



Spectroscopic and structural study of the newly synthesized heteroligand complex of copper with creatinine and urea



Debraj Gangopadhyay^a, Sachin Kumar Singh^b, Poornima Sharma^a, Hirdyesh Mishra^c, V.K. Unnikrishnan^d, Bachcha Singh^b, Ranjan K. Singh^{a,*}

^a Department of Physics, Banaras Hindu University, Varanasi 221005, India

^b Department of Chemistry, Banaras Hindu University, Varanasi 221005, India

^c Physics Department, MMV, Banaras Hindu University, Varanasi 221005, India

^d Centre for Atomic and Molecular Physics, Manipal University, Manipal 576 104, India

ARTICLE INFO

Article history:

Received 18 June 2015

Received in revised form 12 August 2015

Accepted 22 October 2015

Available online 24 October 2015

Keywords:

Creatinine

Urea

Metal complexation

Raman spectroscopy

UV–Vis spectroscopy

Fluorescence spectroscopy

ABSTRACT

Study of copper complex of creatinine and urea is very important in life science and medicine. In this paper, spectroscopic and structural study of a newly synthesized heteroligand complex of copper with creatinine and urea has been discussed. Structural studies have been carried out using DFT calculations and spectroscopic analyses were carried out by FT-IR, Raman, UV–vis absorption and fluorescence techniques. The copper complex of creatinine and the heteroligand complex were found to have much increased water solubility as compared to pure creatinine. The analysis of FT-IR and Raman spectra helps to understand the coordination properties of the two ligands and to determine the probable structure of the heteroligand complex. The LIBS spectra of the heteroligand complex reveal that the complex is free from other metal impurities. UV–visible absorption spectra and the fluorescence emission spectra of the aqueous solution of Cu–Crn–urea heteroligand complex at different solute concentrations have been analyzed and the complex is found to be rigid and stable in its monomeric form at very low concentrations.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Creatinine (Crn; C₄H₇N₃O) is a body waste which is generated by the spontaneous cyclization of its precursor creatine (Cr) during muscular activity [1]. This metabolic cyclization process; Cr → Crn is catalyzed by the enzyme creatine kinase [2] and takes place through the formation of phosphocreatine as an intermediate product. This process has been mimicked in vitro in acidic environment on several occasions [2–8] and in a study by our group [9] the in vitro cyclization mechanism has been visualized with the help of Raman spectroscopic and DFT techniques. The Crn thus produced is transported through the bloodstream to the kidneys. Most of the Crn is filtered out by the kidneys and excreted through urine [10–12]. In case of renal dysfunction or other kidney-related diseases, there is an increase in serum creatinine levels in human body. This condition is called azotemia and is usually accompanied by the increase in blood urea nitrogen (BUN) levels too [13]. Urea (CH₄N₂O) plays a very important role in renal function by contributing to the establishment of an osmotic gradient in the medulla and in forming concentrated urine in the collecting ducts. It is synthesized in the body as the primary product of the urea cycle [14] and is removed through urine as a carrier of waste nitrogen.

The study of the structural and chemical properties of Crn and urea is very important in life sciences, medicine and molecular physics [11–17]. In recent years various studies on different metallic complexes of Crn [18–29] and urea [30–36] have been done leading to interesting observations regarding their coordination properties. The crystal structure of Crn and its coordination complexes with certain metals have been reported using X-ray crystallography [17,18,26,27]. Density Functional Theory based study of the complexes of Crn and urea with certain metals has also been done recently [18,28,29]. Raman spectroscopy and surface enhanced Raman scattering have also been used for studying and correlating the amounts of creatinine and urea in human serum and urine [37–39]. In a previous work by our group [40] conformational stability of Crn at room temperature and the temperature dependent variation in hydrogen bonding character was studied using Raman spectral analysis and DFT calculations. In another work by Bayrak et al. [29], geometries of Crn and its complexes with Cu, Zn, Cd and Hg were optimized using DFT calculations and the metal–ligand binding mode was confirmed.

Both Crn and urea show a tendency to readily form complexes with d-block metals (Cu, Zn, Cd, Hg etc.). Such complexation changes the structural as well as chemical properties of Crn and urea. The knowledge of these changes might be useful in reducing the harmful effect of elevated Crn and BUN levels in blood. However in order to achieve this goal various facets of structural and functional changes in Crn and

* Corresponding author.

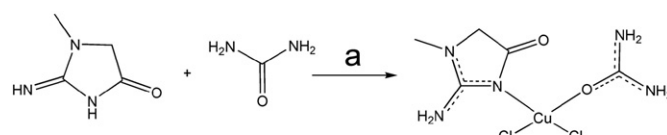
E-mail address: ranjankingsingh65@rediffmail.com (R.K. Singh).

urea upon metal complexation need to be analyzed systematically by specialized techniques. In the present work we have synthesized a new heteroligand complex $\{\text{Cu}(\text{Crn})(\text{urea})\text{Cl}_2\}$ of creatinine and urea with copper along with separate Cu–Crn and Cu–urea complexes. The Cu complex was preferred over other metals because of two reasons. Firstly, Cu is an essential trace element which is present in human body and helps in proper functioning of metabolic processes and in keeping the organs healthy. Secondly, Cu complex is found to be most readily soluble in water compared to other d-block metal complexes. The structural and functional properties for the newly synthesized complex have been studied with the help of vibrational FT-IR and Raman spectroscopic techniques. Comparison of the FT-IR and Raman spectra of pure Crn and urea with their respective Cu complexes gives clear idea about the site for metal coordination in Crn and urea. Based on these results the structure of the newly synthesized heteroligand complex has been predicted. UV–visible absorption and fluorescence studies have also been done for the newly synthesized Cu–Crn–urea heteroligand complex at different concentrations and the absorption and emission spectra have been analyzed in details. Laser Induced Breakdown Spectroscopy (LIBS) is a multi-elemental analysis technique [41,42] giving the characteristic elemental composition of a material. LIBS spectrum of the synthesized complex has been obtained to verify its purity.

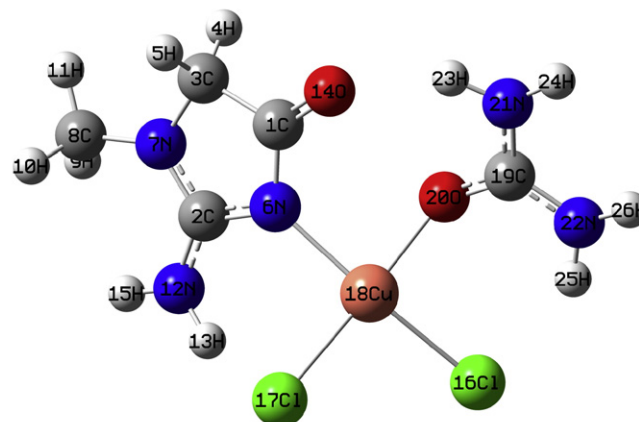
2. Experimental methods

The creatinine powder was purchased from Merck® (Darmstadt, Germany) and urea purchased from Aldrich® Chemicals, USA were directly used without further purification. The synthetic scheme based on co-ordination chemistry suggested by Muralidharan et al. and Mitewa et al. [20–22] was adopted to prepare the heteroligand complex of creatinine and urea with copper. The specific procedure to prepare the heteroligand complex is as follows: copper chloride dehydrate (0.170 g, 1 mM), creatinine (0.113 g, 1 mM) and urea (0.060 g, 1 mM) were dissolved in dry methanol (10 mL) separately. The solutions of creatinine and urea were mixed together in a round bottom flask. The solution of copper chloride was added drop wise to the ligand solution prepared as above with continuous stirring for 2 h. A microcrystalline precipitate started to appear after a few minutes. The complex thus precipitated was filtered off, washed repeatedly with water and water/methanol (1:1, v/v), and then dried under reduced pressure. The reaction scheme of above procedure is given (Fig. 1(a); Scheme 1).

Solubility of the pure Crn powder in water was measured to be $\sim 90 \text{ g L}^{-1}$ while that of the Cu–Crn and the Cu–Crn–urea heteroligand complex were measured to be $\sim 270 \text{ g L}^{-1}$ and $\sim 450 \text{ g L}^{-1}$ respectively. In order to obtain precise structural and functional characterization FT-IR and Raman spectra for all the complexes were recorded and compared with those of pure urea and Crn. The FT-IR spectrometer used was the PerkinElmer Spectrum 65. The FT-IR spectra were recorded in the range $400\text{--}4000 \text{ cm}^{-1}$. The laser Raman set-up used for the present work consists of a 514.5 nm Ar^+ laser as an excitation source delivering $\sim 5 \text{ mW}$ intensity at the sample, a microscope from Olympus consisting of $50\times$ objective for proper focusing of laser beam on the desired portion of the sample and a Raman spectrometer (Renishaw RM 1000) having grating of 2400 grooves/mm. The entrance slit was kept at $50 \mu\text{m}$. The spectral resolution was estimated by measuring the highly attenuated laser line under the same conditions as was used for the measurement of Raman spectra. The width of the laser line was $\sim 1 \text{ cm}^{-1}$, which can be taken as the spectral resolution. The Raman spectra were recorded in the range $200\text{--}3500 \text{ cm}^{-1}$. Spectrometer scanning, data collection and processing were done using Gram Wire software on a dedicated computer. The Origin 6.1 software was used for further analysis of band shape. The UV–visible absorption spectra were measured using a PerkinElmer® Lambda 35™ Spectrophotometer in the wavelength range $200\text{--}500 \text{ nm}$ and the fluorescence emission spectra were



(a) Scheme 1: a. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1 equiv.), methanol (dry), stirring, 2h



(b) Cu–Crn–urea heteroligand complex

Fig. 1. (a) Schematic chemical equation depicting the synthesis of Cu–Crn–urea heteroligand complex from Crn and urea. (b) DFT/B3LYP/(6-311++g(d,p), LANL2DZ) optimized structure of the synthesized heteroligand complex $\{\text{Cu}(\text{Crn})(\text{urea})\text{Cl}_2\}$.

measured using the Edinburgh Instruments® FLS900™ fluorescence spectrometer which employs a 450 W Xenon lamp as a probe for steady state experiments. The details of the LIBS set-up are explained elsewhere [43].

3. Theoretical details

The geometries of the complexes of Crn with Cu, Zn, Cd and Hg were optimized earlier by Bayrak et al. [29]. In the present work, the geometry of the Cu–Crn–urea heteroligand complex has been optimized and its theoretical Raman and IR spectra have been calculated using Gaussian 03 [44] and the results have been viewed by GaussView 4.1 [45]. DFT calculations were done using the B3LYP functional [46,47] with two different basis sets; 6-311++G(d,p) for the ligand and LANL2DZ split-valence basis set for the metal core. The LANL2DZ basis set [48] serves the purpose of including the pseudopotential of the core electrons in atoms of heavy elements (the metal atoms). Furthermore, this basis set is also compatible with other organic elements viz. C, N, H, and O, which are present in the complexes. The optimized structure of $\{\text{Cu}(\text{Crn})(\text{urea})\text{Cl}_2\}$ is shown in Fig. 1(b). In order to achieve better correlation between the experimental and theoretical wavenumbers, two different scaling factors were employed [29,49]; 0.98 for wavenumbers less than 1800 cm^{-1} and 0.96 for wavenumbers greater than 1800 cm^{-1} .

4. Result and discussion

4.1. Comparison of FT-IR and Raman spectra of pure urea, urea–Cu complex, pure Crn, Crn–Cu complex, and Cu–Crn–urea heteroligand complex

The experimental IR spectra of pure urea and the Cu–urea complex are shown in Fig. 2. The vibrational bands have been assigned by comparing the results with earlier works [29,32]. The important vibrational bands for pure urea, Cu–urea complex, pure Crn, Cu–Crn complex and Cu–Crn–urea heteroligand complex are listed in Table 1. The N–H stretching modes of NH_2 group are assigned to 3450 and 3347 cm^{-1} for pure urea as well as for the Cu–urea complex. The C=O stretching

Download English Version:

<https://daneshyari.com/en/article/1231794>

Download Persian Version:

<https://daneshyari.com/article/1231794>

[Daneshyari.com](https://daneshyari.com)