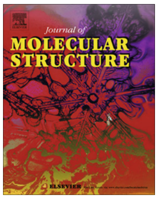
Journal of Molecular Structure 1074 (2014) 271–278

Contents lists available at ScienceDirect

Journal of Molecular Structure

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



Syntheses, crystal structures and spectroscopic characterization of two new octahedral nickel(II) complexes of a Schiff base ligand derived from pyridoxal and 2-(pyrid-2-yl)ethylamine

Senjuti Mandal, Ritwik Modak, Yeasin Sikdar, Barnali Naskar, Sanchita Goswami *

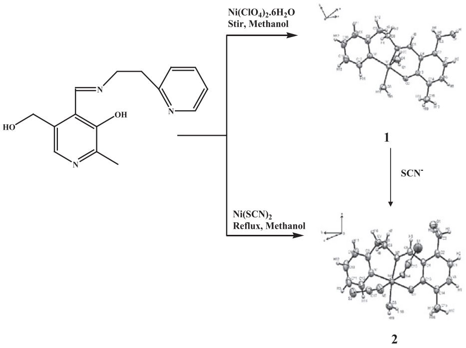
Department of Chemistry, University of Calcutta, 92, A.P.C. Road, Kolkata 700009, India

HIGHLIGHTS

- Two new octahedral nickel(II) complexes have been synthesized.
- The Schiff base is derived from pyridoxal hydrochloride and 2-(pyrid-2-yl)ethylamine.
- Complex **1** is a one dimensional coordination polymer.
- Complex **2** gives rise to a three dimensional zig-zag layer like architecture.

GRAPHICAL ABSTRACT

Two new octahedral nickel(II) complexes, $\{[Ni(HL)(H_2O)_2](ClO_4)_2\}_\infty$ **(1)** and $[Ni(HL)(H_2O)(SCN)_2]$ **(2)** are synthesized from pyridoxal based Schiff base ligand and structurally characterized.



ARTICLE INFO

Article history:
Received 10 April 2014
Received in revised form 4 June 2014
Accepted 4 June 2014
Available online 14 June 2014

Keywords:
Pyridoxal based Schiff base
Distorted octahedral Ni(II)
Crystal structures

ABSTRACT

Two new coordination compounds based on ONN donor Schiff base ligand derived from pyridoxal and 2-(pyrid-2-yl)ethylamine, namely $\{[Ni(HL)(H_2O)_2](ClO_4)_2\}_\infty$ (**1**) and $[Ni(HL)(H_2O)(SCN)_2]$ (**2**) have been synthesized and structurally characterized by single-crystal X-ray diffraction along with other physical techniques, including elemental analysis, IR spectra and UV–Vis studies. X-ray studies suggest that both **1** and **2** are mononuclear nickel(II) complexes and exhibit distorted octahedral geometry. In these compounds the pyridoxal based Schiff base ligand displays different coordination modes constructing various architectures.

Introduction

The biologically active form of vitamin B_6, pyridoxal 5- phosphate (PLP), is a versatile enzyme cofactor responsible for amino acid metabolism in all organisms from bacteria to human [1–3]. From a mechanistic standpoint, a pyridoxal-5-phosphate mediated transamination most likely begins with the formation of a Schiff base at the N-terminus [1,4]. Hence, the study of metal complexes derived from pyridoxal Schiff bases will be important for a complete understanding of the mechanism of action of pyridoxal in vivo, and also for developing novel bioactive compounds. Therefore, it can be said that the study of metal complexes derived from pyridoxal containing Schiff bases are bio-inspired since any ligand, containing pyridoxal moiety always lends a biological significance to the resulting system. In order to unveil the mode of

---

* Corresponding author. Tel.: +91 9433125290.
E-mail address: sgchem@caluniv.ac.in (S. Goswami).

http://dx.doi.org/10.1016/j.molstruc.2014.06.016

function of transition metals in biological systems, it is essential to gain knowledge of the molecular geometries of the metal centers in the different biomolecules. Long ago, spectroscopic studies indicated that the Ni-containing active site of [FeNi] hydrogenase isolated from *Thiocupsa rosepersicina* consists of a pentacoordinated Ni(II) center with two sulfur donor atoms in the first coordination sphere while the remaining coordination sites are occupied by nitrogen donor ligands [5,6]. It is well documented that mononuclear Ni(II) complexes play an important role in modelling metalloprotein sites [7]. Bioinspired nickel coordination chemistry has flourished in recent years and the resulting synthetic models for the active sites of nickel-containing enzymes are reviewed [8]. Nickel is present in the environment originating from natural and anthropogenic sources and also important in modern industry [8]. It is shown that nickel may also be a serious enemy in human organism and a threat to oxidative stress [9]. Recently a few examples of valuable Ni(II) catalyst precursors have been reported in the literature [10–16].

We have recently been exploring the syntheses of complexes derived from 3d metal ions and pyridoxal based Schiff bases and their characteristics in detail in order to draw a correlation between the nature of the ligand and the patterns of reactivity. We have previously reported a copper(II) complex of a Schiff base ligand derived from pyridoxal hydrochloride and 2-(pyrid-2-yl)ethylamine, that exhibited selective quenching of the fluorescence [17]. Our first results have been very encouraging which stimulated further development in this field. As a continuous work in this less trodden field, we have reported the first example of nickel(II) complexes derived from pyridoxal hydrochloride and N,N-dimethylethylenediamine and N,N-dimethylethylenediamine [18]. As an extension of our work, herein we report syntheses, crystal structures, electronic and luminescence spectra and cyclic voltammogram of two hexacoordinated Ni(II) complexes, $\{[Ni(HL)(H_2O)_2](ClO_4)_2\}_\infty$ (**1**) and $[Ni(HL)(H_2O)(SCN)_2]$ (**2**) of the pyridoxal containing Schiff base ligand derived from pyridoxal hydrochloride and 2-(pyrid-2-yl)ethylamine.

Experimental

Materials and physical methods

Pyridoxal hydrochloride and 2-(pyrid-2-yl)ethylamine were purchased from Sigma–Aldrich and used as received. All other materials were of reagent grade quality. The Schiff base ligand was synthesized by a known procedure as reported by Mauryaa et al. [19]. Elemental (C, H and N) analyses were performed on a Perkin–Elmer 2400 II analyzer. IR spectra were recorded in the region 400–4000 cm^{-1} on a Bruker-Optics Alpha– T spectrophotometer with samples as KBr disks. Electronic spectra were obtained by using a Hitachi U-3501 spectrophotometer. Luminescence property was measured using LS-55 Perkin Elmer fluorescence spectrophotometer at room temperature (298 K) by 1 cm path length quartz cell. Cyclic voltammetric (CV) measurements were done using a BASi Epsilon-EC electrochemical analyzer. The concentration of the supporting electrolyte, tetrabutylammonium perchlorate (TBAP) was 0.1 M, while that of the complex was 1 mM. Cyclic voltammetric measurement is carried out in DMF solution at 295 K with a glassy carbon disk working electrode and the scan rate was 100 mVs^{-1}.

Caution: Salts of perchlorate as well as their metal complexes are potentially explosive and should be handled with great care and in small quantities.

Preparation of ligand (HL)

Pyridoxal hydrochloride (0.203 g, 1 mmol) was dissolved in absolute methanol (10 mL) in the presence of KOH (0.056 g, 1 mmol) with stirring. After 1 h of stirring, the separated white solid (KCl) was filtered and the obtained clear solution was added to a solution of 2-(2-aminoethyl)pyridine (0.122 g, 1 mmol) in methanol (10 mL) with stirring and the resulting reaction mixture was refluxed for 2 h. The ligand was obtained as a clear yellow solution and its purity was checked by performing thin layer chromatography. The ligand was not isolated and used directly for the preparation of complexes **1** and **2**.

Synthesis of $\{[Ni(HL)(H_2O)_2](ClO_4)_2\}_\infty$ (1)

To the methanolic solution of $Ni(ClO_4)_2{\cdot}6H_2O$ (0.365 g, 1 mmol), methanolic solution of HL (1 mmol) was added dropwise and resulting green solution was stirred for 6 h. Then it was filtered to remove any suspended particle and allowed to stand for slow evaporation. After a few weeks dark green block shaped single crystals suitable for X-ray diffraction were obtained from the filtrate. Yield: 67%. Anal. Calcd for $C_{15}H_{21}N_3O_{12}Cl_2Ni$(%): C, 31.89 ; H, 3.74; N, 7.43. Found: C, 31.23; H, 3.82; N, 7.27.

Synthesis of $[Ni(HL)(H_2O)(SCN)_2]$ (2)

To the methanolic solution of HL (1 mmol), methanolic solution of $Ni(SCN)_2$ (0.175 g, 1 mmol) was added slowly and resulting light green solution was refluxed for 6 h. Then it was filtered and the filtrate was allowed to stand for slow evaporation. X-ray diffraction quality rhombus shaped single crystals were grown from DMF:methanol = 1:2 solvent mixture. Yield: 74%. Calcd for $C_{17}H_{20}N_5O_3S_2Ni$(%): C, 43.85; H, 4.33; N, 15.05. Found: C, 43.37; H, 4.19; N, 14.87.

X-ray crystal structure analysis

The crystallographic data of the compounds (CCDC No. 931533 and 961742 for **1** and **2** respectively) is summarized in Table 1. Diffraction data were collected on a Nonius APEX-II diffractometer with CCD-area detector at 296 K using graphite-monochromated Mo Ka radiation (k = 0.71073 Å). Crystal structures were determined by direct methods and subsequent Fourier and difference Fourier syntheses, followed by full-matrix least-squares refinements on F^2 using SHELXL-97 [20]. Absorption correction was done by SADABS method. The second perchlorate anion in **1** was disordered and restraints were applied to the geometrical and displacement parameters of the disordered perchlorate anion to refine this. Hydrogen atoms were located and refined freely. The hydrogen atoms were refined isotropically, while the non hydrogen atoms were refined anisotropically.

Results and discussion

Synthesis and IR spectra of the complex

The interaction of $Ni(ClO_4)_2{\cdot}6H_2O$ and $Ni(SCN)_2$ with HL produced crystals of compounds **1** and **2** respectively (Scheme 1). The isolated complexes were characterized by single crystal X-ray crystallography, FTIR and UV–Vis spectroscopy. Both the complexes are air stable.

In complex **1** (Fig. S1), a very broad absorption band was centered at 3376 cm^{-1}. This broad band can be safely assigned to the stretching frequency, ν(O—H) of the —CH_2OH group of the pyridoxal part of the ligand. ν(C═N) absorption appears at 1630 cm^{-1} due to stretching vibration of azomethine (C═N) group of the complex **1**. Absorption band at 1610 cm^{-1} may be due to —OH vibration of the coordinated water molecule to the metal center.