



Original Article

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

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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 d^8 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

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<https://doi.org/10.25073/2588-1140/vnunst.5152>

which showed *cis* geometries cemented by intramolecular π - π interactions [6, 7]. In this paper, a new Ni(II) complex with anthracene-based thiosemicarbazone (**NiL**) is presented. Spectroscopic data such as $^1\text{H-NMR}$, 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 $^1\text{H NMR}$ spectra were recorded on an AVANCE Bruker-500MHz spectrometer in $\text{DMSO-}d_6$ 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 $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). 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: $\nu_{\text{max}}/\text{cm}^{-1} = 3399$ (m), 3216 (m), 3062 (w), 2926 (w), 1523 (s), 1436 (m), 1204 (s), 1077 (w), 890 (w), 732 (m), 607 (w). $^1\text{H NMR}$ ($\text{DMSO-}d_6$): 11.67 (s, 1H, $\text{N}^{(2)}\text{H}$), 9.27 (s, 1H, $\text{CH}=\text{N}$), 8.70 (s, 1H, H_{10}), 8.49 (d, 2H, $\text{H}_{1,8}$), 8.32 (q, 1H, $\text{N}^{(4)}\text{H}$), 8.14 (d, 2H, $\text{H}_{4,5}$), 7.65–7.56 (m, 4H, $\text{H}_{2,3,6,7}$), 3.01 (d, 3H, CH_3).

Crystal Data for HL: orthorhombic, space group $\text{Pna}2_1$ (no. 33), $a = 16.7442(14) \text{ \AA}$, $b = 15.8556(10) \text{ \AA}$, $c = 5.2324(4) \text{ \AA}$, $V = 1389.15(18) \text{ \AA}^3$, $Z = 4$, $T = 0.0 \text{ K}$, $\mu(\text{MoK}\alpha) = 0.229 \text{ mm}^{-1}$, $D_{\text{calc}} = 1.403 \text{ g/cm}^3$, 3923 reflections measured ($7.078^\circ \leq 2\theta \leq 56.448^\circ$), 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 %.

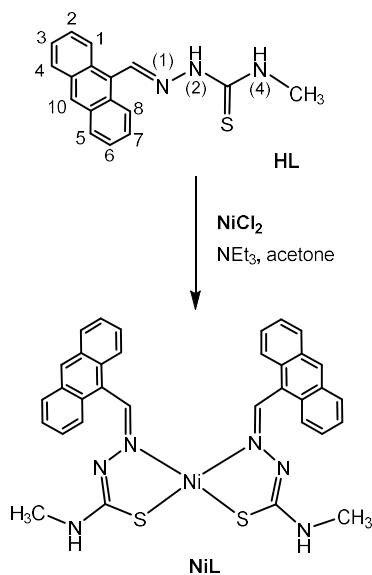
Spectroscopic Data for NiL. IR: $\nu_{\text{max}}/\text{cm}^{-1} = 3309$ (s), 3020 (w), 2833 (w), 1518 (s), 1405 (m), 1262 (m), 1190 (m), 887 (w), 739 (m), 616 (w). $^1\text{H NMR}$ ($\text{DMSO-}d_6$): 8.71 (s, 2H, H_{10}), 8.12 (m, 4H, $\text{H}_{4,5}$), 7.83 (s, 2H, $\text{CH}=\text{N}$), 7.45 (m, 4H, $\text{H}_{3,6}$), 6.78 (q, 2H, NH), 2.41 (d, 6H, CH_3). ESI-MS: m/z 642.9, $[\text{M} + \text{H}]^+$.

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 ^1H NMR spectroscopy were adopted to characterize the complex. ESI-MS result reveals major cluster peak responsible for molecular ion $[\text{NiL} + \text{H}]^+$ 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 $\nu(\text{C}=\text{N})$ 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 $\nu(\text{C}=\text{S})$ 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 $\text{C}=\text{S}$ bond is converted to $\text{C}-\text{S}$ and then $\text{C}-\text{S}-\text{Ni}$ linkages upon complexation [11].

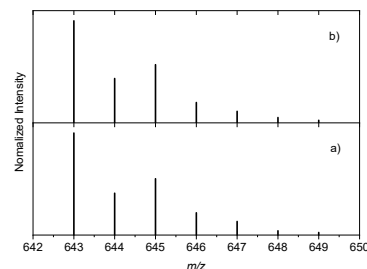


Figure 1: a) Simulated isotopic pattern for $[\text{NiL} + \text{H}]^+$; b) ESI-MS cluster peak for $[\text{NiL} + \text{H}]^+$.

The ^1H NMR spectra of **HL** and **NiL** in $\text{DMSO}-d_6$ 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 $\text{N}^{(2)}-\text{H}$ 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, $\text{N}^{(4)}$ -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 $\text{N}^{(4)}\text{H}$ 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 ($\text{H}_{1,8}$ and $\text{H}_{4,5}$), and two triplets ($\text{H}_{2,3,6,7}$). Unexpectedly, only three proton signals responsible for H_{10} (8.71 ppm), $\text{H}_{4,5}$ (8.12 ppm), $\text{H}_{3,6}$ (7.46 ppm) in anthracene rings in **NiL** are observed (Figure 2b). Besides, the disappearance of proton signals arising from $\text{H}_{1,8,2,7}$ 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 $\pi-\pi$ stacking. Especially, $\text{H}_{1,8,2,7}$ 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).

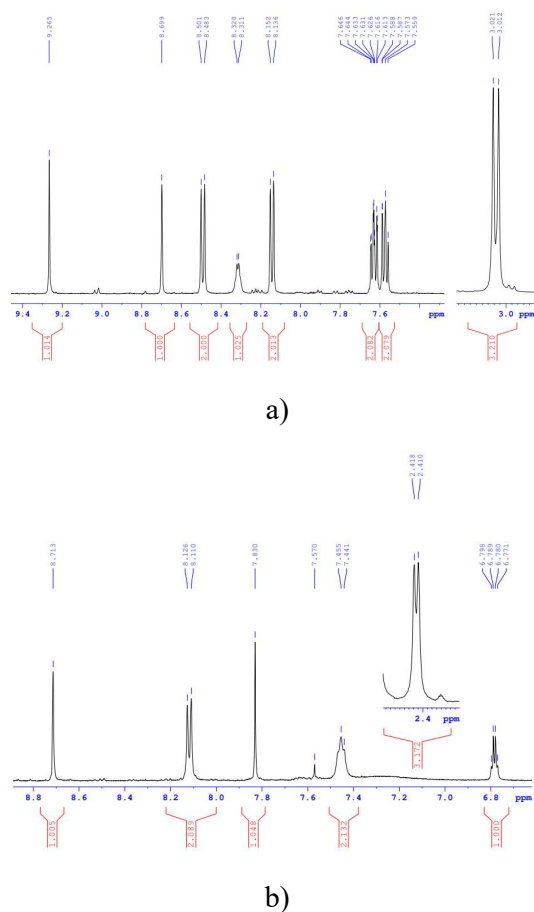


Figure 2: ^1H NMR spectrum of a) **HL** and b) **NiL** in $\text{DMSO-}d_6$.

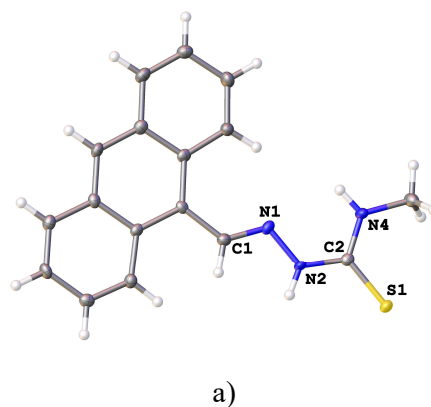
3.2. Characterization of **HL** by X-ray crystallography

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 ($\sim 120^\circ$) 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 π – π 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 ($^\circ$) 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)



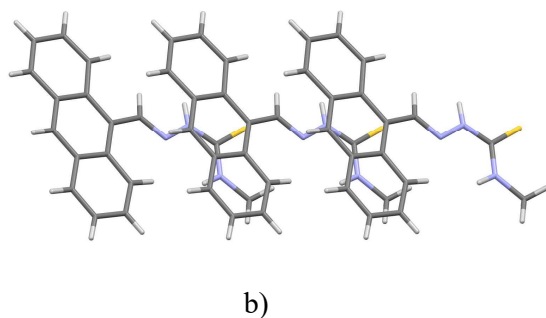


Figure 3: a) X-ray structures of **HL**; b) Solid-state packing of **HL**. Color scheme: S, yellow; C, gray; N, blue; H, white.

3.2. UV-Vis and Photoluminescence Characterizations of **NiL**

UV-Vis absorption and emission spectra of **HL** and **NiL** in CH_2Cl_2 are presented in Figure 4 and Figure 5, respectively. The structureless absorption band at ~ 405 nm assigned to $\pi \rightarrow \pi^*$ 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].

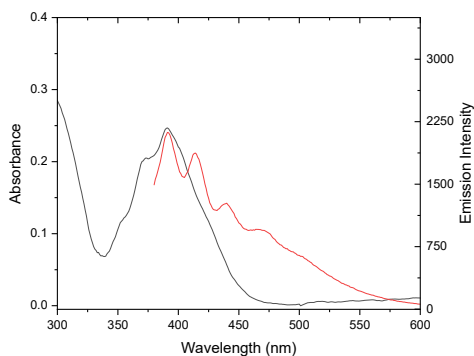


Figure 4: Absorption (black curve) and emission (red curve) spectra of **HL** in CH_2Cl_2 at room temperature. Excitation wavelength = 330 nm.

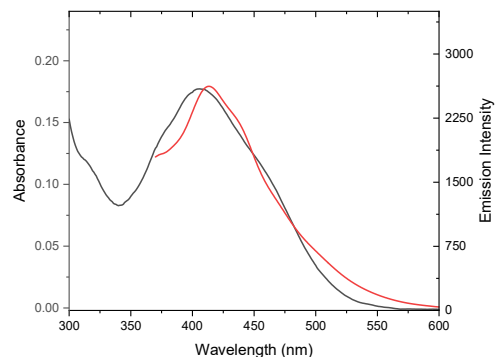


Figure 5: Absorption (black curve) and emission (red curve) spectra of **NiL** in CH_2Cl_2 at room temperature. Excitation wavelength = 330 nm.

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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