Inorganica Chimica Acta 363 (2010) 2720–2727

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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

Azo-containing pyridine amide ligand. A six-coordinate nickel(II) complex and its one-electron oxidized species: Structure and properties

Anuj Kumar Sharma, Saikat Biswas, Suman Kumar Barman, Rabindranath Mukherjee *

Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur 208 016, India

ARTICLE INFO

Article history:
Received 17 February 2010
Received in revised form 18 March 2010
Accepted 23 March 2010
Available online 27 March 2010

Dedicated to Professor Animesh Chakravorty on the occasion of his 75th birthday

Keywords:
Azo group containing pyridine amide ligand
Ni(II) complex
Crystal structure
Redox properties
Electrochemically-generated nickel(III)
EPR spectra

ABSTRACT

A new potentially tridentate ligand HL^{11} consisting of 2-pyridinecarboxamide unit and azo functionality has been used, in its deprotonated form, to prepare a nickel(II) complex which has been structurally characterized. The ligand $L^{11}(-)$ affords a bis-complex $[Ni^{II}(L^{11})_2]$ (**1**). In **1**, the two $L^{11}(-)$ ligands bind to the Ni^{II} center in a *mer* configuration. The relative orientations within the pairs of pyridyl-N, deprotonated amido-N, and azo-N atoms are *cis*, *trans*, and *cis*, respectively. The $Ni^{II}N_2(pyridyl)N'_2(amide)N''_2(azo)$ coordination environment is severely distorted from ideal octahedral geometry. The $Ni–N_{am}$ (am = amide) bond lengths are the shortest and the $Ni–N_{azo}$ bond lengths are the longest. Complex **1** exhibits a quasi-reversible Ni^{III}/Ni^{II} redox process. Moreover, the complex displays two ligand-centered (azo group) quasi-reversible redox processes. Spectroscopic (absorption and EPR) properties have been studied on coulometrically-generated nickel(III) species. To understand the nature of metal-ligand bonding interactions Density Functional Theory (DFT) calculations have been performed on **1** at the B3LYP level of theory. Calculations have also been done for closely related nickel(II) complexes of deprotonated pyridine amide ligands and comparative discussion has been made using observed results.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Amide bonds are ubiquitous in biochemistry, because they provide the linkages that held together two of the most important types of biopolymers, nucleic acids and proteins. The interest in the study of amide complexes [1] derives from their ability to model active sites present in some metallo-proteins [2], to act as effective catalysts for important organic transformations [1,3], and the search for a better understanding of the physicochemical properties of such complexes, especially to modulate the structural, stereochemical, and electronic properties of transition metal centers [1,4–10]. From this perspective, the ligand systems based upon 2-pyridinecarboxamide [1,4–7] and 2,6-pyridinecarboxamide [1,8–10] are noteworthy. Using electronically/sterically demanding pyridine/pyrazine amide ligands HL^1–H_2L^{10} (Fig. 1), in their deprotonated form, we have developed interesting coordination chemistry of a variety of transition metal ions to demonstrate noteworthy molecular structural, electronic structural, and redox properties [4,8].

In pursuit of designing new pyridine amide ligands that will incorporate azo functionality (well known group as π-acceptors [11,12] to stabilize low oxidation state of metal ions) in this work we have directed our attention to a new ligand HL^{11}. In order to evaluate the ability of this new potentially tridentate 2-pyridinecarboxamide ligand, appended with azo functionality, to modulate the structural and electronic properties of transition metal ions, we have chosen nickel(II) as a test case. To reveal the stereochemical changes around the nickel(II) center caused by ligand-structure modification of deprotonated pyridine/pyrazine amide ligands upon changing from $L^4(2-)$ [8c]/$L^5(2-)$ [6o]/$L^9(2-)$ [6n]/$L^{9*}(2-)$ [4d] to $L^{11}(-)$ (Fig. 1), we have determined the crystal structure of the new complex $[Ni^{II}(L^{11})_2]$ (**1**), revealing $Ni^{II}(N_{pyridine})_2(N_{amide})_2(N_{azo})_2$ coordination environment. Room-temperature magnetic and spectroscopic properties of **1** have also been investigated. Given the strong σ-donating properties of amide ligands [1,13] and encouraged by our previous experience [4c,8c] of generating/isolating nickel(III) and nickel(IV) complexes [14] we wished to investigate whether or not for the present complex such a possibility exists. Cyclic voltammetric experiments reveal that stabilization of nickel(III) state could be achieved with new deprotonated ligand $L^{11}(-)$. We report the characterization of coulometrically-generated one-electron oxidized form of **1** and confirm that the oxidation process is metal-centered (EPR spectra). Moreover, as it has been demonstrated that pyridine amide ligands

---

* Corresponding author. Tel.: +91 512 2597437; fax: +91 512 2597436.
E-mail address: rnm@iitk.ac.in (R. Mukherjee).

0020-1693/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2010.03.056

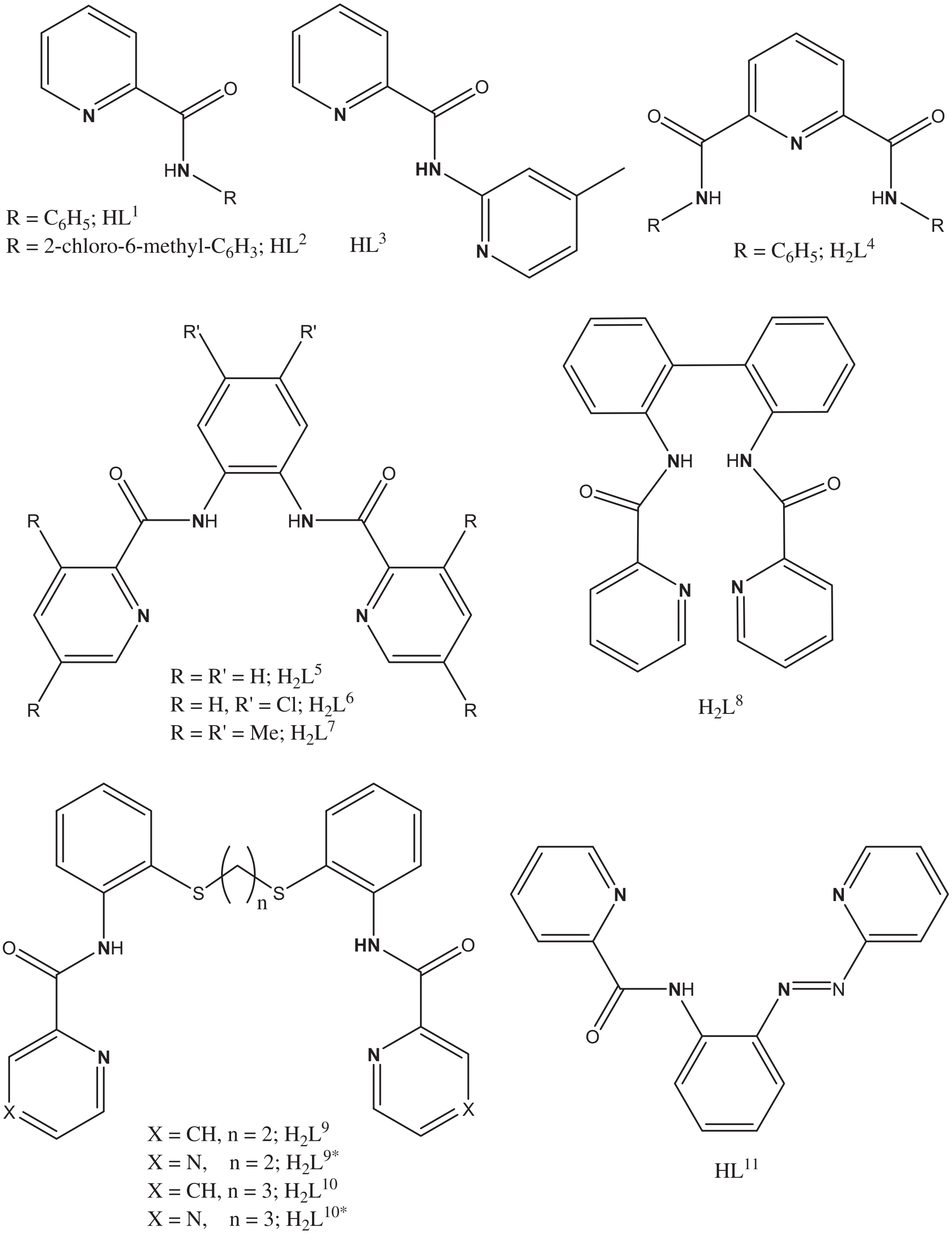

Fig. 1. The ligands of our concern.

are non-innocent [4e,6b,7,8a,15] we have investigated the nature of metal–ligand bonding interactions in **1** and two reported six-coordinate nickel(II) complexes with $Ni^{II}(N_{pyridine})_2(N_{amide})_4$ [8c] and $Ni^{II}(N_{pyridine})_2(N_{amide})_2(S_{thioether})_2$ [4d] coordination sphere. This analysis has given us an opportunity to rationalize the trend in $E_{1/2}$ values of the Ni^{III}/Ni^{II} redox process for the chosen group of complexes.

2. Experimental

2.1. Materials

All reagents were obtained from commercial sources and used as received. Solvents were dried and purified according to reported procedures [4,8]. Tetra-*n*-butylammonium perchlorate (TBAP) was

Download English Version:

https://daneshyari.com/en/article/1306879

Download Persian Version:

https://daneshyari.com/article/1306879

Daneshyari.com