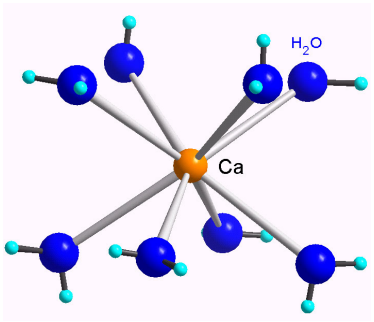
Extended X-ray Absorption Fine Structure (EXAFS) Spectroscopy

This powerful technique for probing the local structure around almost any specific element in the periodic table (except the lightest) gives information on the number and chemical identities of near neighbours and the average interatomic distances up to 5-6 Å. EXAFS studies can be performed at trace levels (< 1000 ppm), which is useful e.g., for studying metal complexes on surfaces, catalysis and metal sites in bioinorganic samples. The X-ray source is *synchrotron radiation*, allowing the EXAFS technique to be used for atoms in any aggregation state (solid, liquid or gas) in all kinds of environment: crystalline solids, glasses, amorphous phases, liquids and solutions. Some examples of how EXAFS can be used in solution chemistry follow below.

Hydration of Calcium(II). This is a notoriously difficult problem due to the flexible hydration shell in solution, which is also the key to the many important biochemical functions of this ion. By combining several techniques, EXAFS, Molecular Dynamics simulations and large angle X-ray scattering, we could conclude that 8 water molecules form a flexible square anti-prism with an asymmetric distribution of the Ca-O bond distances.



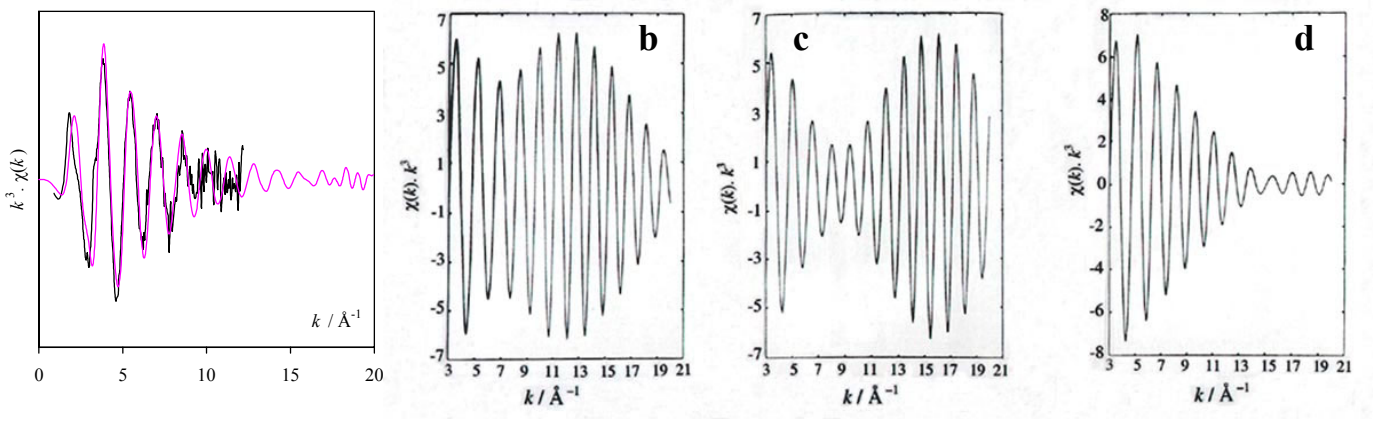


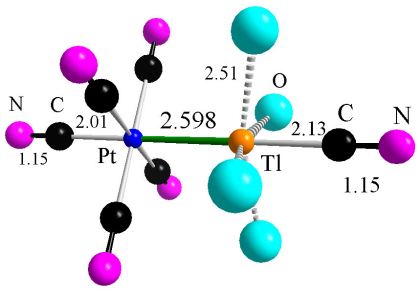
Figure 1. ***a)*** *$CaCl_2$ aqueous solution (1 M); experimental Ca K-edge EXAFS compared with a theoretical oscillation calculated from an average of a large number of snapshots from an MD-simulation (——). The mean Ca-O distance is 2.46(1) Å for an asymmetric distribution of the 8 Ca-O bond distances of the hydrated $[Ca(H_2O)_8]^{2+}$ ion;* ***b-c)*** *Simulated EXAFS oscillations for 3 different MD-snapshots of Ca surrounded by water molecules.* In ***d****, where the Ca-O distances happened to be the same, the EXAFS oscillation is similar to the experimental data.*

Farideh Jalilehvand
University of Calgary

EXAFS Studies on Pt-Tl Cyano Complexes. The two-electron transfer redox reactions in the Tl^{III} – Pt^{II} – CN^- system provide a model system for light-to-energy conversion processes for solar energy conservation. As intermediates in this electron transfer process four binuclear complexes with the general composition $[(NC)_5Pt\text{-}Tl(CN)_{n-1}]^{(n-1)-}$ (n = 1-4) can be obtained in aqueous solution:

$$[Pt(CN)_4]^{2-} + [Tl(CN)_n]^{(3-n)} \rightleftharpoons [(NC)_5Pt\text{-}Tl(CN)_{n-1}]^{(n-1)-} \quad (n= 1\text{-}4)$$

By measuring both the Pt L_{III}-edge and Tl L_{III}-edge EXAFS, we could determine the local structure around the metal centres of these species in aqueous solution.



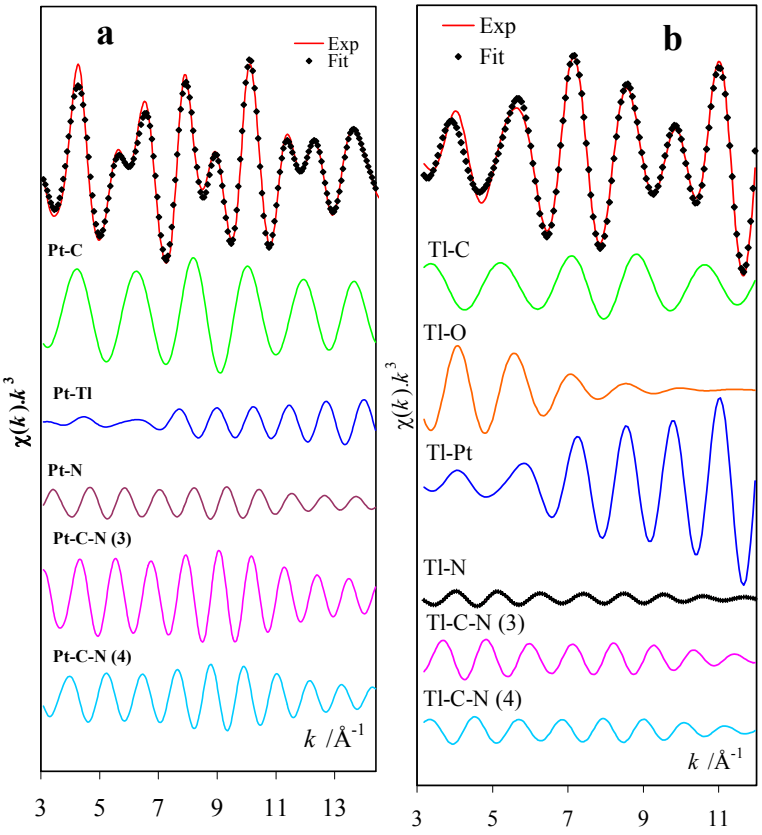


*Figure 2. Structural determination of $[(NC)_5PtTl(CN)]^-$ in aqueous solution (distances in Å): **a)** Pt L_{III}-edge EXAFS spectrum; **b)** Tl L_{III}-edge EXAFS spectrum, showing contributions of different single- and multiple scattering paths.*

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Farideh Jalilehvand
University of Calgary