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Spectrometric characterisation of the solid complexes formed in the interaction of cysteine with As(III), Th(IV) and Zr(IV)

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ABSTRACT

The aminoacids play important roles in biological systems as they participate in key chemical reactions for life, usually involving complexation with metal and metalloid {metal(loid)} ions. In this work, the solid complexes prepared after mixing arsenic(III), thorium(IV) and zirconium(IV) solutions with *l*-cysteine at pH 8.0 were spectrometrically characterised. The X-ray diffraction, together with secondary electron microscopy/energy dispersive-X ray spectrometry, allowed us to obtain information about the crystallinity, morphology and elemental composition of the solid metal(loid)–cysteine complexes. Photoluminescence of the prepared solid complexes was also evaluated by confocal microscopy. The functional groups responsible of the complexation processes were elucidated by Raman and infrared spectrometry. The participation of the thiol group from the *l*-cysteine molecule in the complexation of As(III) was effectively noted by Raman spectrometry. Nonetheless, Th(IV) and Zr(IV) were bound to *l*-cysteine through the oxygen atoms of the carboxylate group, according to the FT-IR results.

1. Introduction

The aminoacids are the basic building blocks of proteins playing important roles in biological systems. Cysteine is one of the commonly-seen aminoacids in human body. Cysteine participates in key physiological functions, including anti-oxidation, anti-aging and detoxification. Many of the chemical reactions involve formation of soluble and/or solid complexes with many toxic and beneficial metal(loid)s, usually under the neutral conditions present in the biological fluids. The chemical structure of *l*-cysteine (2-amino-3-thiol propane carboxylic acid) (Cyst) contains three functional groups and, consequently, its molecular dynamic shows special interest when used as complexing agent for metals in chemistry and biological systems. Two polymorphic phases, orthorhombic and monoclinic, of *l*-cysteine, *gauche*- and *trans*-conformations, are known, both of them usually showing the zwitterionic structure [1]. Intermolecular hydrogen bonds dominate conformations of cysteine molecules in each phase, where the amine nitrogen atom acts as a donor in the hydrogen bonding with the carboxylate oxygen atoms from an adjacent molecule. In addition, hydrogen bonds observed in the monoclinic phase also involves the thiol hydrogen atom taking part as a donor in the bonding to a carboxylate oxygen atom from a neighbouring molecule [2]. Contrarily, in the orthorhombic phase, a positional disorder of the sulphur and hydrogen atoms has been noted [3]. However, these conformations can be altered as a result of interactions with different metal and metalloid species.

Large abundance of many metal(loid) species, including arsenic {As(III)}, thorium {Th(IV)} and zirconium {Zr(IV)}, can show important environmental and biological implications. Arsenic is a ubiquitous toxic metalloid, from which the water-soluble inorganic species, As(III) (arsenite) under reducing conditions and As(V) (arsenate) under conditions of moderate or high redox potential, are predominant [4]. However, As(III) is the most toxic arsenic species. Thorium constitutes a good nuclear fuel largely used through the ^{232}Th–^{233}U cycle [5], being also employed for age-dating in geology [6]. When thorium passes into the natural waters, both mono- and poly-nuclear hydroxylated species co-existing with colloids and/or solid oxides and hydroxides are usually formed [7]. The environmental and biological chemistry of thorium requires to know additional chelating analysis. Zirconium is used to build nuclear reactors, as well as in the production of explosives, fireworks, tracer bullets, and small rockets. Other applications include the use of zirconia, the most important refractory zirconium material. Some zirconium-organic complexes have been used in developing adhesives, sealants, and coatings for different materials [8]. Although some products containing zirconium can cause skin

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rashes, zirconium is regarded as relatively safe, being largely used in clinical chemistry. Nonetheless, continued vigilant monitoring of the use of these compounds in medicine should be warranted.

Mobility of the metal(loid) ions in biological and natural environments is largely affected by complexation with dissolved organic matter. So, knowledge about the chemical interaction between the As(III), Th(IV) and Zr(IV) ions and small organic molecules, such as *l*-cysteine, is of the greatest concern. Evaluation of these interactions provides a better understanding and assessment of the physicochemical properties, speciation and distribution of these complexes in environmental and biological systems. A few vibrational studies have already been focused on the structural elucidation of the solid arsenic-cysteine complex [9,10]. However, nothing is known about the structures of the Th(IV) and Zr(IV) ions when bounded to organic ligands, including *l*-cysteine, in solid phase. The aim of the present work was to obtain information about the solid compounds formed by mixing As(III), Th(IV) and Zr(IV) solutions together with *l*-cysteine at neutral pH. The wide variability in the chemical properties of these metal(loid)s was the reason for their selection, taking the As(III) ion as a reference to carry out this study. X-ray diffraction (XRD), secondary electron microscopy/energy diffraction-X ray spectrometry (SEM/ED-XRS) allowed us to derive conclusive information about the crystalline, morphology and elemental composition of the solid metal(loid)-cysteine complexes. Raman and Fourier transform-infrared (FT-IR) spectrometries were used to derive vibrational information related to the structural dynamic of the solid compounds formed, as compared with solid *l*-cysteine standards. In addition, photoluminescence characteristics were evaluated by confocal microscopy.

2. Experimental

2.1. Instrumentation

2.1.1. XRD

A Philips PW1830 (high voltage generator) powder X-ray diffractometer with a Philips PW1710/00 (diffractometer controller), working in Bragg–Brentano diffraction geometry and equipped with a sample spinner, was used to acquire diffractograms. The current and voltage used were of 30 mA and 40 kV, respectively. Powdered samples were mounted in the form of a thin layer on a zero background Si(911) substrate using Cu(K_α) as incident radiation. The scattered intensities were recorded in the 2θ span of 15–55°. Prior to spectral acquisition the instrument was properly aligned and checked for its figure of merit by conducting a run on α-quartz. Joint Committee on Powder Diffraction Standards (JCPDS)-International Center for Diffraction Data (ICDD) sticks were used to carry out spectral indexing [11]. In the present case, λ was assumed to be 0.154060 nm, which is the Cu $K_{\alpha1}$ line. Contribution from the Cu $K\alpha_2$ line was minimal under the conditions used. In our particle size analysis, machine contribution to the broadening was subtracted from the observed full width at half maximum (FWHM).

2.1.2. SEM/ED-XRS

Electron microprobe analysis of the nanoparticle surface was performed in a JEOL scanning electron microscope (Model JSM-6100), equipped with an energy-dispersive X-ray detecting system (LINK), and operated under recommended conditions (15 kV acceleration voltage and 5 nA probe current).

2.1.3. Raman spectrometry

Raman spectra were recorded in the back scattering geometry and at room temperature. All Raman spectra were obtained using a BWTEK portable Raman spectrometer, i-Raman model, fitted with a refrigerated CCD detector. Raman spectrometry measurements were performed using the 785 nm line laser, CleanLaze model (>300 mW) as the excitation source; the power level was set nominally at 100%, but it had to be reduced on several occasions due to saturation of the detector. The usual experimental conditions were 10 s accumulation time and 1 min acquisition time; spectra were scanned from 100 to 3300 cm^{-1} with resolution 4 cm^{-1}. The results were processed using KnowItAll software.

2.1.4. FT-IR spectroscopy

Infrared spectra in the 500–4000 cm^{-1} region were recorded on a Perkin Elmer System 2000 Fourier transform spectrometer (Norwalk, CT, USA) equipped with an air-cooled deuterium tryglicine sulphate (DTGS) detector. The attenuated total reflection (ATR) accessory utilised was a Perkin Elmer in-compartment HATR ACCY-FLAT (2000), with flat top-plate fitted with a 25-reflection, 45°, 50-mm ZnSe crystal, allowing simple sampling of solids, polymer films and powders. Reproducible contact between the crystal and the sample was ensured by use of a variable pressure clamp assembly (2000/GX). Prior to each analysis, a ZnSe background was scanned at 2 cm^{-1} resolution for each spectrum; 400 scans were coadded. In an effort to minimize problems from baseline shifts, the spectra were baseline-corrected and normalised using the maximum-minimum normalisation in the KnowItAll software.

2.1.5. Fluorescence microscopy

Fluorescence imaging was performed on a Nikon Eclipse C1si model Spectral Laser Scanning Confocal Microscope, equipped with three lasers: diode (408 nm), argon (488 nm) and helium–neon green (543 nm), three detection channels and one transmitted light detection channel.

A pH-meter (Crison model Digit 505) was used to measure acidity of the aqueous phase, when necessary. A Mettler AE 240 semi-micro analytical balance (sensitivity ± 0.01 mg) was used for weighing the chemicals and samples. A centrifuge Digicen 20 (Orto Alresa, Madrid, Spain) was used at 9000 rpm for 30 min to separate the precipitate at room temperature.

2.2. Chemicals

Stock solutions of As(III) (10 000 mg L^{-1}), Th(IV) (20 000 mg L^{-1}) and Zr(IV) (20 000 mg L^{-1}) were prepared in distilled, deionised water. Hydrochloric acid (d = 1.19, 37.9% w/w) and 1 M sodium hydroxide solutions were employed to adjust pH. All containers and glassware were washed with 3 M nitric acid for at least 24 h and rinsed three times with distilled, deionised water before use. Distilled, deionised water with a specific resistivity of 18 M cm, from a Millipore water purifier system, was used for the preparation of the samples and standards. The working solutions were prepared immediately prior to their use by serial dilutions of the stock solutions. *L*-cysteine (Merck), As_2O_3 (Merck), $ZrOCl_2$ (Merck) and ThO_2 (Fluka) were of analytical reagent grade. Solid *l*-cysteine was used in three ways, solid *l*-cysteine as received (compact solid standard), grinded solid *l*-cysteine (powdered solid standard) and treated solid *l*-cysteine (solid treated at 348 K). The last way refers to the solid *l*-cysteine standard submitted to exactly the same dissolution/precipitation procedure than that used with the metal(loid)/cysteine compounds.

2.3. Procedure

The solid As(III)–Cyst, Th(IV)–Cyst and Zr(IV)–Cyst complexes were prepared by the reaction created on mixing As(III) (7×10^{-4}–0.05 M), Th(IV) (0.02 M) and Zr(IV) (0.06 M) solutions with *l*-cysteine (0.25 M) in different mole ratios, at pHs in the range 5–10 and stirring on a hot plate. The reaction was carried