Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 118 (2014) 146–153

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Complex formation equilibria of binary and ternary complexes involving 3,3-bis(1-methylimidazol-2yl)propionic acid and bio-relevant ligands as 1-aminocyclopropane carboxylic acid with reference to plant hormone

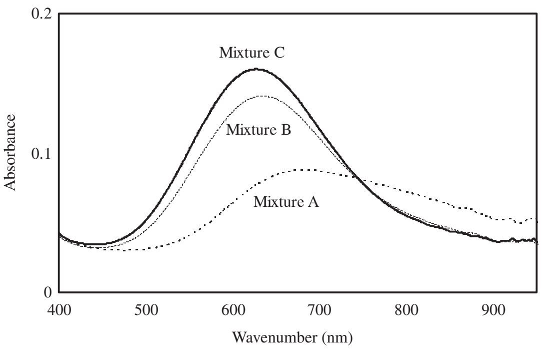
Mohamed M. Shoukry [a,b,*], Safaa S. Hassan [b]

[a] *Department of Chemistry, Faculty of Science, Islamic University, Madinah, Saudi Arabia*
[b] *Department of Chemistry, Faculty of Science, University of Cairo, Egypt*

HIGHLIGHTS

- The Cu(II) complex involving bio-relevant ligands was investigated.
- The manuscript is in the domain of SAA as it deals with spectral and potentiometric study.
- The activation of amino acid ester hydrolysis was studied.
- The results is expected to contribute to the chemistry of plant hormone.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 June 2013
Received in revised form 7 August 2013
Accepted 15 August 2013
Available online 30 August 2013

Keywords:
3,3-bis(1-methylimidazol-yl)propionic acid
1-aminocyclopropane carboxylic acid
Equilibrium studies
Plant hormone

ABSTRACT

The formation equilibria for the binary complexes of Cu(II) with 1-aminocyclopropane carboxylic acid (ACC) and 3,3-bis(1-methylimidazol-2-yl)propionic acid (BIMP) were investigated. ACC and BIMP form the complexes 110, 120 and 11−1. The ternary complexes of Cu(II) with BIMP and biorelevant ligands as some selected amino acids, peptides and DNA constituents are formed in a stepwise mechanism. The stability constants of the complexes formed were determined and their distribution diagrams were evaluated. The kinetics of hydrolysis of glycine methyl ester in presence of $[Cu(BIMP)]^+$ was investigated by pH-stat technique and the mechanism was discussed.

Introduction

The gaseous plant hormone ethylene, regulates many processes of plant development and defense such as pigmentation, fruit ripening, and senescence [1]. It is directly biosynthesized from 1-aminocyclopropane carboxylic acid (ACC) [2,3], a metabolite of methionine. The last step of ethylene biosynthesis is catalysed by ACC oxidase (ACCO). ACCO is known as the ethylene-forming enzyme. The crystallographic structure of ACCO from *Petunia hybrida* that was recently solved reveals the active site contains a metal ion linked with a side chain of two imidazole and one carboxylate groups, and a member of metal complex involving nitrogenous ligands having imidazole and carboxylate groups as enzyme active sites [4].

---

* Corresponding author at: Department of Chemistry, Faculty of Science, University of Cairo, Egypt. Tel.: +2 1001834458; fax: +20 2 35728843.

E-mail address: shoukrymm@hotmail.com (M.M. Shoukry).

http://dx.doi.org/10.1016/j.saa.2013.08.070

Parallel to the discovery of ACC to be the direct precursor of the plant hormone ethylene, it was shown that 1-aminocyclopropane carboxylic acid and numerous derivatives thereof exhibit herbicidal activity and influence plant growth, caused by intervention in the metabolism [5]. In addition, very small amounts of ACC bring about body weight gain and promotion of protein synthesis in microorganisms and animals [6].

Although, structural characteristics of ACC and 3,3-bis(1-methylimidazol-2-yl)propionic acid complexes were extensively investigated [7], no equilibrium data are available on their equilibria in solution. Work in our laboratories focused on the studies of metal complexes of biological significance [8–12]. It is of considerable interest to study the complex formation equilibria involving 1-aminocyclopropane carboxylic acid, glycine, alanine, glycylglycine and 3,3-bis(1-methylimidazol-2-yl)propionic acid. The latter ligand is considered as a model for ACCO having two imidazole and one carboxylic groups. The results of this investigation will support the biological significance of this class of complexes. In the present study, the complex formation equilibria of binary and ternary complexes of copper(II) invovingACC and a model for ACCO is investigated. The formation constants of the complexes formed in solution are determined and their concentration distribution diagrams will be evaluated. The catalysis of amino acid ester hydrolysis through complex formation with Cu-3,3-bis(1-methylimidazol-2-yl)propionate complex will be investigated.

Experimental

Materials and reagents

1-aminocyclopropane carboxylic acid, glycine and alanine were obtained from Aldrich Chem. Co. The peptides used were glycinamide, glycylglycine, asparagines and glutamine are provided by the Sigma Chem. Co. The DNA constituents investigated are inosine, uracil, uridine, thymine and thymidine and obtained from Aldrich Chem. Co. 3,3-bis(1-methylimidazol-2-yl)propionic acid (BIMP) was prepared as sodium salt as described previously [13]. BIMP and amino acids solutions were prepared in the protonated form with standard HNO_3 solution. $Cu(NO_3)_2{\cdot}4H_2O$ was provided by BDH. The copper content of solutions was determined by complexometric EDTA titrations [14]. Carbonate-free NaOH (titrant) was prepared and standardized against potassium hydrogen phthalate solution. All solutions were prepared in deionized H_2O.

Apparatus and measuring techniques

Potentiometric measurements were made using a Metrohm 686 titroprocessor equipped with a 665 Dosimat (Switzerland-Herisau). The titroprocessor and electrode were calibrated with standard buffer solutions, prepared according to NBS specification [15]. Electronic spectra were measured using a Shimadzu UV-2101 recording spectrophotometer. All titrations were carried out at 25 ± 0.1 °C, in a double-walled glass cell, through the outer jacket of which water was circulated from a constant temperature bath.

Equilibruim studies

The acid-dissociation constants of the ligands were determined potentiometrically by titrating the ligand (40 cm^3) solution (2.5×10^{-3} Mol L^{-1}) of constant ionic strength 0.1 Mol L^{-1}, (adjusted with $NaNO_3$). The stability constants of the binary complexes were determined by titrating 40 cm^3 of a solution mixture of Cu^{II} (1.25×10^{-3} Mol L^{-1}), the ligand (2.5×10^{-3} Mol L^{-1}) and $NaNO_3$ (0.1 Mol L^{-1}). The condition for measuring stability constants of the ternary complexes were the same as those adopted for the binary ones, however the solutions contained equivalent amounts of Cu^{II}, 3,3-bis(1-methylimidazol-2-yl)propionate (BIMP) and amino acid, peptide or DNA constituent (1.25×10^{-3} Mol L^{-1}). All titrations were performed in a purified N_2 atmosphere, using aqueous 0.05 Mol L^{-1}NaOH (in 0.1 Mol L^{-1} $NaNO_3$).

The general three component equilibrium can be written as follows (charges are omitted for simplicity):

$$pM + qL + rH \rightleftharpoons (M)_p(L)_q(H)_r \qquad (1)$$

for which the formation constants are given by

$$\beta_{pqr} = \frac{[(M)_p(L)_q(H)_r]}{[M]^p[L]^q[H]^r} \qquad (2)$$

Calculations were performed using the computer program [16]MINIQUAD-75. The model selected was that which gave the best statistical fit and which was chemically consistent with the titration data without any system bias in residuals [16]. The results obtained are listed in Tables 1–3. The concentration distribution diagrams were obtained using the program SPECIES (L. Pettit, Personal communication) under the experimental conditions described.

Kinetic measurements

The kinetics of the hydrolysis of the complexed ester were monitored by the pH-stat technique [17], by using the titroprocessor operated in the SET mode. The hydrolysis was investigated using an aqueous solution (40 cm^3) containing a mixture of Cu(II) (0.25 mmol), 3,3-bis(1-methylimidazol-2-yl)propionate (0.25 mmol) and amino acid ester (0.05 mmol) and the ionic strength was adjusted to 0.1 Mol L^{-1} with $NaNO_3$. The [Cu^{2+}]:[BIMP]:[ester] ratio in the mixture was adjusted to 5:5:1, so as to maximize the amount of complexed ester present. The pH of the mixture was progressively raised to the desired value. The reaction was monitored by the addition of NaOH solution to maintain the given pH. The data fitting was performed with the OLIS KINFIT set of programs [18] as described previously [18].

Spectrophotometric measurements

Spectrophotometric measurements of the binary and ternary complexes were performed by scanning the UV–visible spectra of solution mixtures (*A*–*C*), where (*A*) = 0.02 mmol of Cu(II) + 0.02 mmol of BIMP + 0.06 mmol of NaOH; (*B*) = 0.02 mmol of Cu(II) + 0.02 mmol of BIMP + 0.02 mmol of glycylglycine + 0.08 mmol of NaOH and (*C*) 0.02 mmol of Cu(II) + 0.02 mmol of BIMP + 0.02 mmol of glycylglycine + 0.10 mmol of NaOH. Under these prevailing experimental conditions and after neutralization of the hydrogen ions released, associated with complex formation, it is supposed that the complex formation is nearly complete. In each mixture the volume was brought to 10 cm^3 by addition of deionized water and ionic strength is kept constant at 0.1 Mol L^{-1} $NaNO_3$.

Results and discussion

Complex formation equilibria of 1-aminocyclopropane carboxylic acid

The acid dissociation constants (pK_a) of 1-aminocyclopropane carboxylic acid (HL) in the protonated form were determined by direct potentiometric measurements. The pK_a values were found to be 2.28 ± 0.01 and 8.15 ± 0.01 and corresponding to the carboxylic and protonated amino group. The stability constants of the Cu(II) complex with 1-aminocyclopropane carboxylic acid were