIC. 41012-Sevilla (Spain). <sup>3</sup>ESRF, 6rue Jules Herowitz, BP220, 38043-Grenoble Cedex (France)

## REPORT

During the 12 shifts corresponding to the above-indicated experiment carried out at beamline BM29 the following samples were measured:

-Aqueous solutions of the following salts:

- a) Cu(ethylenediamine)<sub>2</sub> , Cu(histidine)<sub>2</sub> , Cu(glycine)<sub>2</sub> and Cu(PrP-C) complexes.
- b) Ir(trifluoromethanesulfonate)<sub>3</sub>
- c) PdCl<sub>4</sub>K<sub>2</sub> , Pd(NH<sub>3</sub>)<sub>4</sub>(ClO<sub>4</sub>)<sub>2</sub> and Pt(NH<sub>3</sub>)<sub>4</sub>(ClO<sub>4</sub>)<sub>2</sub>
- d) trans-PdCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>
- e) cis- and trans-PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>
- f) Lu(trifluoromethanesulfonate)<sub>3</sub> and Tm(trifluoromethanesulfonate)<sub>3</sub>

-Solid samples:

- a) Cu(phthalocyanine)<sub>2</sub> and Cu(glycine)<sub>2</sub>
- c) PdCl<sub>4</sub>K<sub>2</sub> and Pt(NH<sub>3</sub>)<sub>4</sub>(ClO<sub>4</sub>)<sub>2</sub>

d) trans-PdCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>

e) cis- and trans-PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>

For the case of Ir, Pt, Lu and Tm, in addition to the L<sub>III</sub> -edge, the XANES spectra for the L<sub>II</sub> and L<sub>I</sub> edges were also recorded.

**Figure 1.-** XANES K-edge for different Palladium complexes in solid state and in aqueous solutions

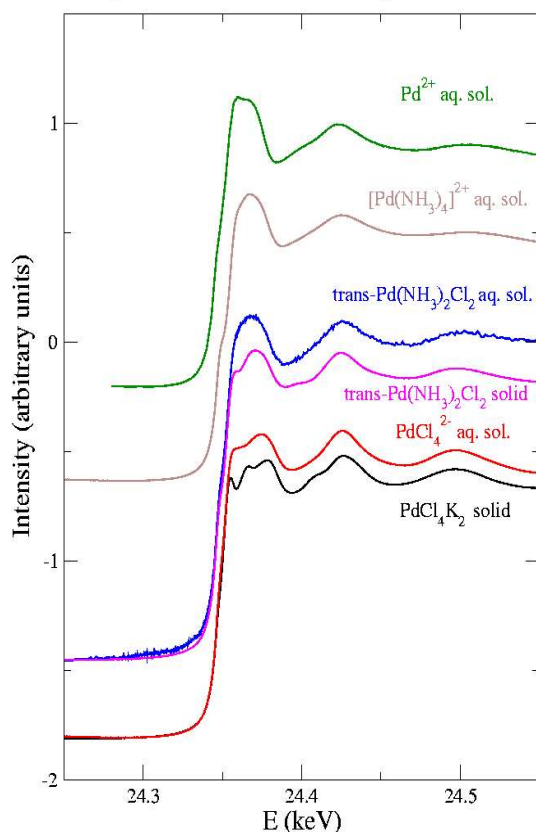
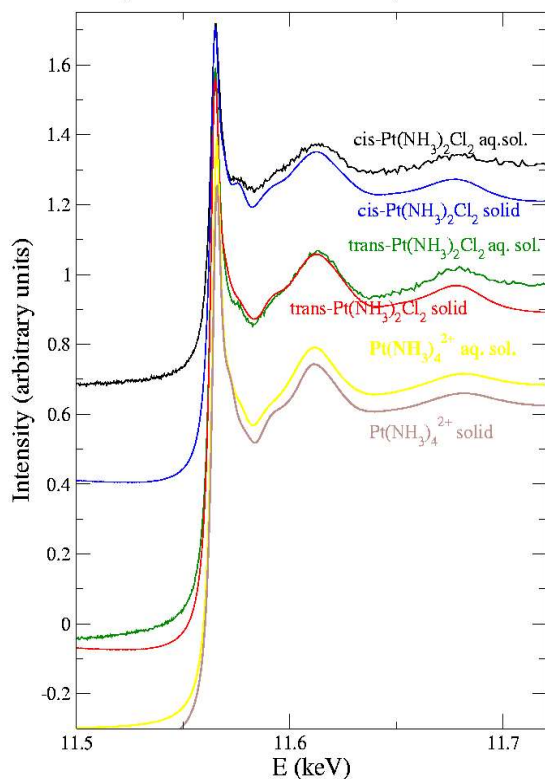


Figure 1 summarizes a set of XANES spectra for the Pd(II) in solid state and aqueous solutions. The closest environment of the palladium atom is formed by four oxygen atoms from water molecules for the case of Pd(II) in aqueous solutions and by four chloride atoms in the solid state PdCl<sub>4</sub>K<sub>2</sub> or in the aqueous solution of the same compound. In the aqueous solution containing [Pd(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> the local coordination environment is formed by four nitrogen atoms. Intermediate situations are also examined by obtaining the corresponding spectra for trans-Pd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> both in solid state and in aqueous solution. It is observed that features on the spectra are different enough to justify additional prospection of

the interplay between the structure and the shape of spectra. Chloride anions in the first coordination shell induce characteristic features in the spectra. A general smoothing of the spectrum is observed when going from the solid to liquid sample (e.g. black vs. red lines for [PdCl<sub>4</sub>]<sup>2-</sup>, and pink vs. blue lines for trans-Pd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>).

Figure 2 shows the XANES spectra corresponding to the L<sub>III</sub> edge of platinum for several amino and chlorocomplexes of Pt(II) in solid and aqueous solutions. It is worth pointing out the fact that the cis and trans geometrical isomers of Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> in solid state exhibit spectra well differenced. A more detailed analysis is needed to reach the same conclusion for the corresponding aqueous solutions of these two isomers, as signal/noise ratio is worse. Moreover an interconversion between both isomers could take place. (cf. Red and blue spectra of the solid samples with green and black spectra of the aqueous solution samples). The low solubility of the

**Figure 2.-** XANES  $L_{III}$ -edge for different Platinum complexes in solid state and in aqueous solutions



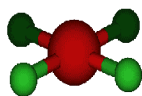
trans -isomer in aqueous solution, ca. 0.001M, made it difficult to obtain a high quality signal/noise ratio. On the contrary, the concentration reachable for  $[Pt(NH_3)_2]^{2+}$  aqueous solutions allows good quality spectrum (yellow line).

A third group of results concerns the EXAFS spectra and analysis of the series of N-coordinated Cu (II) complexes. The knowledge of the complexes formed by N-coordinating ligands and Cu(II) ions is of relevance to understand the interactions of this ion with biomolecules. Within this framework, we have investigated Cu(II) complexation with mono and polydentate ligands, such as

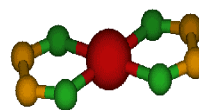
ammonia, ethylenediamine (en) and Phthalocyanine (Pc). In addition to first shell formed by 4 N atoms in square planar arrangement around metal cation, information on higher coordination shells of the chelate ligands can be extracted by EXAFS, thus allowing the discrimination among the different coordination modes. Figure 3 shows schematic representation for the closest environment around Cu(II) for the different ligands studied. This knowledge has been used to elucidate the structure of the complex  $Cu(His)_2$ , formed by Cu(II) ions with Histidine, the amino acid showing the highest affinity for Cu(II) ions, since the in-solution structure of the complex is not clear yet, probably due to the various possible coordination modes. In Figure 3 is given the two most invoked coordination mode, the first one is histamine-histamine like and the second histamine-glycine like.

The EXAFS spectra of the five complexes dissolved in aqueous solutions have been plotted in Figure 4. The EXAFS function becomes increasingly complex when the number of atoms in the ligand becomes larger: it is a *quasi* simple wave in the tetrammine, it shows a beating at around  $5.5 \text{ \AA}^{-1}$  in the

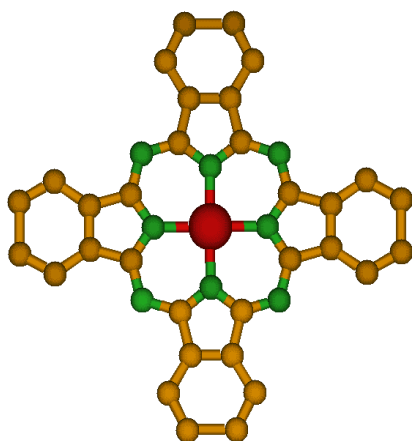
Figure 3.- Cu(II) complexes simplified structures. Cu:red; N:green, C:orange; O:blue



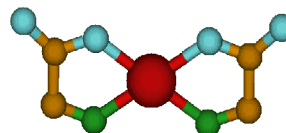
$[\text{Cu}(\text{NH}_3)_4]^{2+}$



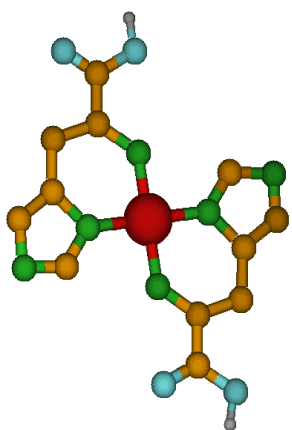
$[\text{Cu}(\text{en})_2]^{2+}$



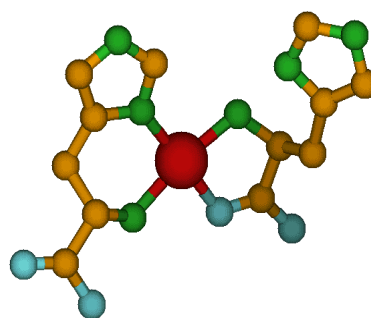
CuPc



Cu(Gly)<sub>2</sub>



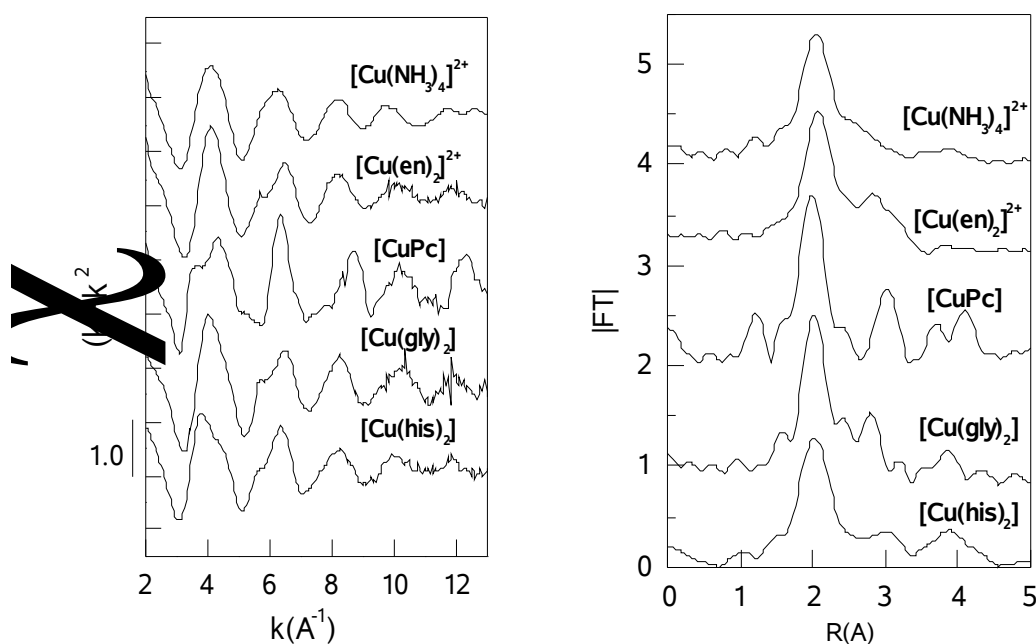
Histamine-Histamine



Histamine-glycine

$\text{Cu}(\text{His})_2$

$[\text{Cu}(\text{en})_2]^{2+}$  spectra and in the complex formed with the tetradentate ligand phthalocyanine, the function is rather complex. Figure 4b shows the Cu-N phase-corrected FT of the spectra included in Figure 4a. A peak centered at around 2.00 Å, which should be ascribed to Cu-N first coordination shell, is the main contribution in all spectra. Additional contributions appear beyond 2.8 Å, thus allowing the determination of structural properties of higher coordination shells



**Figure 4.** (a) (b)

The obtained Cu-N coordination distances were 2.01 Å for  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ; 2.02 Å for  $[\text{Cu}(\text{en})_2]^{2+}$  and 1.95 Å for CuPc. The shorter bond distance found for CuPc together with an extremely small value of mean square deviations is attributed to the macrocyclic effect. The results of the EXAFS analysis point to the fact that the predominant coordination mode is the so-called *histamine-histamine*, in which both histidine molecules coordinate Cu(II) cations through N atoms from the amino group and from the imidazole ring, thus histamine forms two six-membered chelate rings. The obtained coordination distance for the first Cu-N shell is 1.99 Å. In this coordination mode imidazole rings are coplanar with the 4 N atoms forming the first coordination shell of the complex. For this reason multiple scattering contributions become relevant, thus

allowing the determination of higher shells. To investigate the related coordination modes of histidine, the complex formed by Cu(II) ions with the aa Glycine has also been investigated. A comparison of the Cu-glycine coordination with the so-called *glycine-histamine* coordination mode has been considered, and it has been concluded that the coordination histamine-histamine mode seems to be more probable.