



	Experiment title: EXAFS study of the dynamics of the formation of inner and outer-sphere Cr-Cl complexes in aqueous solutions	Experiment number: CH-527
Beamline: BM 29	Date of experiment: from: 10-10-98 to: 12-10-98	Date of report: 26-2-99
Shifts: 6	Local contact(s): Dr. D. Bowron	<i>Received at ESRF:</i> 01/03/99

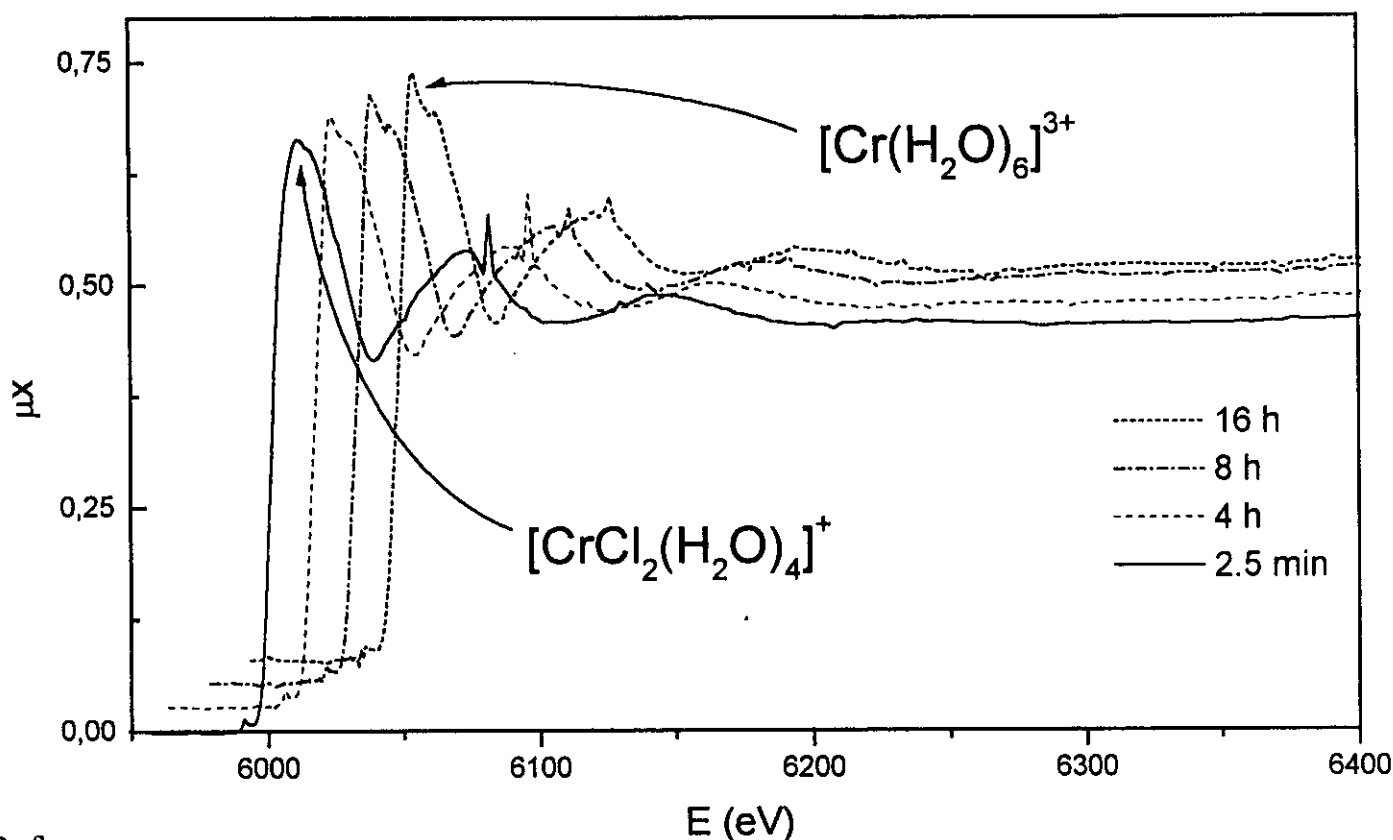
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Reports

Ligand substitution reactions around metal centres in solution are ones of the most basic chemical reaction which takes place in solution.[1,2] A wide variety of techniques, mainly based on thermodynamic and spectroscopic properties has been used to get insight into the mechanism and reactivity. As a general rule, these tools are largely efficient to supply the formal parameters of kinetics as well as sometimes evidence on the nature of intermediates.[3] Direct structural information on the close environment around the metal centre in solution has been limited to the application within the last twenty years of X-ray and neutron diffraction, and EXAFS technique.[4-6] However, time-dependent experiments with these techniques have been initiated during the last decade and are mainly devoted to solid phase processes,[7-11] being very scarce the corresponding studies of liquid solutions. This could be due to the experimental difficulties and particularly to the high reaction rates usually shown by reaction involving dissolved inorganic species. One of the reaction showing a rate slow enough is the aquation of chromium chloro complexes. Based on our previous knowledge of these species[12] a kinetic study of this reaction for $[\text{CrCl}_n(\text{H}_2\text{O})_{6-n}]^{(3-n)+}$ for $n=2,1$ was performed by following the changes in the XANES spectra of Cr-K edge. The spectra were recorded in transmission mode on station BM29 in a specially designed EXAFS cell[13] every 2.5min. The evolution of three different solutions was monitored, two of them containing $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$ 0.5 and 0.1M, and the third one containing $[\text{CrCl}(\text{H}_2\text{O})_5]^{2+}$ 0.5M. The evolution of the systems was followed until no changes was observed in the spectrum,

which meant 16 hours for the first system and 6 hour for the other two. Figure 1 includes the four XANES spectra recorded during the evolution of the first system, the first and the last ones and two intermediates. The preliminary analysis of the results shows that the rate of aquation reaction increases when the initial concentration of the complex is reduced. This unexpected effect could be explained on the basis of reverse reaction ($[\text{CrCl}(\text{H}_2\text{O})_5]^{2+} + \text{Cl}^- \rightarrow [\text{CrCl}_2(\text{H}_2\text{O})_4]^+ + \text{H}_2\text{O}$) that becomes important when the initial complex concentration and concomitantly free chloride concentration is big enough.



References

- [1] R.G.Wilkins, "Kinetics and Mechanisms of Reactions of Transition Metal Complexes". 2nd Ed. VCH Publishers: New York. (1991)
- [2] J. Burgess, "Metal Ions in Solution". John Wiley: New York. (1978).
- [3] K.J. Laidler, "Chemical Kinetics". 3rd Ed. HarperCollins: New York. (1987)
- [4] M.Magini, G.Licheri, G.Paschina, G.Piccaluga, "X-Ray Diffraction of Ions in Aqueous Solutions: Hydration and Complex Formation". CRC Press: Boca Raton. (1988).
- [5] H.Ohtaki, T. Radnai, Chem.Rev. 93, 1157 (1993).
- [6] D.T.Richens, "The Chemistry of Aqua Ions". John Wiley: Chichester. (1997).
- [7] J.M.Lee, M.A.Paesler, D.E.Sayers, A.Fontaine, Physica B, 158, 52 (1989).
- [8] M.Epple, U.Sazama, A.Reller, N.Hilbrandt, M.Martin, L.Troger, Chem. Commun. 1755 (1996).
- [9] D.Hecht, R.Frahm, H.-H.Strehblow, J. Phys. Chem., 100, 10831 (1996).
- [10] J.E.Lorenzo, J.M.Tranquanda, D.J.Buttrei, V.Sachan, Phys. Rev. B, 51, 3126 (1995).
- [11] W. M. Small, J.H.Root, D.Khatamian, J. Nucl. Mat., 256, 102 (1998).
- [12] S.Díaz-Moreno, A. Muñoz-Páez, J.M.Martínez, R.R.Pappalardo, E.Sánchez Marcos, J. Am. Chem. Soc., 118, 12654 (1996).
- [13] E.Sánchez Marcos, M.Gil, J.M.Martínez, A.Muñoz-Páez, A.Sánchez Marcos, Rev. Sci. Instrum. 65, 2153 (1994); A.Muñoz-Páez, M.Gil, J.M.Martínez, E.Sánchez Marcos, Physica B, 208-209, 241 (1995).