Complex formation of copper(II), nickel(II) and zinc(II) with ethylophosphonoacetohydroxamic acid : solution speciation, synthesis and structural characterization.

Autorzy

Małgorzata Ostrowska

Irina A. Golenya

Matti Haukka

Igor O. Fritsky

Elżbieta Gumienna-Kontecka

Rok wydania

2019

Czasopismo

New Journal of Chemistry

Numer woluminu

43

Strony

10237-10249

DOI

10.1039/c9nj01175g

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

The first example of a Cu(II) 12-MC-4 hydroxamic metallacrown containing an ethylphosphonate group as an additional donor function in the β-position with respect to the hydroxamic group is described. The solution equilibrium of ethylphosphonoacetohydroxamic acid (PAHEt) with Cu(II) was investigated in aqueous solution by a combination of potentiometry, mass spectrometry, UV-Vis and EPR spectroscopies, and isothermal titration calorimetry. A model containing mononuclear [CuL], $[CuL_2]^{2-}$ and $[CuL_2H_{-1}]^{3-}$ and pentanuclear $[Cu_5(LH_{-1})_4]^{2-}$ species is proposed. The predominance of the $[Cu_5(LH_{-1})_4]^{2-}$ species in solution over the pH range 4–9 was confirmed by the signals present in the ESI-MS spectra, as well as the absence of the EPR signal. In addition, the results of isothermal titration calorimetry indicated the stoichiometry of the complex form at pH 5.5 as 1.25. Even if forming a less stable MC complex, PAHEt offers the formation of 12-MC-4 in a broad pH range, which distinguishes it especially from α-aminohydroxamic acids. The compound corresponding to the pentameric metallacrown complex was isolated in the solid state as $\{Na_4(H_2O)_6(Ac)[Cu_5(PAHEt\text{-}3H)_4(Ac)]\}_2 \cdot 3H_2O$ (**1**), whose crystal structure was determined by X-ray analysis. The centrosymmetric decanuclear complex anion of (**1**) consists of two pentanuclear 12-MC-4 fragments formed by five Cu(II) ions and four triply deprotonated residues of the phosphonoacetohydroxamate ligand, and is associated with eight sodium cations, two acetate anions and twelve water molecules taking part in sodium cation coordination, as well as solvate water molecules. The stability of MCs under conditions of competitive complex formation, as well as their reactivity with respect to a strong chelating agent, 2,2′-dipyridyl (dipy), was examined, and as a result a 1D coordination polymer featuring mixed-ligand mononuclear units $\{[Cu(dipy)(PAHEt\text{-}2H)]\}_n \cdot 1.86nH_2O$ (**2**) was formed. In addition the chelating capacity of this ligand toward Ni(II) and Zn(II) ions was studied in solution.

Adres publiczny

http://dx.doi.org/10.1039/c9nj01175g