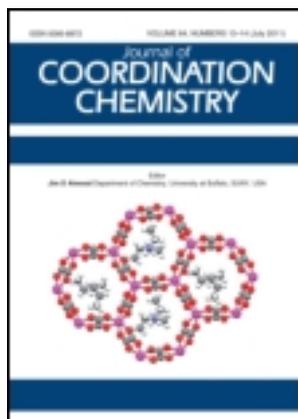


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## Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gcoo20>

### Nickel(II) and copper(II) complexes of allyl 2-(thiophen-2-ylmethylene)hydrazinecarbodithioate: synthesis, X-ray crystal structures, and theoretical study

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Available online: 05 Apr 2012

To cite this article: Reza Takjoo, Roberto Centore, Lydia Rhyman & Ponnadurai Ramasami (2012): Nickel(II) and copper(II) complexes of allyl 2-(thiophen-2-ylmethylene)hydrazinecarbodithioate: synthesis, X-ray crystal structures, and theoretical study, *Journal of Coordination Chemistry*, 65:9, 1569-1579

To link to this article: <http://dx.doi.org/10.1080/00958972.2012.675058>

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## Nickel(II) and copper(II) complexes of allyl 2-(thiophen-2-ylmethylene)hydrazinecarbodithioate: synthesis, X-ray crystal structures, and theoretical study

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(Received 24 December 2011; in final form 3 February 2012)

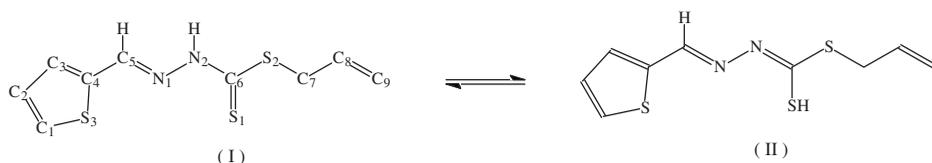
We report allyl 2-(thiophen-2-ylmethylene)hydrazine-carbodithioate (HL) and its Ni(II) and Cu(II) complexes, [ML<sub>2</sub>]. The compounds were fully characterized by elemental analysis, IR, <sup>1</sup>H-NMR, UV-Vis, and molar conductivity. The crystal structure analysis indicates that the metal is four-coordinate square planar and that a parallel stacking of the molecular planes is present in the crystals, with stacking distances of 3.642 and 3.676 Å for the Ni(II) and Cu(II) complexes, respectively. Gas phase DFT computations indicate that the thione tautomeric form of the free ligand is more stable than the thiol form by 14.52 kJ mol<sup>-1</sup>. For HL and ML<sub>2</sub>, comparison between the computed and experimental data shows good agreement.

**Keywords:** NNS donor ligand; S-Allyl dithiocarbamate; Metal complexes; Crystal structure; B3LYP

### 1. Introduction

Dithiocarbamate compounds are an important class of Schiff bases which can be easily obtained by condensation of dithiocarbazides with aldehydes or ketones [1]. The presence of nitrogen and sulfur donors gives dithiocarbazates ability to coordinate metal ions and interesting properties to the resulting metal complexes [2]. Dithiocarbazates possess versatile structural features, existing in two tautomeric forms, thione (I) and thiol (II) (scheme 1) [3]. These compounds generally behave as bidentate (N,S) ligands forming five-membered chelate rings [4]. Interest in these complexes is due to the large spectrum of properties that have been reported, antibacterial [5], antifungal [6], antitumor [7], antituberculosis [8], antipoxvirus drug [9], semiconductor nanoparticles [10], photo-electrochemical solar cells [3], molecular conductors [11], radiopharmaceuticals [12], metal extraction [13], and DNA binding

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Scheme 1. Thione (I) and thiol (II) forms of HL.

and cleavage activity [14]. However, applications of dithiocarbamate compounds in these areas depend on the metal and substituent groups present in the complex.

Recently, we reported the X-ray structure of  $[M(L)_2]$  (HL: *N*-(2-hydroxyethyl)-2-(thiophene-2-ylmethylene)hydrazinecarbothioamide,  $M = Ni, Cu$ ) with thiosemicarbazone as the ligand [15]. In continuation of our studies on metal complexes of (N,S) bidentate ligands, we report herein the syntheses, spectroscopic, X-ray structural, and density functional theory (DFT) studies of two new Ni(II) and Cu(II) complexes with allyl-2-(thiophen-2-ylmethylene)hydrazine-carbodithioate, whose structure is shown in scheme 1. The ligand was chosen for interest in thiophene containing conjugated compounds in organic electronics [16].

## 2. Experimental

### 2.1. Analytical and physical measurements

All chemicals were reagent grade and used as purchased without purification. FT-IR spectra of the compounds were recorded as KBr pellets with a FT-IR 8400-SHIMADZU spectrophotometer. Elemental analyses were determined on a Thermo Finnigan Flash Elemental Analyzer, model 1112EA. UV-Vis spectra were obtained with a SHIMADZU model 2550 UV-Vis spectrophotometer (250–900 nm) in DMF.  $^1\text{H-NMR}$  spectra were recorded on a Bruker BRX 100 AVANCE spectrometer. The molar conductances of  $10^{-3} \text{ mol L}^{-1}$  solutions of the metal complexes in DMF were measured at  $30^\circ\text{C}$  using a Metrohm 712 conductometer.

### 2.2. Synthesis of allyl 2-(thiophen-2-ylmethylene)hydrazine-carbodithioate

*S*-Allyl dithiocarbamate was prepared by previously described methods [17] by condensation of *S*-allyl dithiocarbamate (1.48 g, 10 mmol) with 2-thiophenecarbaldehyde (1.12 g, 10 mmol) in ethanol (20 mL). The solution was heated at reflux for 1 h and then chilled. The yellow product was filtered off, recrystallized from ethanol and finally dried in a desiccator over silica gel. Yield: 2.13 g, 88%. m.p.:  $129.5^\circ\text{C}$ . Anal. Calcd for  $\text{C}_9\text{H}_{10}\text{N}_2\text{S}_3$  ( $242.38 \text{ g mol}^{-1}$ ) (%): C, 44.60; H, 4.16; N, 11.56; S, 39.69. Found (%): C, 43.85; H, 4.10; N, 11.45; S, 39.21. IR,  $\text{cm}^{-1}$ :  $\nu(\text{NH})$  3101 m,  $\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N})$  1589 s,  $[\beta(\text{NH}) + \nu(\text{C}-\text{N})]$  (thioamide I) 1528 s,  $[\nu(\text{C}-\text{N}) + \beta(\text{NH})]$  (thioamide II) 1304 s,  $\nu(\text{C}=\text{S})$  1096 m,  $\nu(\text{N}-\text{N})$  1026 s,  $[\nu(\text{C}=\text{S}) + \nu(\text{C}-\text{S})]$  (thioamide IV) 856w,  $\rho(\text{ring})$  718 s. UV-Vis (DMF),  $\lambda_{\text{max}}$ , nm ( $\log \epsilon$ ,  $\text{L mol}^{-1} \text{ cm}^{-1}$ ): 273 (3.61), 355 (4.14), 368 (4.08)sh.  $^1\text{H-NMR}$  (100 MHz,  $\text{DMSO-d}_6$ ):  $\delta = 13.2$  (s, 1 H,  $\text{N}^2\text{H}$ ; exchangeable with  $\text{D}_2\text{O}$ ), 8.4 (s, 1 H,

C<sup>5</sup>H), 7.7 (d, 1 H, C<sup>1</sup>H), 7.5 (d, 1 H, C<sup>3</sup>H), 7.1 (t, 1 H, C<sup>2</sup>H), 5.6–6.2 (m, 1 H, C<sup>8</sup>), 5.2 (t, 2 H, C<sup>9</sup>), 3.8 (d, 2 H, C<sup>7</sup>).

### 2.3. Preparation of metal complexes

For the preparation of metal complexes, a hot ethanol solution of HL was added to ethanol solution of the metal acetate in 2:1 molar ratio (L:M), and the resulting solution was refluxed for 1 h. After cooling, the solid obtained was separated, washed with ethanol and dried in a desiccator over silica gel.

**2.3.1. Bis(allyl 2-(thiophen-2-ylmethylene)hydrazine-carbodithioato)nickel(II) NiL<sub>2</sub> (1).** Red. Yield: 72%. m.p.: 227.5°C. Molar conductivity ( $1 \times 10^{-3}$  mol L<sup>-1</sup>, DMF):  $13 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . Anal. Calcd for C<sub>18</sub>H<sub>18</sub>N<sub>4</sub>NiS<sub>6</sub> (541.45 g mol<sup>-1</sup>) (%): C, 39.93; H, 3.35; N, 10.35; S, 35.53. Found (%): C, 39.23; H, 3.33; N, 10.27; S, 35.01. IR, cm<sup>-1</sup>:  $\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N})$  1581 s,  $\nu(\text{N}-\text{N})$  1019 s, [ $\nu(\text{C}=\text{S}) + \nu(\text{C}-\text{S})$ ] (thioamide IV) 825w,  $\rho(\text{ring})$  710 s. UV-Vis (DMF),  $\lambda_{\text{max}}$ , nm (log  $\epsilon$ , L mol<sup>-1</sup> cm<sup>-1</sup>): 276 (4.02), 341 (4.51)sh, 354 (4.60), 368 (4.49)sh, 444 (3.88)sh. <sup>1</sup>H-NMR (100 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 8.2 (s, 1 H, C<sup>5</sup>H), 7.9 (d, 1 H, C<sup>1</sup>H), 7.4 (d, 1 H, C<sup>3</sup>H), 7.3 (t, 1 H, C<sup>2</sup>H), 5.5–6.1 (m, 1 H, C<sup>8</sup>), 5.0 (t, 2 H, C<sup>9</sup>), 3.8 (d, 2 H, C<sup>7</sup>).

**2.3.2. Bis(allyl 2-(thiophen-2-ylmethylene)hydrazine-carbodithioato)copper(II) CuL<sub>2</sub> (2).** Brown. Yield: 64%. m.p.: 176.5°C. Molar conductivity ( $1 \times 10^{-3}$  mol L<sup>-1</sup>, DMF):  $17 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . Anal. Calcd for C<sub>18</sub>H<sub>18</sub>CuN<sub>4</sub>S<sub>6</sub> (546.30 g mol<sup>-1</sup>) (%): C, 39.57; H, 3.32; N, 10.26; S, 35.22. Found (%): C, 39.17; H, 3.29; N, 10.19; S, 34.64%. IR, cm<sup>-1</sup>:  $\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N})$  1581 s,  $\nu(\text{N}-\text{N})$  1026 s, [ $\nu(\text{C}=\text{S}) + \nu(\text{C}-\text{S})$ ] (thioamide IV) 817w,  $\rho(\text{ring})$  710 s. UV-Vis (DMF),  $\lambda_{\text{max}}$ , nm (log  $\epsilon$ , L mol<sup>-1</sup> cm<sup>-1</sup>): 298 (4.06), 338 (3.64)sh, 358 (4.18)sh, 370 (4.19), 462 (3.47)sh, 761 (3.36).

### 2.4. Crystal structure determination

Single-crystals of **1** and **2** suitable for X-ray analysis were grown from DMF. Data were collected on a Bruker-Nonius Kappa-CCD diffractometer using graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 173 K. Absorption correction was performed using the multi-scan method [18]. Structures were solved by direct methods [19] and refined by full-matrix least-squares [20] on  $F^2$  against all reflections using anisotropic displacement parameters for non-H atoms. Hydrogen atoms, whose positions were determined stereochemically, were refined by the riding model with  $U_{\text{iso}} = 1.2U_{\text{eq}}$  of the carrier atom. In both complexes, the allyl tail is disordered over two sites. The two split positions were refined with isotropic displacement parameters for some of the carbons involved and with some restraints on bond lengths for **2**. A summary of crystal, collection, and refinement data is shown in table 1.

Table 1. Crystal, collection and refinement data for **1** and **2**.

Compound	<b>1</b>	<b>2</b>
Empirical formula	(C <sub>9</sub> H <sub>9</sub> N <sub>2</sub> S <sub>2</sub> ) <sub>2</sub> Ni	(C <sub>9</sub> H <sub>9</sub> N <sub>2</sub> S <sub>2</sub> ) <sub>2</sub> Cu
Formula weight	541.43	546.26
Temperature (K)	173(2)	173(2)
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>C</i> 2/ <i>c</i>
Unit cell dimensions (Å, °)		
<i>a</i>	9.937(4)	15.340(6)
<i>b</i>	14.993(6)	15.186(6)
<i>c</i>	7.520(3)	20.425(8)
$\beta$	97.11(2)	106.53(3)
Volume (Å <sup>3</sup> ), <i>Z</i>	1111.7(8), 2	4561(3), 8
Calculated density (g cm <sup>-3</sup> )	1.617	1.591
Absorption coefficient (mm <sup>-1</sup> )	1.450	1.520
Reflections collected	8192	23,022
Max. $\theta$ (°)	27.49	25.00
Independent reflection	2547 [ <i>R</i> (int) = 0.0293]	4006 [ <i>R</i> (int) = 0.0895]
Data/restraints/parameters	2547/0/139	4006/2/258
<i>R</i> , <i>wR</i> [ <i>I</i> > 2( <i>I</i> )]	0.0275, 0.0610	0.0673, 0.1504
<i>R</i> , <i>wR</i> (all data)	0.0372, 0.0656	0.0966, 0.1621
Largest difference peak and hole (e Å <sup>-3</sup> )	0.517 and -0.370	0.892 and -0.961

## 2.5. Computational methods

All computations were performed using the DFT with B3LYP functional as implemented in the Gaussian 03 suite of program [21]. The 6-311+G(d,p) basis set was used for all the atoms but nickel and copper, for which the LANL2DZ ECP basis set was used. The B3LYP functional [22] and the 6-311+G(d,p) [23] and the LANL2DZ ECP basis sets [24] have proved to be appropriate for the current research. The ligand and complexes were fully optimized with tight criteria and frequency computations carried out to verify the nature of the stationary points.

## 3. Results and discussion

### 3.1. Syntheses and characterization

The new bidentate ligand allyl 2-(thiophen-2-ylmethylene)hydrazine-carbodithioate (HL) having an (N,S) donor set was synthesized by 1 : 1 condensation of thiophene-2-carbaldehyde with *S*-allyl dithiocarbamate in ethanol. Reaction of HL with Ni(II) or Cu(II) acetate, in 1 : 2 molar ratio, gave the corresponding metal complexes. The yield, color, melting points, elemental analysis, solution electrical conductivity, infrared (IR), UV-Vis, and <sup>1</sup>H-NMR spectra of the synthesized compounds are presented in the experimental section. All spectral and analytical data are in agreement with the proposed structures. The complexes are soluble in organic solvents. Molar conductivities of complex solutions indicate non-electrolytic behavior for these compounds. The ligand can exhibit thione–thiol tautomerism and *Z/E* isomeric forms since it has a thioamide functional group –NH–C(=S)SR [25] (scheme 1). Spectral properties of these complexes are described below in detail.

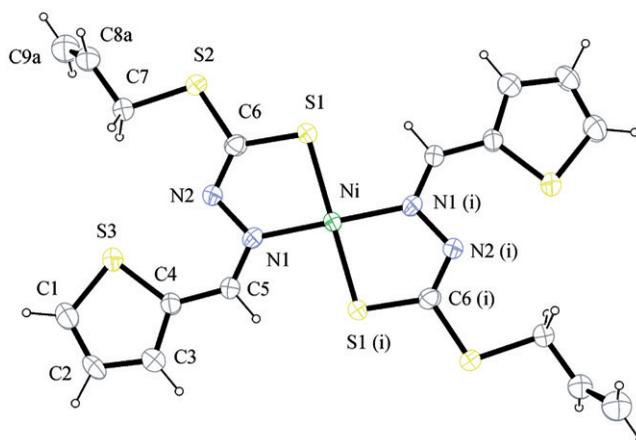


Figure 1. Ortep drawing of **1**. Thermal ellipsoids are drawn at 50% probability level. Only one position of the disordered allyl tail is shown. Symmetry code: (i) =  $-x, -y, -z$ .

The solid state IR spectrum and  $^1\text{H-NMR}$  spectrum in  $\text{CDCl}_3$  of the ligand does not reveal any  $\nu(\text{S-H})$  band at *ca*  $2600\text{ cm}^{-1}$  and S-H resonance peak near  $\delta = 4\text{ ppm}$  [26], indicating that in the solid state and in solution it is present in the thione form (scheme 1).

The  $\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N})$  is observed at  $1589\text{ cm}^{-1}$  in the free ligand and shifts to lower frequency after coordination, evidence for coordination *via* the azomethine in the complexes. The  $\nu(\text{N-H})$  of HL at  $3101\text{ cm}^{-1}$  is not present in IR spectra of the complexes; the acidic proton is extracted by acetate, affording the anionic ligand. The  $\nu(\text{C}=\text{S})$  of HL at  $1096\text{ cm}^{-1}$  also disappears in the complexes [27], as well as thioamide I and thioamide II bands [28]. For **1** and **2**, the thioamide IV band ( $\nu(\text{C}=\text{S}) + \nu(\text{C}-\text{S})$ ) at  $856\text{ cm}^{-1}$  in the free ligand undergoes a red-shift ( $825\text{--}817\text{ cm}^{-1}$ ), pointing to sulfur of thiol as a coordination site [29]. Coordination of the thione sulfur results in a decrease in frequency of thioamide IV in spectra of the complexes compared with HL [30].

$^1\text{H-NMR}$  data are given in the experimental section and the numbering scheme of the free ligand is given in figure 1. The  $^1\text{H-NMR}$  spectrum of HL exhibits a signal at 13.2 ppm for the thioamide  $-\text{NH}(\text{CS})$  proton which disappears on  $\text{D}_2\text{O}$  exchange. This supports the presence of the thione form in solution. The discrepancy between the NH signal at 13.2 ppm and the usual values of  $\delta$  8–9 [31] is attributed to intramolecular H bonding and *Z* configuration for the  $\text{C}=\text{N}$  bond [15, 32], see below. The NH singlet is not found in the spectrum of **1**, confirming deprotonation and thiolate form in the complex. The methine proton  $\text{C}^5\text{H}$ , observed as a singlet at 8.4 ppm in HL, shifts downfield after complexation, indicating coordination *via* the azomethine nitrogen. The signals due to thiophene ring protons appear as two doublets for  $\text{C}^1\text{H}$  and  $\text{C}^3\text{H}$ , and a triplet for  $\text{C}^2\text{H}$  at 7.7, 7.5, and 7.1 ppm, respectively, in the free ligand; the signals at 3.8, 5.6–6.2, and 5.2 ppm corresponding to  $\text{C}^7\text{H}_2$ ,  $\text{C}^8\text{H}$ , and  $\text{C}^9\text{H}_2$ , respectively, all show slight variation upon complexation.

The electronic spectra of the compounds were recorded in DMF. The Schiff base exhibits two  $n \rightarrow \pi^*$  bands of the dithiocarbazate and thiophene at 355 and 368 nm, respectively [15]. A band at 273 nm is assigned to  $\pi \rightarrow \pi^*$  of the dithiocarbazate group. Upon coordination with the metal, the  $n \rightarrow \pi^*$  band is shifted.  $\text{S} \rightarrow \text{d}$  charge transfer

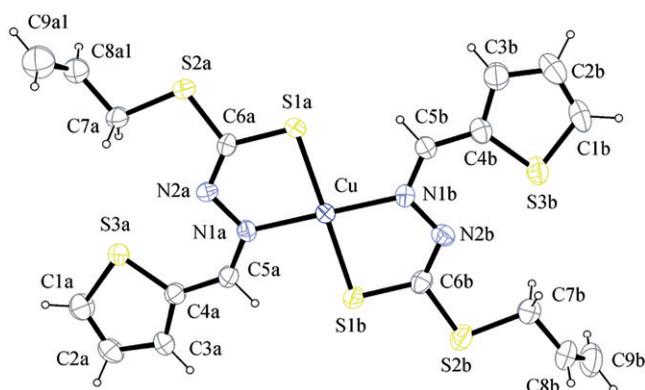


Figure 2. Ortep drawing of **2**. Thermal ellipsoids are drawn at 50% probability level. Only one position of the disordered allyl tail C8a–C9a is shown.

(LMCT) bands appeared at 368 and 370 nm in the Ni and Cu complexes, respectively. The square planar Ni(II) complex is expected to show three spin allowed bands corresponding to the  $^1A_{1g} \rightarrow ^1A_{2g}$ ,  $^1A_{1g} \rightarrow ^1B_{1g}$ , and  $^1A_{1g} \rightarrow ^1E_g$  transitions. However, the presence of S  $\rightarrow$  M charge transfer band hides some d–d transitions and only the  $^1A_{1g} \rightarrow ^1A_{2g}$  band is observed at 444 nm. The Cu(II) complex shows a band at 761 nm which is related to the  $^2B_1 \rightarrow ^2A_1$  transition in square planar geometries [33].

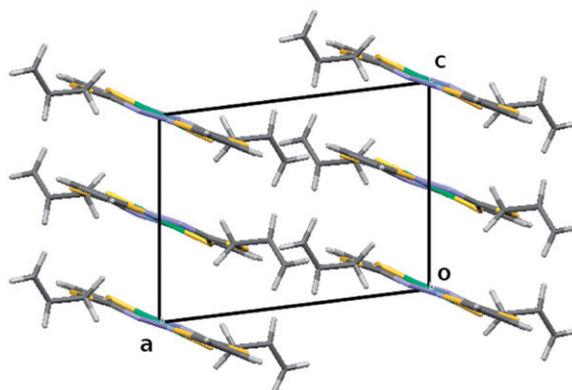
### 3.2. Crystal structure description of **1** and **2**

The X-ray structures of **1** and **2** are shown in figures 1 and 2, respectively, with selected bond lengths and angles given in table 2. In both cases, the metal adopts square planar coordination geometry and is bound to two chelating ligands *trans* through imino nitrogen and thiolate sulfur. The square-planar coordination geometry is fairly regular in both complexes; the four bond angles around the metal are close to 90°, with the bite angles corresponding to the formation of the five-membered rings slightly contracted (they are close to 85°) and the others slightly enlarged (about 95°). In both complexes, the metal-to-nitrogen distances are, on average, 0.2 Å shorter than the metal-to-sulfur distances. In addition, in comparing **1** with **2**, distances involving Cu are, on average, 0.1 Å longer than Ni; this is expected because of the larger ionic radius of Cu(II) as compared with Ni(II) [34]. For **1**, molecules lie on crystallographic inversion centers, with  $C_i$  point symmetry. The inspection of the bond lengths indicate that, in both complexes, the coordinated ligand is in the thiolato form, indicated by bond lengths C5–N1 (1.293(2) Å in **1**, 1.282(9), 1.316(9) Å in **2**) and C6–N2 (1.280(2) Å in **1**, 1.279(9), 1.296(9) Å in **2**), which take values close to those expected for a double bond.

In both complexes, the allyl tail is located from the same side of the thiophene ring as a result of C7 being in the *trans* position with respect to S1. In this way, the ligand takes on an overall bent shape. The conformation around C4–C5 is *S-cis* in the two complexes, i.e., with S3 from the same side of N2. This conformation is probably taken because it allows coplanar arrangement of the thiophene ring with the coordination plane of the metal; in fact, the dihedral angles between the mean plane of the thiophene

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2** with esd's in parentheses.

Compound	<b>1</b>	<b>2</b>
M–N1	1.913(2)	2.012(6), 2.016(6)
M–S1	2.1664(9)	2.258(2), 2.255(2)
C4–C5	1.426(3)	1.44(1), 1.411(9)
C5–N1	1.293(2)	1.282(9), 1.316(9)
N1–N2	1.405(2)	1.387(8), 1.379(8)
C6–N2	1.280(2)	1.279(9), 1.296(9)
C6–S1	1.723(2)	1.734(7), 1.731(7)
C6–S2	1.742(2)	1.745(7), 1.754(7)
N1–M–N1	180.00(9)	175.4(2)
S1–M–S1	180.00(4)	175.5(1)

Figure 3. Crystal packing of **1** viewed down **b**.

ring and the mean coordination plane of the metal are  $6.27(8)^\circ$  in **1** and  $8.8(2)^\circ$  and  $2.5(3)^\circ$  in **2**. Actually, the molecules have a substantially flat overall geometry, with the only exception the terminal alkenyl group.

The flat geometry of the molecules has effects on their packing. In both cases, the plane of the independent molecule is parallel to the crystallographic **b** axis and, in the monoclinic system, this implies that the packing is made up by parallel molecules. In particular, in **1** molecules lie on crystallographic planes of the family  $(1\ 0\ -2)$  and, consistently, the  $1\ 0\ -2$  reflection is very intense (it is the second most intense reflection of the diffraction pattern). The spacing of the family of planes, which is also the average stacking distance of the molecular planes, is  $3.642\ \text{Å}$ . In **2**, the pattern is analogous, with the molecules lying on the planes of the family with Miller indices  $4\ 0\ 0$  (reflection  $4\ 0\ 0$  is the second most intense of the whole diffraction pattern), whose spacing is  $3.676\ \text{Å}$ . A suitable projection of the crystal packing of the two compounds is shown in figures 3 and 4.

The close stacking of the molecular planes determines, in particular for **2**, some close contacts involving the metal, carbon and sulfur ( $\text{Cu}\cdots\text{S1B}(\text{i}) = 3.149(3)\ \text{Å}$ ,  $\text{C5}\cdots\text{C5A}(\text{i}) = 3.37(1)\ \text{Å}$ ,  $\text{C5B}\cdots\text{S3A}(\text{ii}) = 3.493(8)\ \text{Å}$ , (i) =  $1-x, y, 0.5-z$ ; (ii) =

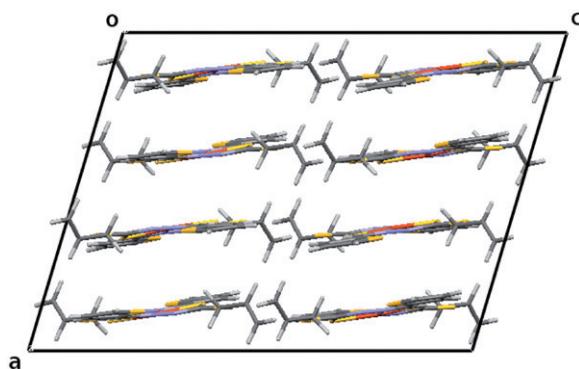


Figure 4. Crystal packing of **2** viewed down **b**.

$1.5 - x, 0.5 + y, 0.5 - z$ ). We note that crystal structures with close parallel stacking of planar conjugated cores are receiving interest as organic or metallorganic semiconductors [16].

### 3.3. DFT computations

IR and NMR data indicate that the thione tautomer of the free ligand is present both in the solid state and in solution, probably related with the strength of intermolecular H bonding. In the thione tautomer, the sulfur of the thiocarbonyl is a good H bonding acceptor [35] and the amido N–H a very good donor. In the thiol form, S–H is a very weak donor [35], while imino N is a good acceptor. However, we have performed gas phase DFT calculations of both tautomeric forms of HL, and the results indicate that in the absence of intermolecular interactions, the thione tautomer is the most stable species, but only by  $3.5 \text{ kcal mol}^{-1}$  over that for thiol. For a useful comparison, we note that in the case of the dithiocarbazate ligand that we have recently studied, *S*-allyl-3-(2-pyridyl-methylene)-dithiocarbazate, the calculated energy difference between the thiol and thione form was  $14.65 \text{ kcal mol}^{-1}$ , due to the presence of a strong intramolecular H bonding in the thione form, not allowed in the thiol [36]. Figure 5 displays the gas phase optimized structures of the two tautomeric forms of 2-(thiophen-2-ylmethylene)hydrazine-carbodithioate. In the optimized structure of the thione form, figure 5(a), the CH=N bond is in the *Z* configuration and this allows a weak intramolecular interaction between N–H donor and thiophene S acceptor through the formation of a six-membered ring (N–H =  $1.017 \text{ \AA}$ , H...S =  $2.436 \text{ \AA}$ , N...S =  $3.152 \text{ \AA}$ , and N–H...S =  $126.8^\circ$ ). In the thiol tautomer, figure 5(b), the CH=N bond is in the *E* configuration, and a weak H bonding interaction can be established between the S–H donor and N1 acceptor through formation of a five-membered ring (S–H =  $1.355 \text{ \AA}$ , H...N =  $2.153 \text{ \AA}$ , N...S =  $2.959 \text{ \AA}$ , and S–H...N =  $113.1^\circ$ ). The intramolecular H bonding interactions of the thione and thiol tautomers are both weak. In the first case because S of the thiophene ring is a very weak acceptor [35], and in the second because thiol S–H is a very weak donor. This is consistent with the small calculated energy difference.

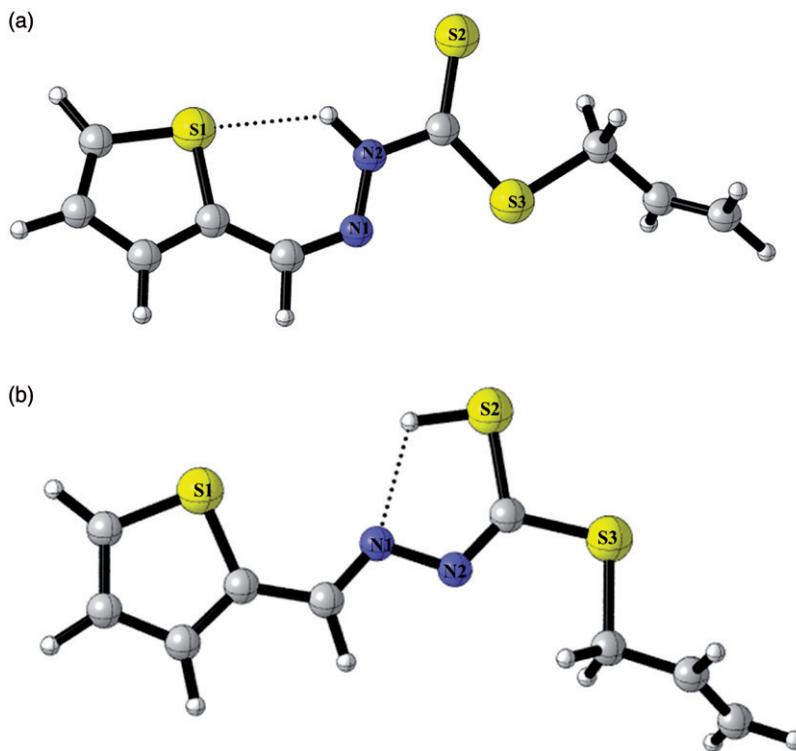


Figure 5. Optimized structures of the HL ligand; (a) thione and (b) thiol.

Table 3. Selected structural data for the optimized structure of Cu and Ni complexes.

	Theoretical	Experimental
Cu-S1A	2.349	2.258(2)
Cu-S1B	2.347	2.255(2)
Cu-N1A	2.033	2.012(6)
Cu-N1B	2.034	2.016(6)
Ni-S1	2.248	2.1664(9)
Ni-N1	1.950	1.913(2)
S1A-Cu-S1B	159.1	175.5(1)
N1A-Cu-N1B	160.5	175.4(2)
S1-Ni-S1	180.0	180.00(4)
N1-Ni-N1	180.0	180.00(9)

Some selected data for the optimized structures of the Ni(II) and Cu(II) complexes are reported in table 3. The nickel complex adopts a nearly square-planar configuration, whereas for the copper complex some deviations from the square planarity are calculated. If we impose  $C_s$  symmetry to the square planar structures of these complexes, our computations yield four imaginary frequencies for both complexes. We have compared some computed parameters with those available from X-ray data.

The root mean square error for bond length and bond angle for the Ni complex are 0.079 Å (27 data set) and 1.82° (41 data set), respectively, and 0.084 Å (50 data set) and 3.36° (80 data set), respectively, for the copper complex. Therefore, taking deviations into account together with inspection of the data (Supplementary material), we deduce that there is a good agreement between the computed and experimental parameters.

#### 4. Conclusion

We have described a new ligand, HL, and its Ni(II) and Cu(II) complexes. The compounds were characterized by elemental analysis, IR, <sup>1</sup>H-NMR, UV-Vis, and molar conductivity. The IR and <sup>1</sup>H-NMR spectra of the free ligand show that in the solid state, the ligand remains in the thione form. The structure of the complexes was determined by single-crystal X-ray analysis. In both complexes, HL is monoanionic NS bidentate through deprotonation of the corresponding thiol tautomer. The computational study in B3LYP basis set reveal that the thione form of the ligand is more stable than the thiol form (14.52 kJ mol<sup>-1</sup>) by formation of the six-membered intramolecular H bonding ring. In addition, there is a good comparison between the experimental and theoretical structural parameters.

#### Supplementary material

CCDC 855655 and 855654 contain the supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge *via* <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

#### Acknowledgments

Thanks are due to CIMCF of the University of Naples “Federico II” for the X-ray facility. R.T. was supported by Ferdowsi University of Mashhad grant 1/16651 (89-14 – 1389/11/10).

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