Introduction: Scytonemin is a cyanobacterial sheath pigment with potent UV (UV-A, UV-B and UV-C) absorbing properties[1] which has been spectroscopically well characterized[2,3]. Di- and tetramethoxy derivatives of scytonemin, scytomin and scytonemin-imine have also been found and described in the literature[4,5]. The importance of these biomolecules is their photoprotective function, which is one of the major survival strategies adopted by extremophiles in environmentally stressed conditions. The existence of the cyanobacterial stromatolitic colonies on early Earth, with the scytonemin protection afforded against radiation exposure in the early atmosphere and dating from about 3.5 Gya in our geological record, therefore could imply that such an occurrence could have pertained on Mars[6]. Scytonemin has been identified as a prime biomarker in the search for extinct or extant life on planetary surfaces and subsurfaces. The molecular vibrational modes of the scytonemin family molecules and their theoretically predicted Raman spectra have already been established with the purpose of their recognition and differentiation both in terrestrial and extraterrestrial scenarios [7-10]. In this work, iron complexes of two scytonemin molecules in which iron is sandwiched between two scytonemin molecules are proposed.

An iron complex of two scytonemin molecules

Scytonemin Family molecules: Apart from scytonemin, di- and tetramethoxy derivatives of scytonemin, scytomin and scytonemin-imine that have been isolated experimentally, hypothetical iron(III) complexes of scytonemin and its di- and tetramethoxy derivatives predicted by modeling and theoretical calculations are suggested to facilitate the movement of iron through the rock matrix[7,8,9]. Also, a novel theoretically plausible, structure is proposed for oxidized scytonemin[10].

Computations: DFT calculations have been carried out at the B3LYP/6-31G* level for optimizations and frequency calculations making use of the program package Gaussian09.

Conclusions: The theoretical analysis illustrates novel feature characteristic of some important complex structures of scytonemin which may form by iron complexation and provides the potential for their recognition in extreme scenarios. This work indicates potentially novel structures and aims to add to the previous diagnostic Raman spectral database for scytonemin and its derivatives which are predicted to be stable for cyanobacterial colonies in iron-rich environments [11].