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SYNTHESIS, STRUCTURAL, SPECTROSCOPIC AND MAGNETIC SUSCEPTIBILITY STUDIES OF A Cr(III)-HEIDA (2-HYDROXYETHYLIMINODIACETIC ACID) COMPLEX.

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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 at a specific pH (5.5) in aqueous media led to the isolation of complex $(NH_4)[Cr\{HOCH_2CH_2N(CH_2COO)_2\}_2]\cdot 2H_2O$ (**1**). The complex was 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)*

Introduction

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 (Ramos, 1994), doping (Peter, 1996) of advanced materials for the modification of the efficiency and lifetime of the photorefractive signals (i.e. the "memory' '-type signals in connection with hologram recording) (Fö1dvári, 1995), heterogeneous catalysts, electrochromic devices and, more recently, in gas sensors (Moseley, 1991; Schierbaum, 1991; Meixner, 1996), and b) direct or indirect involvement in plants, animals, and humans (Bae, 2005). 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) (Toepfer, 1977; Zetic, 2001) by preventing mild forms of diabetes (Morris, 1995) and arteriosclerosis in humans, and to be involved in nucleic acid synthesis (Richard, 1991).

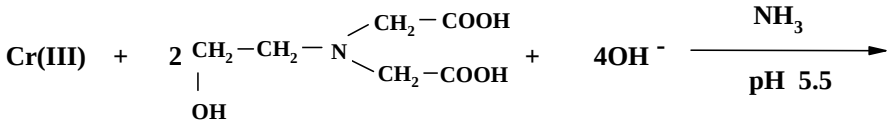
In a widely diverse coordination environment, through which Cr(III) develops its activity, a field of avid research activity has emerged. In this field of research, the role(s) of Cr(III) in biological systems is inevitably associated through its aqueous chemistry with lipids, proteins, and amino acids 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.

Experimental

In the course of this study, we investigated the aqueous synthetic chemistry of the binary chromium(III)- hydroxyethyliminodiacetic acid system.

The synthesis of $(NH_4)[Cr\{HOCH_2CH_2N(CH_2COO)_2\}_2] \cdot 2H_2O$ (**1**) was carried out in aqueous media, under specific pH conditions (ammonia was used to adjust the pH specifically at the value of 5.5). The addition of ammonia, for the adjustment of the pH, took place after one day of continuous stirring. Following addition of ethanol at 4^oC, the reaction afforded red crystals. The stoichiometric reaction for

the synthesis of complex of Cr(III) with hydroxyethyliminodiacetic acid is given below:



$$[Cr(C_6H_9O_5N)_2]^- + 4\ H_2O \qquad \text{Reaction 1}$$

Results and Discussion

Positive identification on the crystalline product was achieved by elemental analysis, spectroscopic, structural, thermal, EPR and magnetic susceptibility studies.

The FT-Infrared spectrum of **1** in KBr exhibits the presence of vibrationally active carboxylate groups. Antisymmetric as well as symmetric vibrations for the carboxylate groups in the coordinated 2-hydroxyethyliminodiacetic ligand were present. Specifically, antisymmetric stretching vibrations $\nu_{as}(COO^-)$ for the carboxylate carbonyls appeared at 1630 cm^{-1} for **1**. Symmetric vibrations $\nu_s(COO^-)$ for the same groups appeared at about 1397 cm^{-1} for **1**.

The UV/Visible spectrum of **1** was taken in water. The spectrum shows a band around 506 nm (ε 60). At higher energies a well-formed major peak appears at 362 nm (ε 39). The absorption features are likely due to d-d transitions, which are typical of a Cr(III) d^3 octahedral species.

The structure of the complex is presented in Figure 1. The structure consists of a mononuclear core unit, assembled by a central Cr(III) ion, and two 2-hydroxyethyliminodiacetate ligands. The latter ligands bind to the metal ion through the two carboxylates oxygens and the amine nitrogen, promoting the formation of two stable metallacyclic rings. The second 2-hydroxyethyliminodiacetate ligand coordinates Cr(III) in the same mode due to the presence of center of

inversion. The hydroxyl group is not deprotonated and does not bind Cr(III). It dangles away from the site of metal coordination.

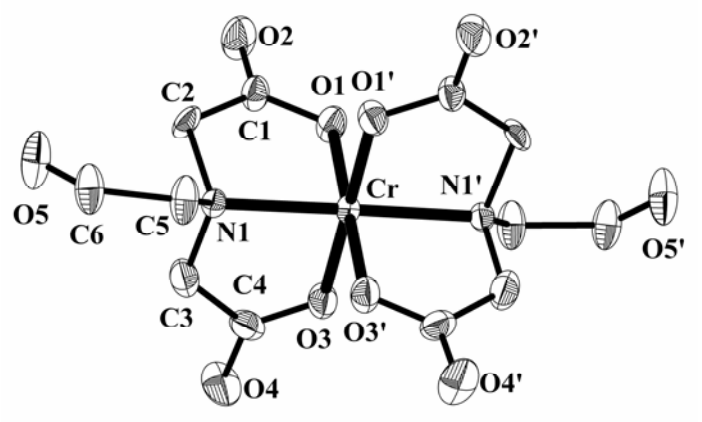


Fig. 1. Partially labeled ORTEP plot of the $[Cr[HOCH_2CH_2N(CH_2COO)_2]_2]^{-1}$ anion with thermal ellipsoids drawn at the 30% probability level.
Symmetry operation: (') *x*, *-y*, *-z* (Hydrogen atoms have been omitted for clarity).

Conclusions

In the course of the herein presented research, the ability of hydroxyethyliminodiacetic acid to promote complexation chemistry with Cr(III) was examined. Our synthetic studies were carried out in aqueous media and at a pH specific value. In particular, chromium(III) reacted with hydroxyethyliminodiacetic acid in aqueous solution, at pH~5.5, and afforded the mononuclear anion $[Cr\{HOCH_2CH_2N(CH_2COO)_2\}_2]^{1-}$, which was isolated in a crystalline form and was 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.

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