



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

An integrated experimental and theoretical investigation of the vibrational modes and molecular structure of a chelate, tetraaqua cysteine aluminum(III)

Thaís Tenório ^{a,*}, André Tenório ^b

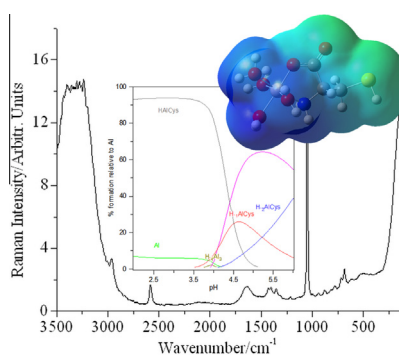
^a Department of Chemistry, Pontifícia Universidade Católica do Rio de Janeiro, Rua Marquês de São Vicente, 225, Edifício Cardeal Leme, 7º andar, sala 772A, 22453-900, Rio de Janeiro, RJ, Brazil

^b Instituto Federal de Educação, Ciência e Tecnologia do Rio de Janeiro, Rua Senador Furtado, 121 a 125, 20270-021, Rio de Janeiro, RJ, Brazil

HIGHLIGHTS

- Al³⁺:cysteine system M:L ratios 1:1 and 1:5 were studied in aqueous solution.
- Potentiometry, Raman spectroscopy and DFT calculations were used.
- Cysteine acts as a bidentate ligand in tetraaqua cysteine aluminum(III).
- The geometric arrangement adopted was distorted octahedral.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 17 May 2014

Received in revised form 22 October 2014

Accepted 20 November 2014

Available online 3 December 2014

Keywords:

Aluminum(III)

Cysteine

Coordination mode

Geometric arrangement

Vibrational assignments

ABSTRACT

The complex formed by Al³⁺ and cysteine in aqueous solution has been studied by potentiometry, Raman spectroscopy and DFT calculations (DFT:B3LYP/6-311++G**).

Atomic charges, frontier molecular orbitals, electrostatic potential contour surface, electrostatic potential map and donor–acceptor second order perturbative energies were examined. The [Al(Cys)(H₂O)₄]²⁺ complex adopts a distorted octahedral geometry. Cysteine should act as a bidentate ligand through the oxygen of the carboxylate and the nitrogen of the amino group. The molecule has high HOMO–LUMO energy gap, intense intramolecular charge transfer and positive electrostatic potential.

© 2014 Elsevier B.V. All rights reserved.

Introduction

Alzheimer's disease is a common neurodegenerative disease that affects the older population. It is hallmarked by senile plaques

and neurofibrillary tangles in the brain tissue. Its main protein constituents are, respectively, β-amyloid (Aβ) and tau [1].

The relation between aluminum(III) and Alzheimer's disease was published in 1965 [2]. Aluminum(III) participates in Alzheimer's pathogenesis by favoring oxidative stress, Aβ aggregation, tau phosphorylation and fibril genesis [3–6]. These conditions lead to neuronal degeneration.

Cysteine (Cys) (Fig. S1) is a conditionally essential sulfur-containing amino acid. This amino acid contributes to the

* Corresponding author. Tel.: +55 21 3527 1824; fax: +55 21 3527 1637.

E-mail addresses: tenoriocalc@gmail.com (T. Tenório), tenoriofrj@gmail.com (A. Tenório).

maintenance and integrity of cellular systems and influences organic redox reactions and the cellular capacity to decontaminate toxic compounds, free radicals and reactive oxygen species.

A deficiency or defect in enzymes related to sulfur metabolism can cause disequilibrium in the plasma sulfur concentration. Sulfur homeostasis has an impact on human health, and changes in its concentration provoke homocystinuria, cystinuria, neural tube defects, vascular diseases, Alzheimer's disease and cancer [7–9].

Investigations [10] into a novel drug for Alzheimer's disease based on the addition of a cysteine residue to A β peptide showed positive effects in mice, including increased immunogenicity and reduced A β deposits in the brain, and thereby reduced toxicity.

Antioxidants based on the structure of cysteine, such as S-allyl cysteine and N-acetyl cysteine, also exhibit neuroprotective effects, including against Alzheimer's disease. S-allyl cysteine [11] prevents induced neuronal apoptosis, destabilizes A β fibrils and inhibits A β fibrillation, thereby preventing cognitive decline. N-acetyl cysteine [12] protects neurons against oxidative stress and apoptosis. A study in rats treated by chronic administration of N-acetyl cysteine exposed to aluminum ingestion revealed improvements in memory retention, decreased oxidative damage and a reduction in acetylcholinesterase activity [13].

Furthermore, cysteine is found in dietary supplement, in protein-rich foods and drinks and in parenteral nutrition therapy. Aluminum(III) can be found in some drugs (e.g. antacids, analgesics, etc.), in parenteral nutrition therapy, in food additives and even in water [14,15]. Aluminum(III) is absorbed in the stomach or proximal duodenum. Amino acids help aluminum absorption and distribution *in vivo*. These increase the pH of Al³⁺ precipitation and its gastrointestinal absorption via complexation reactions [16,17].

Studies on complexes formed by aluminum(III) and amino acids such as glycine [18], serine [19], asparagine [19] and histidine [19], among others, can be found in the literature. Some research into cysteine and other metallic ions such as iron(III) [20], chromium(III) [21], bismuth(III) [22], lanthanum(III) [23] and cesium(III) [23] can also be found.

It is important to improve our knowledge about the complexes formed between cysteine and aluminum(III) in living organisms. Investigations have been performed in aqueous solution, using techniques such as potentiometry, Raman spectroscopy and theoretical calculations to analyze [Al(Cys)(H₂O)₄]²⁺ complex. This species was particularly studied because of its great predominance in the acidic pH range before starting an intense hydrolysis.

Experimental

Reagents

All chemicals are analytical-reagent grade. Cysteine (Cys) was purchased from Sigma–Aldrich (Missouri, USA) and used as received. Al(NO₃)₃·9H₂O, HCl, NaOH, ammonium hydroxide, solochrome black indicator, KNO₃, standard solutions of carbonate-free KOH 0.1 mol L⁻¹ and of EDTA Titriplex III 0.1 mol L⁻¹, standard buffer solutions of pH 4.0 and 7.0 were purchased from Merck (Darmstadt, Germany). The solutions were prepared freshly each day with ultrapure and CO₂-free water.

Equipments

Ligand solutions were obtained using an ultrasound machine with induction heating (UltraClean model 1400A, Unique Ultrasonic, Temecula, CA). Potentiometric data were obtained using a system consisted by a titrando automatic microburette (model 809, Metrohm, Herisau, Switzerland), a stirrer (model 801, Metr-

ohm), a dosing system (800 Dosino, Metrohm) and a combined glass electrode. This system was coupled with personal computer and operated using software Tiamo. Raman spectra were recorded by a Raman Spectrometer Model 400 (Perkin Elmer, Massachusetts, USA) with a high performance stabilized 785 nm diode laser with signal-to-noise >40 dB and stability of 0.1 nm. Theoretical calculations were performed using Gaussian 03 W program [24], GaussView molecular visualization programs [25,26] and Chem-Craft program [27].

Procedures

The purity of cysteine was verified by determining the exact concentrations of their solutions using the Gran method [28]. The concentrations of Al³⁺ solutions were obtained via back-titration with standard solution of EDTA 0.1 mol L⁻¹ using solochrome black indicator and ammonia buffer solution [29].

Potentiometry

Aluminum(III) nitrate solution (0.01 mol L⁻¹) and cysteine solutions (0.005 mol L⁻¹ and 0.001 mol L⁻¹) were prepared by dissolving reagents in ultrapure and CO₂-free water. Ligand solutions were prepared using an ultrasound machine to get a solution without precipitate. For the determination of cysteine acid dissociation constants, an aqueous solution of protonated ligand (0.001 mol L⁻¹) was titrated with 0.1 mol L⁻¹ KOH. It was necessary the addition of 1.00 mL of HCl standard 0.1 mol L⁻¹ to induce the ligand's protonation. For the determination of the stability constants of the aluminum(III) complexes, samples with solutions containing cysteine (0.005 mol L⁻¹ or 0.001 mol L⁻¹) and Al³⁺ (0.01 mol L⁻¹) were titrated at metal–ligand ratios (M:L) of 1:5 and 1:1 with 0.1 mol L⁻¹ KOH under the same conditions of the ligand titration. All titrations were performed at 25.0 ± 0.1 °C. The ionic strength was adjusted to 0.1 mol L⁻¹ with KNO₃ in acidic medium.

The stability constants of the ligand and complexes were determined using the Hyperquad 2000 program [30]. Validation curves and species distribution diagrams were determined using the Hyss 2006 program [31]. The ionic product of water was found to be pK_w = 13.77. Hydrolysis constants for Al³⁺ were obtained from the literature [32,33] and employed in the calculations. The constants values were: –5.33 for AlOH, –10.91 for Al(OH)₂, –17.30 for Al(OH)₃, –13.13 for Al₃(OH)₄ and –107.47 for Al₁₃(OH)₃₂.

Raman spectroscopic analyses

All measurements were carried out at room temperature (25.0 ± 0.1 °C) in the dark under the following conditions: 100 mW of laser power, 2 cm⁻¹ of resolution, 20 s exposure time and accumulation of 200 scans.

Aluminum(III) nitrate and cysteine solutions, all in 0.5 mol L⁻¹, were prepared by dissolving reagent in ultrapure and CO₂-free water. Measurements were made on a 4.0 mL quartz cuvette. All Raman spectra were obtained focusing the laser directly on the sample aqueous solutions. The Raman spectra from Cys (aqueous solution) and from Al³⁺:Cys solution at a 1:1 M:L ratio were made in solutions under a specific pH chosen according to the speciation studies. Raman spectrum from the solid ligand was also obtained.

Quantum chemical calculations

In this study theoretical calculations were made using density functional theory (DFT) with B3LYP (Becke's three parameter hybrid functional for the exchange part and the Lee–Yang–Parr (LYP) correlation function) [34–37] hybrid functions and the 6-311++G(d,p) basis set for structures of ligand and binary system. All calculations have considered the molecules in water solvent with polarizable continuum model (PCM).

Download English Version:

<https://daneshyari.com/en/article/1229079>

Download Persian Version:

<https://daneshyari.com/article/1229079>

[Daneshyari.com](https://daneshyari.com)