DFT calculations and Raman spectroscopy of As(III) complexation with thiol ligands

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The extensive arsenic contamination is considered one of the most important toxicological problem \cite{1}. Its poisonousness is mainly due to the high affinity for the sulfhydryl groups present in active biomolecules, such as enzymes and proteins \cite{2}. The significance of the metal pollution, as well as its mobility and bioavailability, depends on arsenic speciation, which represents the distribution of the different chemical species in a given system. The study here reported was based on a previous speciation analysis on As(III)-TMA and As(III)-TMA systems and subsequently on Raman spectroscopic investigations combined with density functional calculations (DFT). The results obtained by means of Raman spectroscopy combined with data provided by DFT calculations give information about the molecular mechanisms of chelation of arsenic with these S-donor ligands.

**Speciation Study**

Raman spectroscopy studies were performed to confirm the complex formation and to obtain information about the way of ligand chelation towards Arsenite. More in detail, these investigations allowed to understand which ligand-chelating group played a key role in the metal - ligand complexation. The figures show the comparison between the Raman spectrum obtained on a free ligand solution (C\textsubscript{L} = 300 mmol L\textsuperscript{-1}) and the one recorded for a metal - ligand containing solution, with a M:L ratio of 1:2 (C\textsubscript{M} = 0.15 M and C\textsubscript{L} = 0.3 M). As it can be observed, the signal relative to the stretching of the S-H bond (\approx 2600 cm\textsuperscript{-1}) is not visible in the spectrum collected on the As(III)-L solutions. Moreover, an increase in intensity of the band at \approx 400 cm\textsuperscript{-1} is observed in the spectrum of the As (III) - ligands systems, probably due to the metal interaction with the sulfur of the thiol group present on the given ligand. In the light of these considerations, it is possible to assert that SH group plays a key role in the complexation of arsenite.

DFT studies, as shown in the graphs alongside, provide an energetic study on the different possible complexes, showing which is the most stable in energy and therefore the one favored.

**References**

\begin{itemize}
\item \cite{1} B. K. Mandal, K.T. Suzuki, *Talanta*, (2002), 58, 201.
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