![ESRF logo] **ESRF**	**Experiment title:**'EXAFS investigation of the hydration structure and ion pairing formation around highly charged cations'	**Experiment number**: CH_775
Beamline: ID26	**Date of experiment**: from: 1st December 1999 to: 5th December 1999	**Date of report**: 26/2/2001
Shifts: 12	**Local contact(s)**: V. A. Sole	*Received at ESRF:*

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Report:

Most stable cations of transition metals form well defined hydrates whose structure has been solved both in solution and solid state.The most frequent hydration number is six, but higher coordination numbers, such as nine (La(III)), eight (Y(III)), or seven (Sc(III)), although it is still controversial, can be also found. Conversely, lower coordination numbers are found for group–10 divalent cations, Pt(II) and Pd(II), where the highly favored square planar geometry points to the existence of four–coordinated hydrates for both cations.

Herewith we present a structural study of the Pt(II) square planar complexes, tetraaquo, $[Pt(H_2O)_4]^{2+}$, and tetrachloro, $[PtCl_4]^{2-}$, both in aqueous solution, combining the quantum mechanical computations and X–ray Absorption spectroscopies, EXAFS and XANES. In addition to the determination of the isolated structures, a detailed investigation of the preferred site for water molecules interaction around the planar complexes was carried out ($[PtCl_4]^{2-}(H_2O)_2$ and $[Pt(H_2O)_4]^{2+}(H_2O)_8$). This was done to check the influence on the XANES spectra of the medium range order solvation structure (Figure 1.), as well as to help in the interpretation of the EXAFS fit of the structures in solution.

From the espectra analysis the following conclusions were obtained (Table 1.):

The Pt^{2+} aquocomplex has a square planar geometry, oxygen atoms being located at 2.02 Å. Similarly, $[PtCl_4]^{2-}$ units are square planar, Pt–Cl distance being 2.30 Å. The MS contribution arising from triangular path has an intensity higher than that found in octahedral complexes since its Debye–Waller factor is similar to that of SS path.

The solvation of the Pt^{2+} aquocomplex is mainly determined by a second hydration shell that form hydrogen bond with the water molecules of the tetraaquo complex in an equatorial arrangement ($Pt-O_{II} \sim 3.95$ Å).

From the analysis of the EXAFS data, and from the combined quantum–mechanical and XANES spectra computations, it can be deduced that axial region of these square planar complexes in solution does not present a potential well which favors restricted orientation of water molecules, so that no coherent contribution to the X–ray absorption spectra is detected neither in the EXAFS nor in the XANES spectra of the $[PtX_4]^{2+/-}$ (X= Cl$^-$, H_2O) complexes.

Previous ascription of a hybridization peak in Pt–Cl XANES spectrum, involving d–atomic Cl orbitals, is supported by this study, where such a peak is observed for experimental and computed spectra of chlorocomplexes in solid state and aqueous solution, but it does not appear in the corresponding spectra of the aquocomplex, in which there are only Pt–O contributions.

Table 1. Best fit parameters obtained from the analysis of the Pt L_{III}–edge EXAFS spectra of the $[Pt(H_2O)_4]^{2+}$, $K_2[PtCl_4]$ in solid state and in aqueous solution.

	R(Pt–X) (Å)	σ_1^2 (Pt–X) (Å^2)	ΔE_o (eV)	$\Re$	χ^2_{red}	Δk	ΔR	Noise amplitude
$[Pt(H_2O)_4]^{2+}$	2.02 ± 0.015	0.003 ± 0.001	6 ± 2	0.08	4.8	2.8–10.4	1.1–3.9	0.007
$K_2[PtCl_4]$	2.304 ± 0.005	0.0021 ± 0.0004	9.6 ± 0.8	0.02	1.4	2.8–11.5	1.1–4.9	0.003

ΔE_0: Inner potential correction; σ_n^2: Debye–Waller factors; R: Coordination distances; R and χ^2_{red}: goodness of fit parameters .
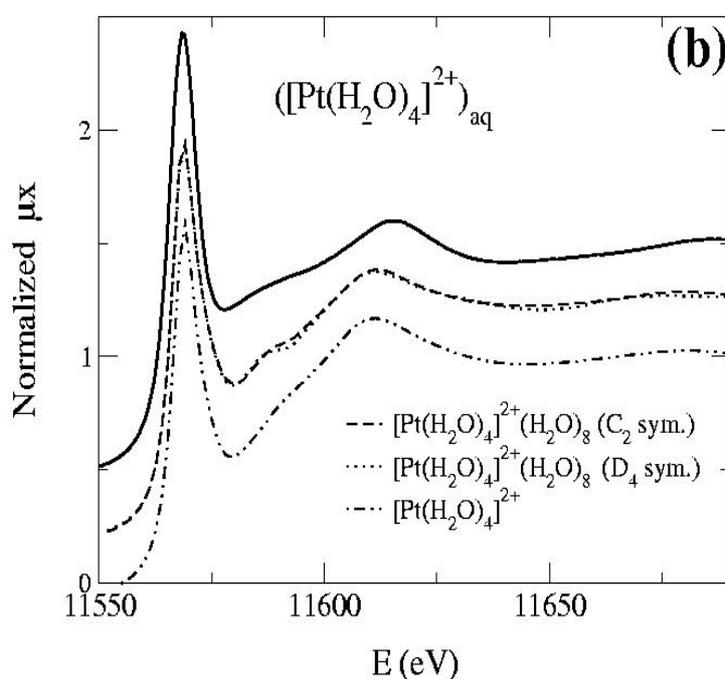

Figure 1. XANES region of the Pt–L_{III}–edge X–ray Absorption spectra of $[Pt(H_2O)_4]^{2+}_{aq}$ complex . Solid lines: Experimental data. Dashed–dotted and dashed lines: spectra calculated using the geometries obtained from quantum mechanical calculations at the MP2 level. Energy axis has been shifted +5 eV for the computed spectra.