XAS Investigation of Arsenic Compounds Relevant to Biological and Environmental Systems

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Drinking water polluted by arsenic has caused severe health risk in many areas. To elucidate toxicity effect of arsenic in molecular basis, it is essential to understand fundamental chemistry of arsenic interacting with biological- and environmental- related molecules. Two themes that we have been focusing on this subject. One is the investigation of arsenic species interacting with humic substances and related organic compounds by various spectroscopic methods and techniques The other is the study of arsenic sulfur species interacting with selenium.

It has been proposed that arsenic related diseases are caused by the binding of arsenic with humic substance. Thus, we were mitivaed to explore the reactions of arsenic with dihydroxybenzoic acid that conatins the functional groups simlar to humic acid. In a reaction of $NaAsO_2$ and 2,3-dihydroxybenzoic acid, an arsenic compound was obtained. To gain the structural information of this arsenic species, the As K-edge XAS was performed. The measurements were carried out at room temperature at the beam line 17C in NSRRC. The data was collected at the energy range of 11840 to 11900 eV. After fitting the experiment data with Tilasite, 4[CaMg(AgO4)F] [American Mineralogist Vol. 57, pp. 1880-1884 (1972)], we not only confirm that arsenic exactly reacts with 2,3-dihydroxybenzoic acid again, but also get the further information about As-O binding length (1.68Å) and the coordination number of 4 (Fig. 1).

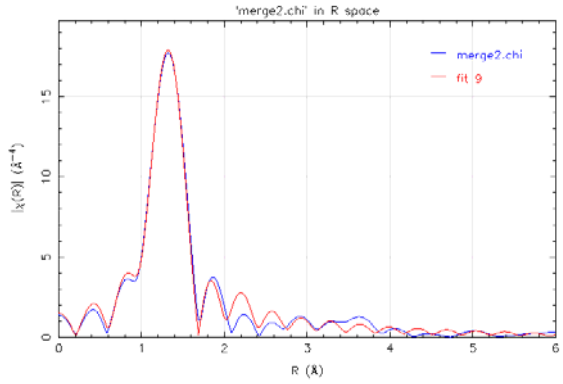

Fig. 1: Fourier transforms of As extended X-ray absorption fine structure (EXAFS) of the reaction adduct from $NaAsO_2$ and 2,3-dihydroxybenzoic acid.

On the other hand, the most observations in mammalian toxicology is that a lethal dose of selenium can be overcome by a lethal dose of arsenic. Some researches discovered glutathione (GSH) in vivo can form an As-Se complexes, which can be excreted from the bile. Against this background, we are prompted to study the chemistry of arsenic thiolate complexes reacting with selenium species. In a reaction of tris(benzenethiolato)arsenic(III) complex with selenic acid, we isolated a reaction adduct. The As K-edge XAS was used to characterized this species. The measurements were also carried out at room temperature at the beam line 17C in NSRRC. The data was collected at the energy range of 11840 to 11900 eV. After fitting the experiment data with $K(H_2AsO_4)$ [Journal of the Physical Society of Japan (2001) 70, 2327-2332], we get the further information about As-O binding length (1.80Å) and the coordination number (CN=4) (Fig. 2). Thus, we concluded that As-Se bond does not form in a reaction of tris(benzenethiolato)arsenic(III) with selenic scid. Futhermore, the reaction caused the dissocation of As-S bond, leading to the formation of As(V) oxo species.

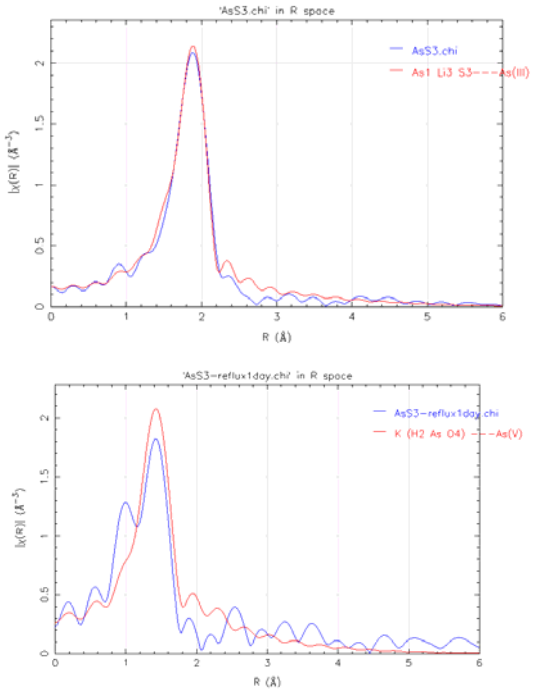

Fig. 2: Fourier transforms of As extended X-ray absorption fine structure (EXAFS) of tris(benzenethiolato)arsenic(III) complex (upper) and the reaction adduct from tris(benzenethiolato)arsenic(III) complex and selenic acid (bottom).