Spectrochimica Acta Part A 79 (2011) 538–547

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Solvatochromaticity and pH dependence of the electronic absorption spectra of some purines and pyrimidines and their metal complexes

Mamdouh S. Masoud[a], Medhat A. Shaker[b], Alaa E. Ali[b,*], Gehan S. Elasal[b]

[a] *Chemistry Department, Faculty of Science, Alexandria University, Egypt*
[b] *Chemistry Department, Faculty of Science, Damanhour University, Egypt*

ARTICLE INFO

Article history:
Received 3 December 2010
Received in revised form 21 February 2011
Accepted 11 March 2011

Keywords:
Uric
6-Amino-2-thiouracil
Complexes
Solvatochromic
Dissociation constants
pH-effect

ABSTRACT

The solvatochromic responses of uric acid (Ua), 6-amino-2-thiouracil (ATU) and a series of their complexes dissolved in ten solvents of different polarity have been measured. The solvent-dependent UV/Vis spectroscopic absorption maxima, λ_{max}, are assigned to the corresponding electronic transitions and analyzed using SPSS program, regression analysis and Kamlet and Taft methods. The observed solvatochromism is discussed using various solute–solvent interaction mechanisms. The electronic absorption spectra of ATU were investigated in aqueous buffer solutions of varying pH and utilized for the determination of dissociation constants. The ranges of pH, where individual ionic species are predominant have been determined.

1. Introduction

Compounds containing pyrimidine and purine play a significant role in many metabolic processes [1], where both exist in nucleic acids, several vitamins, coenzymes and antibiotics. Attention in our laboratory has escalated regarding the potential of those compounds and their complexes owing to their applicability as potential ligands for a large number of metal ions [2–13]. Compounds containing nitrogen and sulphur as donor atoms such as thiouracil (TU) and 6-amino-2-thiouracil (ATU) have an important role to play as anti-cancer and anti-viral activities [14]. In human species, uric acid (Ua) is one of the final degradation products of purine nucleotides [15]. Accumulation of uric acid in kidneys can lead to severe disorders. More particularly, in cancer patients, cellular disorders or aggressive chemotherapy increase purine metabolism and therefore, the release of large quantities of uric acid in blood. To prevent and cure hyperuricemia, it is common to use a nonhuman proteolytic enzyme, e.g. urate oxidase as a drug to oxidize uric acid [16–18]. In order to elucidate the solvent influence on the spectral behaviour of systems in study, the solvent induced spectral shifts can be related to macroscopic parameters such as the dielectric constant (ε) and with microscopic parameters such as Kamlet and Taft's solvatochromic parameters (α, β, π^*) [19–21], which define the solvent characteristics [22] and evaluate solvent dipolarity/polarizability, solvent hydrogen-bond acidity and solvent hydrogen-bond basicity [23–26]. In this work, the objective is to investigate the solvent influence on the UV/Vis spectral changes of Ua, ATU and some of their complexes: Cr–Ua, Co–Ua, Co–$(Ua)_2$, Co_2–$(Ua)_3$, Ni–Ua, Ni–$(Ua)_2$, Cd–Ua, UO_2–$(Ua)_2$, Na_2–Ua, K–Ua and Cu–$(ATU)_2$. The structures and the abbreviations of the investigated compounds are shown in Fig. 1. The UV–Vis absorption spectra of ATU were investigated in aqueous buffer solutions of varying pH and utilized for the determination of dissociation constants. The ranges of pH, where individual ionic species are predominant have been determined.

2. Experimental

2.1. Materials and methods

2.1.1. Reagents

Uric acid (Fluka, Buchs, Switzerland), 6-amino-2-thiouracil (Sigma, St. Louis, MO) and their complexes have been synthesized by direct combination in basic medium. The solvents used in this study were of HPLC grade (Merck, Darmstadt, Germany) and have been used without further purification. The chemicals used throughout the investigation were of analytical grade quality (Merck). All solutions were prepared with de-ionized and CO_2-free water. The buffer used was of the universal type taking 0.04 M of H_3BO_3, H_3PO_4 and CH_3COOH acids and adding the required volume

---

* Corresponding author. Tel.: +20 115799866.
E-mail address: dralaae@yahoo.com (A.E. Ali).

1386-1425/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2011.03.029

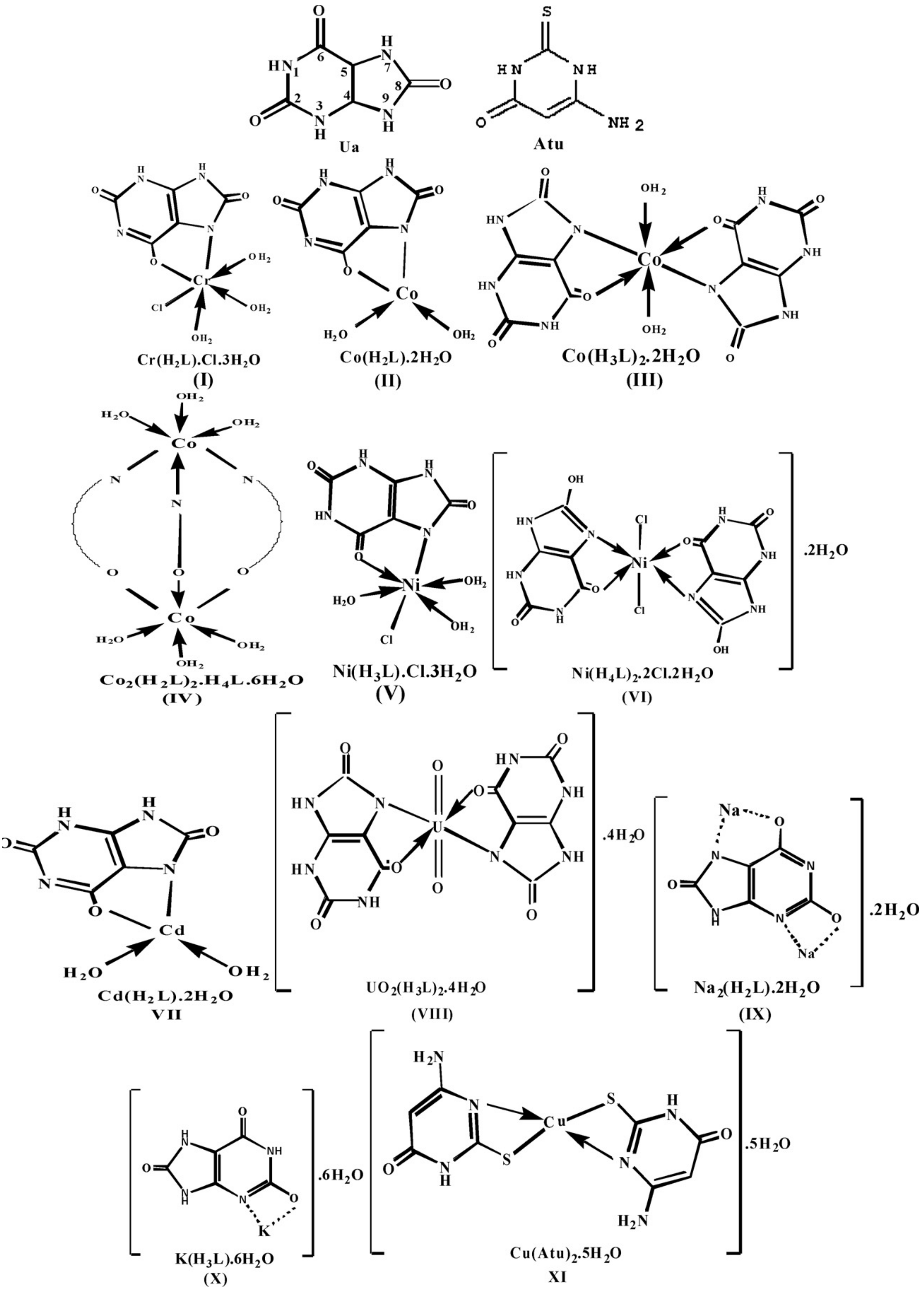

Fig. 1. The structures and the abbreviation of the investigated compounds.