The pH-specific synthesis of three new Cr(III)-heida (2-hydroxyethyliminodiacetic acid) complexes

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Abstract

In our quest to delineate interactions of chromium with ligands often involved in chemistries of toxic and biologically significant manifestations, we have looked into the aqueous structural speciation of the binary system of Cr(III)-heida (2-hydroxyethyliminodiacetic acid). Synthesis in aqueous media led to the isolation of three new complexes Na \([\text{Cr} \{\text{HOCH}_2\text{CH}_2\text{N} (\text{CH}_2\text{COO})_2 \}_2\text{H}_2\text{O}] \) (1), 2 (NeoH) \([\text{Cr} \{\text{HOCH}_2\text{CH}_2\text{N} (\text{CH}_2\text{COO})_2 \}_2\text{OH} \) . \(\text{H}_2\text{O} \) (2), and \([\text{Cr} (\text{H}_2\text{O}) (\text{Phen}) \{\text{HOCH}_2\text{CH}_2\text{N} (\text{CH}_2\text{COO})_2 \}_2\] (NO\(_3\)) .3H\(_2\)O (3). The complexes were characterized by elemental analysis, spectroscopic, structural, thermal, EPR and magnetic susceptibility studies. The physicochemical properties of the new species project the fundamental features of the interaction of Cr(III) with (O,N)-containing biosubstrates potentially involved in toxic effects manifested at the cellular level.

Keywords: chromium(III), heida (2-hydroxyethyliminodiacetic acid) binary system, ternary system

1. Introduction

The Chromium is abundantly present on the earth’s crust. Its use includes a) industrial processes in tanneries, cement industries, plating and alloying industries, corrosive paints [1], doping [2] of advanced materials for the modification of the efficiency and lifetime of the photorefractive signals (i.e. "memory"-type signals in connection with hologram recording) [3], heterogeneous catalysts, electrochromic devices and, more recently, in gas sensors [4,5,6], and b) direct or indirect involvement in plants, animals, and humans [7]. In the case of humans, chromium has been reported to play an important role in regulating cellular physiology through participation in the glucose tolerance factor (GTF [8]) [9] by preventing mild forms of diabetes [10] and arteriosclerosis in humans, and to be involved in nucleic acid synthesis [11]. In a widely diverse coordination environment, through which Cr(III) develops its activity, a field of avid research activity has emerged. In this field of research, the role(s) of Cr(III) in biological systems is inevitably associated through its aqueous chemistry with lipids, proteins, and amino acids free in the cytosol or as components of peptides and lipid membrane structures. In all such cases, soluble and bioavailable forms of Cr(III) promote (bio)chemical activity, thus reflecting the complexity of the aqueous speciation in binary and ternary systems present in biological media. In view of chromium’s involvement in cellular processes, thereby directly or indirectly affecting the physiology of organisms with often deleterious consequences, research efforts have targeted a) the aqueous structural speciation of Cr(III), one of the two major oxidation states of chromium (III,VI), with metal-complexing carboxylate-containing low molecular mass physiological ligands, and b) the study of the physicochemical properties of arising species potentially bioavailable and eliciting interactions with cellular biotargets. To this end, we herein report on the pH-specific synthesis, spectroscopic and structural characterization, and magnetic susceptibility studies of a new aqueous binary Cr(III)-heida species arising from the requisite binary system.

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2. Materials and methods

All experiments were carried out under aerobic conditions. Nanopure quality water was used for all reactions. Cr (NO₃) 3·H₂O and 2-hydroxyethylenediaminodiacetic acid, were purchased from Aldrich. Sodium hydroxide, neocuproin and 1,10-phenanthroline were supplied by Fluka.

3. Results and Discussion

In the course of this study, we investigated the aqueous synthetic chemistry of the binary chromium (III) – hydroxyethylenediaminodiacetic acid system. The synthesis of the new compounds was carried out in aqueous media, under specific pH conditions.

The addition of base, for the adjustment of the pH, took place after one day of continuous stirring. Following addition of ethanol at 4°C, all three reactions afforded red crystals with different shapes. The reactions for the synthesis of the three complexes of Cr(III) with hydroxyethylenediaminodiacetic acid are given below:

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\begin{align*}
\text{Cr(NO}_3\text{)}_3 + 1.5 \text{HEIDA} & \xrightarrow{\text{pH 3}} \text{Na}_4[\text{Cr(HEIDA)}_2] \cdot 2\text{H}_2\text{O} \\
\text{(CH}_3\text{COO)}_2\text{Cr(OH)}_2 + 3 \text{HEIDA} & \xrightarrow{\text{pH 4.5}} 2\text{Na}_2\text{H}[\text{Cr(HEIDA)}_2]\text{(OH) \cdot H}_2\text{O} \\
\text{Cr(NO}_3\text{)}_3 + 1 \text{HEIDA} & \xrightarrow{\text{pH 4.5}} [\text{Cr(HEIDA)(phen)(HEIDA)}]\text{(NO}_3\text{)} \cdot 3\text{H}_2\text{O}
\end{align*}
\]

4. Conclusions

In the course of the herein presented research, the ability of hydroxyethylenediaminodiacetic acid to promote complexation chemistry with Cr(III) was examined.

Our synthetic studies were carried out in aqueous media in a pH specific manner. In particular, chromium (III) reacted with hydroxy ethylenediaminodiacetic acid in aqueous solution, at different pH and afforded the three new mononuclear anions \([\text{Cr}\{\text{HOCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COO})_2\}_2]^- (1)\) and \((2), [\text{Cr(phen)}\text{-(H}_2\text{O)}\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COO})_2]\)^+(3) which were isolated in a crystalline form and were characterized structurally and spectroscopically. The collective physicochemical studies project basic structural features potentially involved in Cr(III) interactions with O,N-containing substrates of low or high molecular mass targets in cellular media. Such well defined species reflect discrete components of aqueous speciation systems involved in benign or biotoxic effects in cellular processes.

References