



Spectra-structure correlation based study of complex molecules of 1-isonicotinoyl-3-thiosemicarbazide with Ni²⁺, Mn²⁺ and Fe³⁺ using Raman, UV–visible and DFT techniques



Priyanka Gautam^a, Om Prakash^a, R.K. Dani^b, M.K. Bharty^b, N.K. Singh^b,
Ranjank K. Singh^{a,*}

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

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

ARTICLE INFO

Article history:

Received 28 November 2015

Received in revised form

21 July 2016

Accepted 22 July 2016

Available online 25 July 2016

Keywords:

Thiosemicarbazide (TSC)

Coordination property

UV–Visible

Raman

DFT

ABSTRACT

In present work, we have analysed the structural property of newly synthesized ligand and its coordination complex molecules with Ni²⁺, Mn²⁺ and Fe³⁺. The spectroscopic techniques UV–visible, IR, Raman and DFT methods are used. The newly synthesized ligand 1-isonicotinoyl-3-thiosemicarbazide (Hintsc) has supramolecular architecture stabilized through various intermolecular interactions viz. N–H⋯O, C–H⋯O, C–H⋯N, N–H⋯S and C–H⋯S type hydrogen bonds as observed in the single crystal of the ligand. The single crystals of the complexes could not be obtained with high degree of homogeneity from the solutions therefore plausible geometry of the complexes have been proposed on the basis of Raman spectroscopy, UV–visible and DFT methods and coordination properties of Ni²⁺, Mn²⁺ and Fe³⁺ with ligand (Hintsc). The ligand Hintsc contains the thiosemicarbazide (TSC) moiety through which Ni²⁺, Mn²⁺ and Fe³⁺ metals are coordinated. Raman spectroscopy is used to investigate the binding of Ni²⁺, Mn²⁺ and Fe³⁺ with ligand (Hintsc). In Raman spectra, the disappearance of N–H bending/ N–H stretching and lower wavenumber region Raman spectra clearly confirms that Ni²⁺ and Mn²⁺ metals are coordinated through –N3 and –O sites of thiosemicarbazide (TSC) and consequently formed the chelate ring {C6–N2–N3–M–O}, where M= Ni²⁺ and Mn²⁺. In Fe complex, Fe³⁺ is coordinated through –N2 and –S sites of TSC and formed the chelate ring {C7–N3–N2–Fe–S}. The structural and molecular property of 1-isonicotinoyl-3-thiosemicarbazide (Hintsc) and its complexes with transition metals Ni²⁺, Mn²⁺, Fe³⁺ have also been studied by DFT technique. By means of UV–visible, Raman spectroscopy and DFT technique, it is found that Ni²⁺, Mn²⁺ and Fe³⁺ exhibit the octahedral coordination property with 1-isonicotinoyl-3-thiosemicarbazide (Hintsc).

© 2016 Published by Elsevier B.V.

1. Introduction

The thiosemicarbazide derivatives are biologically active and pharmaceutically important compounds. They are mostly used as therapeutic antibacterial, antiviral, antimalarial, antifungal etc. drugs [1–10]. The thiosemicarbazide (TSC) group can coordinate easily with wide range of transition metals through the nitrogen, sulphur or oxygen. The coordination behaviour with transition metals influences the biological and chemical property. The structural/ geometrical parameters of the coordination complexes are

important to decide biological and chemical properties of the complexes. The single crystal X-ray diffraction is the most established and commonly used experimental technique to obtain the 3–dimensional (3D) structural information of coordination complex molecules. The single crystal XRD requires a high degree of homogeneity and for some compounds single crystal of required homogeneity is not isolated. In such cases XRD cannot be used to know the structure. The structure and geometry of the molecules can be probed by other spectroscopic techniques as Raman, infrared, UV–visible, NMR, magnetic measurements, mass spectroscopy and many diffraction methods (e.g. X-rays, electron and neutron diffractions etc.) and DFT based quantum chemical calculations [11–13]. Among many spectroscopic techniques, vibrational spectroscopy is the most commonly used techniques that reveal the

* Corresponding author.

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

fingerprint of the molecule. Raman and Infrared spectroscopy provide the information about molecular symmetry and functional groups in the molecules. The vibrational bands in IR and Raman spectra give the clear idea about the coordination of transition metals with ligand. Few interesting studies of analysing the binding sites of coordination compounds especially with transition metals have also been done with spectroscopic techniques *viz.* elemental analyses, UV–visible, Infrared, Raman spectroscopy and DFT method [14–19].

The aim of present study is to determine the structure/geometry of some coordination complex molecules. In this work, we have synthesized a novel ligand 1-isonicotinoyl-3-thiosemicarbazide (Hintsc) which contains the thiosemicarbazide (TSC) moiety. Further, the metal complexes of Hintsc have been synthesized with Ni^{2+} , Mn^{2+} and Fe^{3+} but the single crystal of the complex molecules could not be obtained. Therefore, the structure and geometry of these complex molecules has been probed by means of spectroscopic (UV–visible, IR and Raman) and DFT techniques. The molecular level properties *viz.* charge distribution, HOMO-LUMO and reactive sites for electrophilic attack and nucleophilic reaction of the ligand and complex molecules have also been investigated by DFT based quantum chemical calculations.

2. Experimental details

Isonicotinoyl chloride and thiosemicarbazide were purchased from Sigma Aldrich and the metal salts were obtained from BDH chemicals. All the synthetic manipulations were carried out in open atmosphere and at room temperature. The solvents were distilled before use following the standard procedure. Commercial reagents were used without further purification.

2.1. Synthesis of 1-isonicotinoyl-3-thiosemicarbazide (Hintsc)

The 1-isonicotinoyl-3-thiosemicarbazide (Hintsc) was prepared by refluxing equimolar mixture of isonicotinoyl chloride and thiosemicarbazide in ethanol for 5 h at 65 °C and allowed to cool to room temperature. The solid product obtained was filtered off, washed with water, dried and recrystallized from a mixture of $\text{MeOH}-\text{CHCl}_3$ (50:50 v/v).

2.1.1. Synthesis of Ni (II), Mn(II) and Fe(III) complexes of Hintsc

A methanol-acetonitrile solution (20 mL, 50:50 v/v) of ligand 1-isonicotinoyl-3-thiosemicarbazide (2 mmol) was added slowly to the water (10 mL) solution of metal salts $\{\text{M} = \text{Ni}^{2+}, \text{Mn}^{2+}$ and $\text{Fe}^{3+}\}$ (1.0 mmol), stirred for 2 h, and then refluxed for 1 h at 60 °C. The coloured solution thus obtained was filtered off and kept for crystallization which yielded solid compounds after a few days. The synthesis scheme of the ligand and its complexes with Ni^{2+} , Mn^{2+} and Fe^{3+} has been given in Scheme S1 (Supporting Information). The empirical formula of the complexes are deduced as follow: $\text{Ni}(\text{intsc})_2(\text{H}_2\text{O})_2$, $\text{Mn}(\text{intsc})_2(\text{H}_2\text{O})_2$ and $\text{Fe}(\text{intsc})_2(\text{H}_2\text{O})_2\text{Cl}$. Here, it is noted that intsc is deprotonated form of Hintsc.

2.2. Single crystal XRD, UV–visible and Raman measurements

Carbon, hydrogen, nitrogen and sulphur contents were estimated on a CHN Model CE-440 Analyzer and on an ElementarVario EL III Carlo Erba 1108. The analytical data, color, melting point and percentage yield of ligand and the metal complexes are shown in Table 1. The X-ray data collection for 1-isonicotinoyl-3-thiosemicarbazide (Hintsc) was performed on an Oxford Diffraction Gemini diffractometer equipped with CrysAlis CCD using a graphite mono-chromated $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation source at 273 K. The structure was solved by direct method (SHELXL-2013)

and refined against all data by full matrix least-squares on F^2 using anisotropic displacement parameters for all non-hydrogen atoms. All the hydrogen atoms were included in the refinement at geometrically ideal positions and refined with a riding model [20]. The MERCURY package and ORTEP-3 programs were used for generating molecular structures [21,22]. The UV–Visible spectra were recorded on a SIMADZU 1700 UV–visible spectrophotometer at room temperature. The magnetic susceptibility/moment measurement was performed at room temperature on a Cahn Faraday balance using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as the calibrate. The laser Raman spectra were recorded on a Raman spectrometer from Renishaw Model: RM 1000 having grating of 2400 grooves/mm giving spectral resolution of 1 cm^{-1} at 50 micron slit opening. The 514.5 nm Ar^+ -laser was used as an excitation source delivering 5 mW intensity at the sample.

3. Computational details

The DFT calculations of 1-isonicotinoyl-3-thiosemicarbazide (Hintsc) and its metal complexes have been carried out with Gaussian 03 and Gauss View 4.1 program packages [23]. The optimized geometry and vibrational frequency of Hintsc and its Ni^{2+} , Mn^{2+} and Fe^{3+} complexes have been calculated using DFT/B3LYP/LanL2DZ method [24,25]. The basis set LanL2DZ serves the purpose of including the pseudo potential of the core electrons in the metal atoms and is also compatible with other elements *viz.* C, H, N, S and O. The vibrational assignments of Raman bands of Hintsc and their potential energy distributions were done by using GAR2PED software [26]. The electrostatic potential mapping surface (MEPS) and frontier molecular orbital (FMO) were also estimated by same DFT method at the 0.02 isovalues and 0.0004 isodensity value to illustrate continuous charge distributions and reactive sites of the molecules.

4. Results and discussion

4.1. Crystal structure description of ligand Hintsc

Fig. 1 (a) shows the ORTEP diagram of the Hintsc together with numbering of atoms and the crystallographic data of ligand is given in Table 2. The structural refinement details derived by crystallographic XRD and DFT calculated bond length and bond angle of Hintsc are given in Table S1 (Supporting Information). Crystal packing in unit cell shows that sulphur and oxygen atoms of each molecule in every row are arranged in such a way those they face opposite to each other [Fig. 1(b)]. The C=O bond having bond length 1.239 Å is purely a double bond which takes part in the formation of supramolecular architecture through hydrogen bonding and bond length of C=S (partial double bond) bond is 1.689 Å. The structure of the compound is stabilized via $\text{N}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ intermolecular hydrogen bonds formed between the carbonyl oxygen and N–H hydrogen of TSC and C–H of phenyl ring as shown in Fig. 2(a). Further, the compound is stabilized by $\text{C}-\text{H}\cdots\text{N}$, $\text{N}-\text{H}\cdots\text{S}$ and $\text{C}-\text{H}\cdots\text{S}$ interactions occurring between the thione sulphur and N–H hydrogen of TSC unit of other molecule in the formation of supramolecular architecture [Fig. 2(b)]. It is noticeable that the same number scheme of atoms represented in ORTEP diagram of the Hintsc is used to define the coordination bonds in the complexes in forthcoming section.

4.2. UV–visible and magnetic moment

UV–visible were recorded to approximate the geometries of the metal complexes. The absorption bands and their assignments are given in Table 3. The UV–Visible spectra of Ni^{2+} , Mn^{2+} and Fe^{3+}

Download English Version:

<https://daneshyari.com/en/article/1407558>

Download Persian Version:

<https://daneshyari.com/article/1407558>

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