Inorganica Chimica Acta 362 (2009) 3526–3540

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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

1-Hydroxybenzotriazole (HOBt) acidity, formation constant with different metals and thermodynamic parameters: Synthesis and characterization of some HOBt metal complexes – Crystal structures of two polymers: $[Cu_2(H_2O)_5(OBt)_2(\mu\text{-}OBt)_2] \cdot 2H_2O \cdot EtOH$ (**1A**) and $[Cu(\mu\text{-}OBt)(HOBt)(OBt)(EtOH)]$ (**1B**)

Hassan H. Hammud [a,*], K. Travis Holman [b], Mamdouh S. Masoud [c], Ayman El-Faham [c], Hanan Beidas [a]

[a] Department of Chemistry, Beirut Arab University, 11-5020 Beirut, Lebanon
[b] Department of Chemistry, Georgetown University, 20057-1227 Washington, DC, USA
[c] Chemistry Department, Faculty of Science, Alexandria University, Egypt

ARTICLE INFO

Article history:
Received 7 November 2008
Received in revised form 6 March 2009
Accepted 28 March 2009
Available online 5 April 2009

Keywords:
1-Hydroxybenzotriazole complexes
Copper(II) complexes
Acidity constants
Formation constants
Thermodynamic parameters
Crystal structures
Thermal analyses
Electrical conductivities

ABSTRACT

The dissociation constants of 1-hydroxybenzotriazole (HOBt) and the formation constants of its complexes with cobalt(II), copper(II), nickel(II), iron(III), zinc(II), lead(II), mercury(II), and cadmium(II) were evaluated at different temperatures (20–45 °C) by potentiometric measurements in the presence of different percentages of ethanol–water and dioxane–water media. The thermodynamic parameters were calculated and discussed. HOBt complexes of copper, nickel, cobalt, and zinc were synthesized and characterized by IR, magnetism, elemental analysis and mass spectra. Entropies of activation (ΔS^*) were calculated from differential thermal analysis (DTA) curves of complexes. Electrical conductivity measurements indicated that all the complexes exhibit semiconductor behavior and the electrons in the available orbitals are not of high mobility. The crystal structure of coordination polymer $[Cu_2(H_2O)_5(OBt)_2(\mu\text{-}OBt)_2] \cdot 2H_2O \cdot EtOH$ (**1A**) is composed of helical chains of Cu(II) ions with alternating chromophores bridged by 1-hydroxybenzotriazolate ligand. Copper exhibits octahedral and square pyramidal coordination geometry. Both intra- and inter-molecular $\pi-\pi$ interactions exist in the structure of **1A**.

While **[**$Cu(\mu\text{-}OBt)(HOBt)(OBt)(EtOH)]$ (**1B**) is composed of zigzag polymeric chains of Cu(II) atoms bridged by 1-hydroxybenzotriazolate ligand, the copper has a square pyramidal environment. Both H-bond and $\pi-\pi$ interaction exist in the structure of (**1B**).

1. Introduction

There has been a great interest in the coordination chemistry of benzotriazole (BtaH) and its ring-substituted derivatives because of their anticorrosion action toward certain metals, particularly copper and its alloys [1–5]. Chemical, physical, and structural studies on realistic model complexes are needed to understand the complex surface chemistry that leads to corrosion inhibition and to preparation of new efficient inhibitors. It has been postulated that copper oxide films are prerequisites for successful corrosion inhibition [6]. Nevertheless, the inhibition mechanism model can involve an oligomeric complex of BtaH and copper(I) ions forming a film on the metal surface and protecting the surface from aggressive ions in solution. This is supported by electron spectroscopy for chemical analysis (ESCA) and infrared studies [6,7], surface-enhanced Raman scattering (SERS) [8], and FT-SERS [9]. Thus, the inhibition process can be investigated by studying the coordination chemistry of BtH with copper bound to oxygen-donor ligands (β-diketonate) [10–12], or by studying the complexation of 1-hydroxybenzotriazole (HOBt) that binds to copper metal from nitrogen and oxygen groups [13,14].

Also, benzotriazole and its derivatives found wide application in peptide synthesis. The segment condensation method has been employed for chemical synthesis of large peptides and proteins where a carboxyl component peptide is coupled to an amine component. The use of potent activation reagents to perform the coupling steps converts the carboxyl acid group into an ester fraction with good leaving group. However, this transformation tends to increase the acidity of α-proton and favors the formation of 5(4H)-oxazolone both of which may lead to racemization [15,16]. Racemization suppressors such as HOBt [17] permit the trapping of the vigorously activated intermediate before significant epimerization can occur [18]. $CuCl_2$ was reported to reduce epimerization effectively by acting as oxazolone stabilizer [19]. $CuCl_2$ was also found effective in conjunction with HOBt and

* Corresponding author. Tel.: +961 3 381862; fax: +961 1 3 300110.
E-mail address: hhammud@yahoo.com (H.H. Hammud).

0020-1693/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2009.03.046

hydroxypyridinotriazole (HOAt) [20]. $Cu(OBt)_2$ complex also reduced racemization in solution peptide segment coupling and in solid-phase peptide synthesis [21,22].

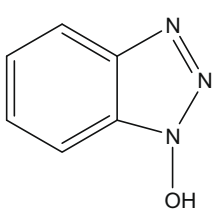
Benzotriazole ligands (BtaH) have shown rich coordination chemistry. They form mononuclear metal complexes and also act as a building block for the preparation of supramolecular complexes of both oligomeric and polymeric types. The crystal structures of 1-methylbenzotriazole (MebtaH) complexes have been determined for the monomeric cobalt [23], and nickel complexes [24], and also for the doubly chloro-bridged dimer and the novel alternating linear-chain polymer [25]. The reaction of the η^3–μ^3 bridging tridentate ligands benzotriazole (btaH) and 5,6 –dimethylbenzotriazole (5,6 diMebtaH) with nickel acetate produces the pentanuclear clusters $[Ni_5(OH)(bta)_5(acac)_4(H_2O)_4]$ [26] and $[Ni_5(OH)(5,6\text{-diMebta})_5(acac)_4(H_2O)_4]$, respectively, where acacH = acetylacetone [26,27]. The nickel assemblies are composed of tetrahedral arrangement of four six-coordinate metal ions centered on the fifth. The analogous copper pentanuclear cluster $[Cu_5(bta)_6(L)_4]$ has also been synthesized and studied by X-ray where L = β-diketonate [28]. A Ni9 complex was formed with benzotriazole ligand $[Ni_9(bzac)_6(Rbta)_{12}(MeOH)_6]$, bzacH = benzoylacetone [29]. The highest nuclearity of such complex is Mn26 cluster $[Mn_{26}O_{17}(OH)_8(OMe)_4F_{10}(bta)_{22}(MeOH)_{14}(H_2O)_2]$ [30].

The new ligand 1-hydroxybenzotriazole HOBt (Fig. 1) acts as a bidentate bridging hydroxybenzotriazolate anion (btaO) through N_2;N_3 in the trinuclear complex $[Ni_3(btaO)_6(NH_3)_6]$ [31]. Higher-nuclearity Ni(II) clusters: hydroxo and azido complexes Ni13 have also been obtained $[Ni_{13}(OH)_6(O_2CMe)_8(btaO)_{12}(H_2O)_6\text{-}(n\text{PrOH})_4]$ and $[Ni_{13}(N_3)_6(O_2CMe)_{8}\text{-}(btaO)_{12}(MeOH)_{10}]$ [32]. These also act as a bidentate-bridging ligand but through N_3 and O_1 in the ferromagnetic 3D diamond-like copper (II) network $[Cu(btaO)_2(MeOH)]_n$ which exhibits soft magnetic properties [33]. Hydroxybenzoate anion also complexes with Cd(II) forming mononuclear complex $[Cd(btaO)_2(H_2O)_4]\cdot 3H_2O$, with Zn(II) forming 1-D coordination polymer $[Zn(btaO)_2]_n$, [34] and with Mn(II) forming the 2-D coordination polymer $[Mn_3(O_2CMe)_2(btaO)_4(MeOH)_2]_n$ [35].

In the present work, the reaction of copper acetate with HOBt resulted in the preparation of complex **1**A having helical chain structure with alternating chromophore and complex **1B** having a zigzag chain structure as evidenced by X-ray study. Also several complexes of HOBt with the metals(II) (Cu, Co, Ni and Zn) have been synthesized and characterized by IR, elemental, thermal analysis, mass spectra, and conductivity measurement. In order to obtain further information on the nature of the metal–HOBt interactions and solvent effects, the acidity constants of HOBt and its formation constants with different metals(II) Cu, Co, Ni,, Zn, Hg, Cd, and Pb and also Fe(III) in water–ethanol and water–dioxane media have been evaluated, as well as the corresponding thermodynamic parameters.

2. Experimental

The chemicals used were BDH, Merck, and MA Biosystem products. The solvents used were of spectroquality grade.



HOBt

Fig. 1. Structure of hydroxybenzotriazole HOBT.

2.1. Potentiometric measurements

2.1.1. Apparatus

The potentiometric measurements were carried out using Denver instrument Model 225 pH. Ion selective electrode meter was fitted with a combined glass electrode (readings to ±0.01 pH unit). The pH meter was calibrated from time to time at different temperatures using three standard buffers at different pH values. The titrations were carried out in 150 ml thermostat cell. The cell compartment was kept constant at the desired temperature by using a thermostat Model Heto HMT 200 in the temperature range of 20–45 °C (±0.1 °C).

2.1.2. Reagents and materials

All the solutions were prepared in double distilled water. Carbonate-free sodium hydroxide solution (10^{-2} M) was used as a titrant and was standardized against potassium hydrogen phthalate solution. Potassium chloride solution was prepared as a supporting electrolyte ($\mu = 0.30$) to maintain constant ionic strength. The metal ion solutions were prepared and standardized with EDTA.

2.1.3. Procedure

The dissociation constants of the ligands were determined by introducing 50.00 ml of 1-hydroxybenzotriazole ligand (1.00×10^{-3} M) into the thermostated titration cell in the presence of KCl ($\mu = 0.30$) and different percentages (v/v) of the organic solvent–media. The pH readings were taken after the addition of small increments of 1.00×10^{-2} M standard NaOH solution. The solution was maintained free of carbon dioxide by passing through it a stream of purified nitrogen through the whole titration. The obtained K_a values were used to calculate the stability constants at each temperature.

The stability constants were computed using acid–base titration technique: 50.00 ml solution in the thermostated titration cell consisted of 5.00×10^{-4} M metal ions, 1.00 x 10^{-3} M ligand, and KCl (μ = 0.30) (ligand to metal mole ratio equals 2). The pH readings were taken after the addition of small increments of 1.00×10^{-2} M standard NaOH solution. The calculations were restricted to the data obtained before pH 8 to avoid precipitation and complications due to the hydrolysis of the complex species. The model

$$\mathrm{pH} + [\log \overline{n}_A/(1-\overline{n}_A)] = \mathrm{p}K\ \overline{n}_A < 1 \quad (3)$$

selected was that which gave the best statistical fit and proved consistent with the titration data without giving any systematic drifts in the magnitudes of various residuals.

2.2. Physical measurements

Melting points were measured using the Griffin and George MFB 590 010T apparatus. Elemental analysis of C, H, and N was performed by Kanti Labs Ltd. Mississauga, Canada, Microanalysis and Alexandaria University. Electrical conductance measurements (μs/cm) of the metal complexes, using dimethylformamide (DMF) as solvent, were carried out with BA 380 conductivity meter. TLC was performed on Bakerflex silica gel IB-F (2.5–7.5 cm) plates in CH_2Cl_2. Metal and chloride analyses were achieved using published methods. Thermal analysis: 60 mg of the compound was placed in a platinum crucible. Dry nitrogen was flowed over the sample at a rate 10 °C/min. The differential thermal analysis data were achieved with the aid of a Du Pont 9900 computerized thermal analyzer. Spectra were obtained with an Air product LTD-3-110 Heli-Tran Liquid helium transfer refrigerator. The field was calibrated with a powder sample of DPPH ($g = 2.0037$). The infrared spectra in the range of 200–4000 cm^{-1} were recorded using a Schimadzu 8300 FTIR spectrophotometer using the KBr pellet method. Mass spectrometry was provided by the Washington University