ESRF	**Experiment title:** Platinum containing organometallicmacromolecules as gas sensors: metal - gas interaction studied by EXAFS	**Experiment number**: 08-01 803
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Report:

Introduction:

Since the last decade, the electronic, optical and liquid crystal applications of "rigid-rod" organometallic polymers, obtained from transition-metal complexes with alkynyl ligands, have been thoroughly investigated [1], elucidating the correlated intrachain electron and hole migration of model Pt alkynyl mixed valence complexes [2], as well as the charge transport in molecular model Pt acetylides [3], in view of their applications as components for molecular electronics. The research of our group has been focussed to the investigations on the chemical and electronic structure of Pt-containing *rod-like* organometallic polymers [4]. In this framework, binuclear complexes and small oligomers have been successfully used as model molecules for the interpretation of the optoelectronic properties of more complicated systems [5]. In the field of technological applications and more specifically sensor devices, Pt poly-ynes have been used as thin film membranes in surface acoustic wave (SAW) devices [6] showing high sensitivity towards relative humidity and sulphur containing organic vapors [7]. Recent studies on sensors based on analogue poly-metallaynes showed a higher sensitivity towards low relative humidity percentages, when nanostructured membranes were employed [8]. The obtained materials have been extensively studied and conveniently used as sensors; however, the basic understanding of some chemical and physical aspects still needs to be investigated.

Experiment:

In this experiment, we intended to achieve information about the interaction occurring between gaseous molecules such as NO and SO_2 and the transition metal dialkynyl bridged Pt(II) complexes *trans*-$[ClPt(PBu_3)_2(C{\equiv}C\text{-}C_6H_4\text{-}C_6H_4\text{-}C{\equiv}C)Pt(PBu_3)_2Cl]n$ (n=2, 4), that can be considered as models for the study of the more chemically complex organometallic pi-conjugated polymers. EXAFS spectroscopy measurements were performed at the Pt LIII-edge (11564 eV) in transmission mode to investigate the interaction between Pt-DEBPn (Pt-diethynylbiphenyl, n = 2,4) oligomers of different length and geometry (linear and cyclic, depending on the Pt square planar complex configuration, trans or cis respectively) and SO_2, NO molecules. The hypothesized chemical interaction occurring between Pt(II) and S and N containing chemical species was verified and investigated. We believe that this chemical interaction is responsible for the high sensitivity and selectivity of Pt-DEBPn-Cl_2 based mass sensor devices towards sulfur-containing compounds [7]. As a start, we performed EXAFS measurements on the sample pellet in low vacuum conditions (P = 10-3 mBar). Then, we filled up the GILDA's chemical cell with SO_2 at a partial pressure of about 500 mBar, then we performed the same structural characterization. In sit treatments were made possible at GILDA by a small chemical chamber equipped with input and output gas lines, that allows to perform EXAFS measurements on samples in controlled chemical environment [10]. The same procedure was followed to investigate the interaction arising between Pt-DEBPn-Cl_2 samples-and NO.

Results:

EXAFS spectroscopy was employed on purpose to carry on an extensive characterization of the sample before and after exposure to gases. As a result, the chemical interaction arising between Pt(II) centers and sulphur or nitrogen respectively, has been assessed by the spectra analysis. Furthermore, EXAFS data analysis suggested a square-pyramidal geometry around the transition metal with the gas molecule in the apical position for the pentacoordinated platinum units similarly to Pt-DEBPn-Cl_2/H_2S adducts investigated in ref. [9].

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