



Nickel(II) Complex of Pyrrole-2-carboxaldehyde Schiff base of *S*-allyl dithiocarbazate (H_2L): Synthesis, Spectroscopic Properties and X-ray Crystal Structures of H_2L and Nickel(II) Complex

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introduction:

Dithiocarbazic acid and their Schiff bases form an interesting series of ligands and metal complexes. In order to presence of both hard nitrogen and soft sulfur donor atoms in the backbones of dithiocarbazate ligands, they facilitate for coordination with a wide range of transition and non-transition metal ions [1]. Some of which have been shown interesting physical and chemical properties [2] and potentially useful biological activities [3]. We describe here the preparation and characterization of ligand (1) and Ni(II) complex (2), together with the X-ray crystal structure determination of them.

Experimental:

Synthesis of Allyl *N*-[1-(pyrrole-2-yl)methylene]hydrazinecarbodithioate (H_2L , 1)

To a mixture of 5 ml (0.1 mol) hydrazine hydrate and 5.5 g (0.1 mol) KOH in 30 ml of ethanol at 5 °C, was added a solution of 6.1 ml (0.1 mol) of carbon disulfide and 8.6 ml (0.1 mol) of allyl bromide with continuous stirring. To this mixture was added the ethanolic solution (25 ml) of pyrrole-2-carboxaldehyde (9.51 g, 0.1 mol) and heated. The brown product was separated by filtration, washed with water and dried in a vacuum. H_2L was recrystallized from ethanol. Yield 42%; m.p. 115 °C. $C_9H_{11}N_3S_2$ (225.33).

Preparation of bis [*S*-allyl- β -*N*-(2-pyrrol)methylene]dithiocarbazate]nickel(II) (2)

A ethanolic solution (20 cm³) of the ligand (0.225 g, 1 mmol) was mixed with a solution of Ni(NO₃)₂·6H₂O (0.145 g, 0.5 mmol) in the same solvent, the mixture was stirred for 40 min in water-bath temperature. Upon slow evaporation, dark green well-shaped crystals were obtained. Yield 53.25%; m.p. 139.5 °C. $C_{18}H_{20}N_6NiS_4$ (507.35); $\lambda_m = 1.07 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

Results and discussion:



Spectroscopic characterization (^1H NMR, IR, UV-Vis and Mass Spectroscopy)

The mass spectral data of **1** and **2** are exhibit parent ions at 225 and 507 m/z , respectively.

The IR spectra of **1** show bands at 3108 and 3390 cm^{-1} attributed to the *sec* NH group of the thione form and pyrrole ring, respectively. The $\nu(\text{C}=\text{S})$ at 1103 cm^{-1} in **1** that has disappeared in the complex, thus supporting the coordination thiolate S donor atom with metal ion. The coordination of the azomethine nitrogen to the Ni(II) ion is apparent by the red-shift of the $\nu(\text{C}=\text{N})$ band (ca. 17 nm). The $\nu(\text{NH})$ band (3108 cm^{-1}) disappear in the IR spectra of **2** suggesting that the proton attached to the α -nitrogen atom is lost upon complexation [4]. This coordination is confirmed by the presence of new bands at 347 and 432 cm^{-1} that can be assigned to M-S and M-N bonds stretching for complex, respectively.

The electronic spectra of **1** exhibit the two $n \rightarrow \pi^*$ bands (ca. 357 & 426 nm). The $\pi \rightarrow \pi^*$ band at 240 nm may be related to pyrrole ring which is unaffected by complexation. The band at 426 nm result from associated with the thioamide portion of the dithiocarbazate moiety. the band at approximately 439 nm can be assigned to $\text{S} \rightarrow \text{M}^{\text{II}}$ charge transfer. The thioamide $n \rightarrow \pi^*$ intraligand bands are shifted to as high an energy (blue shift) on coordination of the thiol sulfur [5].

The ^1H NMR spectrum of **1** showed two peak at ca. 10.99 and 9.05 ppm attributed to the resonance of NH proton of pyrrole ring and thioamide, respectively. In the spectrum of **2**, the absence of -NH (thioamide), at 9.05 ppm for **1**, confirmed their deprotonation, followed by coordination to Ni center as a uninegatively ligand.

X-ray crystal structure of **1** and **2**

The molecular structures of both the crystals were determined by single crystal X-ray diffraction and the ORTEP drawings of them are shown in Fig. 1.

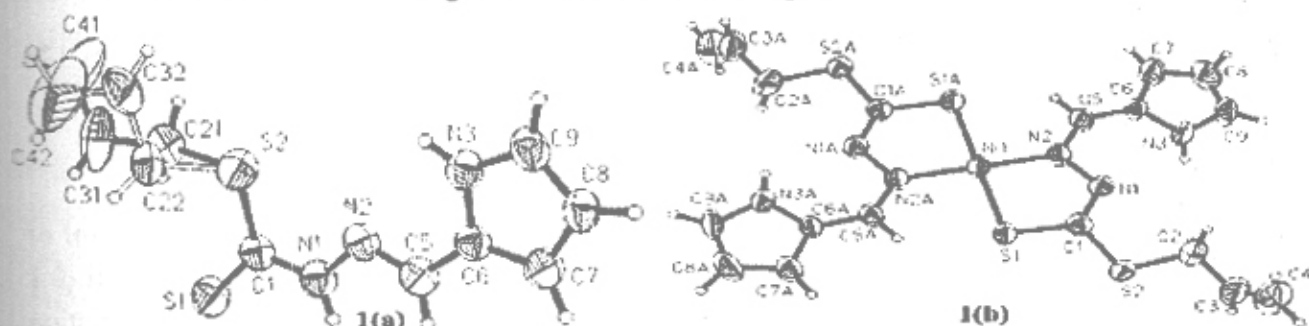


Fig. 1. ORTEP drawing of **1** (1a) and **2** (1b). Ellipsoids correspond to 50% probability.

The compound **1** and **2** crystallizes in an Tetragonal $\text{P4}(2)/n$ and Monoclinic $\text{P2}(1)/c$ space group symmetry, respectively. In dithiocarbazate ligand (**1**) the β -nitrogen atom and the thioketo S atom are in the *trans*-configuration viz. in *E* form around C(1)-N(1). The centrosymmetric structure consists of the neutral molecule **2** and the metal at the center of symmetry. In the complex, the monodeprotonated bidentate ligand shows a *cis*-configuration for the nitrogen N2 and sulfur S atoms to make the 4-coordinate Ni(II) complex with square planar fashion. In the free ligand, however, these centres present a *trans*-configuration, indicating that the complexation occurs after 180° rotation around the C1-N1 and N2-C5



bonds [6]. The Ni(II) coordination is almost square planar with S1A-Ni1-S1 and N2A-Ni1-N2 bond angles (trans angles) of 180° for both of them in compound **2**. The Ni-N bonds for **2** complex is significantly shorter than the Ni-S bonds so that the coordination geometry about the metal ion is more rectangular than square; the cis bond angles in **2** range from $85.8(3)^\circ$ to $94.2(3)^\circ$. The delocalisation of electron density from the coordinating nitrogen onto the Ni(II) gives rise to an elongated N(1)-N(2) bond compared with **1**. The important difference may be due to the distance around atom C(1). In the free ligand (**1**), the bond distances C(1)-N(1) 1.329(3) and C(1)-S(1), 1.637(3) Å suggest that C(1)-N(1) as the single bond and C(1)-S(1) the double bond, while in the complex, the bond distances C(1)-N(1), 1.306(16) and C(1)-S(1), 1.720(14) Å appear that C(1)-N(1) is the double bond and C(1)-S(1) the single bond. Deprotonation and the formation of the metal complex makes the configuration of the ligand quite different.

Conclusion:

In this paper, we have reported the synthesis and the characterization of two new bidentate ligand (**1**) and Ni(II) complex (**2**). The spectroscopic analyses have shown that the Schiff base is in the thione form when in solid state. In case of the complex **2**, both of ligand molecules in its deprotonated thiol form functions as a mononegative bidentate. The neutral **2** complex has distorted square planar environment.

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