Original Article

Synthesis and Spectroscopic Characterizations of Ni(II) Thiosemicarbazone Bearing Anthracene

Dinh Thi Hien¹, Khuat Thi Thuy Ha², Vu Thi Bich Ngoc², Nguyen Tien Dat², Dinh Thi Thao³, Nguyen Minh Hai²*¹

¹ Hanoi National University of Education, 136 Xuan Thuy, Cau Giay, Hanoi, Vietnam
² VNU University of Science, 19 Le Thanh Tong, Hoan Kiem, Hanoi, Vietnam
³ Army Academy 1, Co Dong, Son Tay, Hanoi, Vietnam

Received 29 October 2020
Revised xxx 2021; Accepted xxx 2021

Abstract: The X-ray structure of 9-anthraldehyde-4-methyl-3-thiosemicarbazone was firstly determined. The Ni(II) complex with this ligand was prepared upon reaction with chloride salt. Mass spectrometry result confirms correct formulation of the complex. Unusual ¹H NMR signal pattern of anthracene moiety reveal cis arrangement cemented by intramolecular π–π stackings between aromatic rings. As a result of this interaction, the electronic structure of anthracene ring is perturbed and gives rise to structureless and broad absorption and emission bands.

Keywords: Anthracene, thiosemicarbazone, nickel, spectroscopies, π–π interactions.

1. Introduction

Having a large π system, anthracene has been found useful in many areas such as structural chemistry and fluorescent sensing [1, 2]. In close proximity with parallel arrangement, two anthracene rings are able to give excimer emission with green or greenish yellow color [3]. In order to bring forth this intriguing property, it is important to design a linker that might put the two aromatic rings in such arrangement.

Thiosemicarbazone is a well-known class of ligands that may give rise to unexpected coordination chemistry. Ni(II), a d⁸ metal, tends to form square planar geometries with trans configuration which is more favorable in energy. Nonetheless, many Ni(II) thiosemicarbazone complexes with cis geometries were reported. Indeed, weak interactions such as π–π stackings among the thiosemicarbazone ligands are needed to sustain the cis arrangements [4, 5]. Our group also reported anthracene-based and pyrene-based Ni(II) thiosemicarbazone complexes...
which showed cis geometries cemented by intramolecular \( \pi-\pi \) interactions \([6, 7] \). In this paper, a new Ni(II) complex with anthracene-based thiosemicarbazone (NiL) is presented. Spectroscopic data such as \(^1\)H-NMR, electronic absorption and emission support cis square planar structure around Ni(II) ion.

2. Experimental

2.1. Materials and Instruments

All the solvents used for synthesis and spectroscopic measurements were purified according to literature procedures. 9-Anthraldehyde and 4-methyl-3-thiosemicarbazide were used as received without further purification.

The FT-IR spectra of the compounds were measured on a FT-IR 8700 infrared spectrophotometer (4000-400 cm\(^{-1}\)) in KBr pellets. The \(^1\)H NMR spectra were recorded on an AVANCE Bruker-500MHz spectrometer in DMSO-\(d_6\) solution at room temperature. ESI-MS spectra were recorded on an Agilent LC/MSD SL spectrometer. Absorption and emission spectra of the complexes were measured in dichloromethane at room temperature on Jasco UV-Vis spectrometer and Hitachi fluorescence spectrophotometer.

The intensities for the X-ray determinations were collected on a Bruker D8 Quest instrument with Mo K\(\alpha\) radiation (\(\lambda = 0.71073\) Å). Standard procedures were applied for data reduction and absorption correction. Structure solution and refinement were performed with OLEX2 and SHELXT programs \([8, 9] \). Hydrogen atom positions were calculated for idealized positions.

The synthesis of HL has been reported elsewhere \([10] \).

2.2. Synthesis of HL

To a 10 mL ethanolic solution of 9-anthraldehyde (0.206 g, 1.0 mmol) was added 10 mL acidified aqueous solution of 4-methyl-3-thiosemicarbazide (0.105 g, 1.0 mmol). The resulting mixture was stirred for 4 h at 60°C to afford a pale yellow solid. The product was washed by a large amount of water and then air-dried. Yield: 0.228 g, 78%.

Spectroscopic Data for HL. IR: \( \nu_{\text{max}}/\text{cm}^{-1} = 3399 (\text{m}), 3216 (\text{m}), 3062 (\text{w}), 2926 (\text{w}), 1523 (\text{s}), 1436 (\text{m}), 1204 (\text{s}), 1077 (\text{w}), 890 (\text{w}), 736 (\text{m}), 607 (\text{w}) \). \(^1\)H NMR (DMSO-\(d_6\)): 11.67 (s, 1H, N\(\text{(2)}\)H), 9.27 (s, 1H, CH=N), 8.70 (s, 1H, H\(\text{10}\)), 8.32 (q, 1H, N\(\text{(4)}\)H), 8.14 (d, 2H, H\(\text{4,5}\)), 7.65–7.56 (m, 4H, H\(\text{2,3,6,7}\)), 3.01 (d, 3H, CH\(\text{3}\)).

Crystal Data for HL: orthorhombic, space group Pna2\(_1\) (no. 33), \(a = 16.7442(14)\) Å, \(b = 15.8556(10)\) Å, \(c = 5.2324(4)\) Å, \(V = 1389.15(18)\) Å\(^3\), \(Z = 4\), \(T = 0.0\) K, \(\mu(\text{MoK}\alpha) = 0.229\) mm\(^{-1}\), \(D_{\text{calc}} = 1.403\) g/cm\(^3\), 3923 reflections measured (7.078° ≤ 2\(\Theta\) ≤ 56.448°), 2203 unique \((R_{\text{int}} = 0.0417, R_{\text{sigma}} = 0.0580)\) which were used in all calculations. The final \(R_1\) was 0.0388 (I > 2\(\sigma(I)\)) and \(wR_2\) was 0.0846 (all data).

2.3. Synthesis of NiL

A solution of NiCl\(_2\) (0.009 g, 0.04 mmol) in acetone (5 mL) was added dropwise to a solution of HL (0.023 g, 0.08 mmol) in acetone (15 mL) in the presence of excess triethylamine. The mixture was heated to 60°C and stirred for 5 h in darkness, then filtered, washed with methanol, and lastly dried in vacuum to give dark-red product. Yield: 0.015 g, 58%.

Spectroscopic Data for NiL. IR: \( \nu_{\text{max}}/\text{cm}^{-1} = 3309 (\text{s}), 3020 (\text{w}), 2833 (\text{w}), 1518 (\text{s}), 1405 (\text{m}), 1262 (\text{m}), 1190 (\text{m}), 887 (\text{w}), 739 (\text{m}), 616 (\text{w}) \). \(^1\)H NMR (DMSO-\(d_6\)): 8.71 (s, 2H, H\(\text{10}\)), 8.12 (m, 4H, H\(\text{4,5}\)), 7.83 (s, 2H, CH=N), 7.45 (m, 4H, H\(\text{3,6}\)), 6.78 (q, 2H, NH), 2.41 (d, 6H, CH\(\text{3}\)). ESI-MS: \(m/z\) 642.9, [M + H]\(^+\).

3. Results and Discussion

3.1. Synthesis

The ligand HL was obtained from reaction between 9-anthraldehyde and acidified 4-methyl-3-thiosemicarbazide using previously reported method \([10] \). The ligand was then
allowed to react with NiCl$_2$ in boiling acetone with the aid of an organic base (triethylamine), as shown in Scheme 1. The resulting complex NiL was separated in high yield as dark red solid. Notably, single crystals of HL could be collected from dichloromethane/methanol mixture, making its X-ray crystallography characterization feasible. Unfortunately, numerous attempts to obtain single crystals of NiL failed.

Scheme 1: Synthetic pathway of NiL.

Many physical methods such as infra-red spectroscopy, mass spectrometry (ESI-MS), and $^1$H NMR spectroscopy were adopted to characterize the complex. ESI-MS result reveals major cluster peak responsible for molecular ion [NiL + H]$^+$ at m/z = 643 (Figure 1). The little discrepancy between theoretical and experimental isotopic patterns of the cluster peak help confirm the correct formulation of NiL with one central Ni(II) ion and two thiosemicarbazone ligands. The bathochromic shift of $\nu$(C=N) from 1523 cm$^{-1}$ in HL to 1517 cm$^{-1}$ in NiL in the IR spectra indicated the complexation through imine nitrogen of HL. Moreover, the band due to $\nu$(C=S) at 890 cm$^{-1}$ in NiL is shorter than that in HL by 3 cm$^{-1}$. This is reasonable in light of the tautomerization of the ligands into thiol form in which C=S bond is converted to C–S and then C–S–Ni linkages upon complexation [11].

Figure 1: a) Simulated isotopic pattern for [NiL + H]$^+$; b) ESI-MS cluster peak for [NiL + H]$^+$.

The $^1$H NMR spectra of HL and NiL in DMSO-$d_6$ are given in Figure 2. It is reasonable to confirm square planar geometry of NiL given its sharp signals which are only possible for diamagnetic Ni(II) complexes. The N(2)H signal (11.67 ppm) in HL are not found in the spectrum of NiL, hinting the tautomerization of the ligand upon complexation with Ni(II). Moreover, N(4)-substituted methyl groups in HL and NiL give rise to doublet signal at 3.02 ppm and 2.41 ppm, respectively. A quartet at 6.78 ppm arising from N(4)H in NiL is largely upfield shifted from that in HL (8.32 ppm).

Because of steric effect, mono-substituted anthracene ring is expected to show a typical set of proton signals including one singlet (H$_{10}$), two doublets (H$_{1,8}$ and H$_{4,5}$), and two triplets (H$_{2,3,6,7}$). Unexpectedly, only three proton signals responsible for H$_{10}$ (8.71 ppm), H$_{4,5}$ (8.12 ppm), H$_{3,6}$ (7.46 ppm) in anthracene rings in NiL are observed (Figure 2b). Besides, the disappearance of proton signals arising from H$_{1,8,2,7}$ is detected. The abnormal signal pattern is understandable in view of reported X-ray structures of similar Ni(II) complexes [7]. In the reported structures, anthracene rings are in cis arrangement with intramolecular π–π stacking. Especially, H$_{1,8,2,7}$ experience a large coverage by anthracene and thiosemicarbazone fragments, leading to complete broadening of proton signals. Furthermore, due to the coverage by anthracene ring, the imine proton in NiL is markedly upfield
shifted by 1.44 ppm compared to that in HL (from 9.27 ppm to 7.83 ppm).

3.2. Characterization of HL by X-ray crystallography

Despite the synthesis of HL was previously reported, no X-ray structure of the ligand was achieved so far. Fortunately, we were able to obtain X-ray quality crystals of HL which allow determination of NiL’s molecular structure (Figure 3a). Selected bond lengths and angles of the ligand are given in Table 1. The X-ray structure of HL indicates the presence of 9-anthraldehyde and 4-methyl-3-thiosemicarbazide moieties, confirming the correct condensation reaction. C1–N1 and C2–S1 bond distances are of typical values for double bond while C2–N2 bond distance is close to that of a single bond. The bond lengths imply that HL as the free ligand exists in thione form. All bond angle values (~120°) support \( sp^2 \) hybridization states of C2, N1 and N2 atoms in thiosemicarbazone fragment. More importantly, all the atoms of C, N and S in HL are found to be arranged in the same plane. Consequently, extensive intermolecular \( \pi-\pi \) stackings are detected in the solid state of HL (Figure 3b). Nonetheless, the two anthracene rings are not overlapped. Instead, the aromatic ring is substantially covered by a thiosemicarbazone fragment of the adjacent molecule. The parallel separations between the molecules of HL in the stackings are normal (3.316 Å).

Table 1: Selected bond lengths (Å) and angles (°) of HL.

| Bond lengths   |     |
|----------------|-----|
| S1–C2          | 1.685(3) |
| C1–N1          | 1.291(5) |
| N1–N2          | 1.382(3) |
| N2–C2          | 1.345(4) |
| C2–N4          | 1.339(4) |

| Bond angles    |     |
|----------------|-----|
| C1–N1–N2       | 113.9(3) |
| N1–N2–C2       | 121.2(3) |
| N2–C2–N4       | 116.4(3) |
| N2–C2–S1       | 120.9(2) |
| N4–C2–S1       | 122.7(2) |
3.2. **UV-Vis and Photoluminescence Characterizations of NiL**

UV-Vis absorption and emission spectra of HL and NiL in CH₂Cl₂ are presented in Figure 4 and Figure 5, respectively. The structureless absorption band at ~405 nm assigned to π→π* transition in NiL is in marked contrast to vibronic absorption band in HL [12]. Also, the complex reveals a severely broad emission band with maximum at ~415 nm upon excitation at 330 nm. Meanwhile, a well-resolved and characteristic anthracene-based emission band is observed in the spectrum of HL. This might result from the perturbation by π–π interaction between the two anthracene rings in NiL, as suggested by similar examples [13, 14].

Notably, the Stoke shift in NiL (~10 nm) is not large enough to be considered as excimer emission which are in the typical range of 450–550 nm. Therefore, the broadening of emission band at ~415 nm might be due to steric effect of two closely arranged anthracenyl rings in π–π stacking. The results are consistent with the disappearance of proton signals in ¹H-NMR spectrum of NiL.

4. **Conclusion**

In summary, we have successfully determined the X-ray structure of HL and synthesized its Ni(II) complex. ¹H-NMR spectroscopy showed abnormal signal pattern which is due to intramolecular π–π stacking between anthracene rings in cis square planar Ni(II) complex. The unusual molecular structure of NiL was also supported by the broadening of absorption and emission bands.

**Acknowledgments**

DAAD is thanked for photoluminescence measurement support through RoHan project.
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