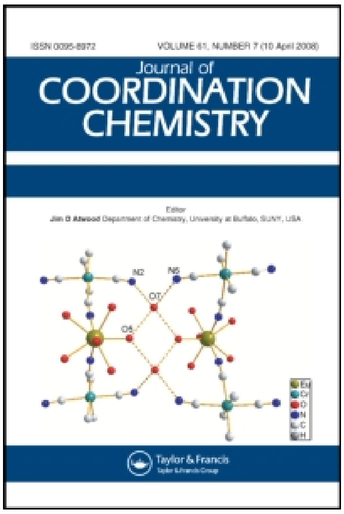

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The preparation, spectroscopic characterization and X-ray crystal structures of the pyrrole-2-carboxaldehyde Schiff base of S-allyldithiocarbazate (HL) and its nickel(II) complex ([Ni(L)$_2$])

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The preparation, spectroscopic characterization and X-ray crystal structures of the pyrrole-2-carboxaldehyde Schiff base of S-allyldithiocarbazate (HL) and its nickel(II) complex ([$Ni(L)_2$])

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A new bidentate Schiff base (HL) derived from the condensation of S-allyldithiocarbazate with pyrrole-2-carboxaldehyde and its complex NiL_2 have been prepared and characterized by elemental analyses, IR, NMR, UV-Vis spectroscopy, mass spectrometry, and molar conductivity measurements. The structures of ligand and NiL_2 complex have been determined using X-ray diffraction analysis. Ligand and Ni(II) complex crystallize in the tetragonal space group $P4_2/n$ with the unit cell parameters $a = 22.1827(18)$ Å, $c = 4.5388(3)$ Å, $V = 2233.4(3)$ Å^3, $Z = 8$ and in the monoclinic space group $P2_1/c$ with the unit cell parameters $a = 9.9998(14)$ Å, $b = 15.1322(16)$ Å, $c = 7.5920(11)$ Å, $\beta = 99.397(17)^\circ$, $V = 1133.4(3)$ Å^3, and $Z = 2$, respectively. X-ray crystallographic structural analysis confirms that two Schiff bases of S-allyldithiocarbazate is coordinated to nickel as a uninegatively charged bidentate NS chelating agent via the azomethine nitrogen and the thiolate sulfur. NiL_2 is square planar with *cis*-configuration.

Keywords: Nickel complex; S-allyldithiocarbazate; Bidentate NS Schiff bases; Crystal structure

1. Introduction

Schiff-bases have been extensively studied in coordination chemistry [1]. Dithiocarbazic acid and their Schiff bases form an interesting series of ligands and metal complexes. Because of the presence of both hard nitrogen and soft sulfur donor atoms in the backbones of dithiocarbazate ligands, they coordinate a wide variety of transition [1a] and non-transition [1c] metals.

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Transition metal chelates of hard–soft nitrogen–sulfur dithiocarbazic acid, its S-alkyl/aryl esters and their Schiff bases have been studied, mainly due to their potential anticancer [2], antifungal [3], antibacterial [4], and insecticidal [5] activities. Various transition and inner-transition metal complexes with NS donor Schiff bases play an important role in biological systems and represent interesting models for metalloenzymes, which efficiently catalyze the reduction of dinitrogen and dioxygen [6, 7]. Macrocyclic derivatives of these Schiff bases have many fundamental biological functions, such as photosynthesis and transport of oxygen in mammalian and other respiratory systems [8]. Publications to date have mainly focused on S-benzyldithiocarbazate (SBDTC) and S-methyldithiocarbazate (SMDTC). Although S-benzoyldithiocarbazate (SBODTC) has been synthesized [9], little work has been reported using this ligand. Complexes of Ni(II) have been reported with Schiff bases of S-methyl and S-benzyldithiocarbazate [10, 11] and other derivatives of thiosemicarbazone [12]. Herein, as part of our efforts in synthesis of SN donor Schiff-base complexes [13], we introduce a new dithiocarbazate derivative (SADTC) containing a pyrrolyl group, pyrrole-2-aldehyde Schiff base of S-allyl dithiocarbazate (HL, **1**) and its nickel(II) complex ($[Ni(L)_2]$, **2**). The crystal structure of the allyl 2-(1H-pyrrol-2-ylmethylidene)-1-hydrazinecarbodithioate (HL) and bis[allyl-2-[1H-pyrrol-2-ylmethylidene]-1-hydrazinecarbodithioato]-nickel(II) have been determined by X-ray structure analysis.

2. Experimental

2.1. *Materials and methods*

All reagents were supplied by Aldrich or Merck and used without purification. Elemental analyses (C, H, N, and S) were performed using Thermo Finnigan Flash 1112EA elemental analyzer and Shimadzu AA-670 atomic absorption spectrometer. Melting points were determined in an electrothermal digital melting point apparatus. IR and far-IR spectra were recorded in KBr discs ($4000–600\,cm^{-1}$) using a Buck 500 Scientific spectrometer and on a Thermo Nicolet NEXUS 870 FT-IR from 700 to $200\,cm^{-1}$ as CsI pellets. ^1H NMR spectra in $CDCl_3$ were recorded on a Bruker BRX 100 AVANCE spectrometer with Me_4Si as internal reference. EI-Mass spectra were obtained on a Varian CH-7 instrument at 70 eV. Electronic spectra were obtained in $CHCl_3$ solution on an Agilent 8453 single beam UV-Vis spectrophotometer.

2.2. *Crystal structure determination*

Well-shaped crystals of **1** and **2** were selected by means of an optical microscope, sealed in thin-walled glass capillaries (Hilgenberg GmbH, Germany) and investigated with a Stoe IPDS with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 291 K. Only a small amount of specimens of both compounds were available, not suffering from intergrowth. Unit cell parameters were determined by least-squares refinements on the positions of 6242 and 1697 strong reflections, distributed equally in reciprocal space in the range $2.90° < \theta < 19.95°$ and $2.10° < \theta < 24.55°$, respectively. In the case of **1** a tetragonal lattice and for **2** a monoclinic lattice was found, and space groups $P4_2/n$ and $P2_1/c$ were uniquely determined. Lp corrections were applied to all the intensity data.

Table 1. Crystal data and structure determination details for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_9H_{11}N_3S_2$	$C_{18}H_{20}N_6NiS_4$
Formula weight	225.33	507.35
Temperature (K)	291(2)	291(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Tetragonal	Monoclinic
Space group	$P4_2/n$	$P2_1/c$
Unit cell dimensions (Å, °)		
a	22.1827(18)	9.9998(14)
b	–	15.1322(16)
c	4.5388(3)	7.5920(11)
β		99.34(2)
Volume (Å^3), *Z*	2233.4(3), 8	1133.4(3), 2
Calculated density (g cm^{-3})	1.340	1.487
Absorption coefficient (mm^{-1})	0.442	1.241
F(000)	944	524
Crystal size (mm^3)	$0.25 \times 0.10 \times 0.10$	$0.30 \times 0.04 \times 0.03$
θ range for data collection (°)	2.60–26.12	2.06–25.99
Limiting indices	$-27 \le h \le 27$, $-27 \le k \le 27$, $-5 \le l \le 5$	$-12 \le h \le 11$, $-18 \le k \le 18$, $-9 \le l \le 9$
Reflections collected	30,147	6597
Independent reflections	2221 [$R_{(int)} = 0.0911$]	2218 [$R_{(int)} = 0.0825$]
Completeness to $\theta = 26.12$ (%)	99.2	99.2
Absorption correction	None	None
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2221/62/155	2218/17/133
Goodness-of-fit on F^2	1.031	1.060
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0411$, $wR_2 = 0.0631$	$R_1 = 0.0932$, $wR_2 = 0.2344$
R indices (all data)	$R_1 = 0.1391$, $wR_2 = 0.0677$	$R_1 = 0.1863$, $wR_2 = 0.2408$
Largest difference peak and hole (e Å^{-3})	0.219 and −0.138	0.835 and −0.232

The structures were solved by direct methods [14] and the positions of all but some of the H atoms of a disordered part of the molecule of **1** were found via ΔF-syntheses. Taking into account a 0.516(9) : 0.484(9) twisting disorder of the allyl group in the crystal of **1**, refinements by full-matrix least-squares calculations on F^2 [15] converged to the indicators given in table 1 (max. shift/esd: 0.000 and 0.000, respectively). Anisotropic displacement parameters were refined for all atoms heavier than hydrogen. Appropriate distance and displacement parameter restraints had to be applied for **2** and the disordered part of **1**. Idealized bond lengths and angles were used for all the CH_2, CH, and NH groups; the riding model was applied for their H atoms. The isotropic displacement parameters of the H atoms were kept equal to 120% of the equivalent isotropic displacement parameters of the parent carbon or nitrogen. A summary of further crystallographic data, data collection parameters, and refinement parameters is collected in table 1.

2.3. *Synthesis of allyl 2-(1H-pyrrol-2-ylmethylidene)-1-hydrazinecarbodithioate (HL, 1)*

A solution of 6.1 mL (0.1 mol) of carbon disulfide and 8.6 mL (0.1 mol) of allyl bromide was added to a mixture of 5 mL (0.1 mol) hydrazine hydrate and 5.5 g (0.1 mol) KOH in

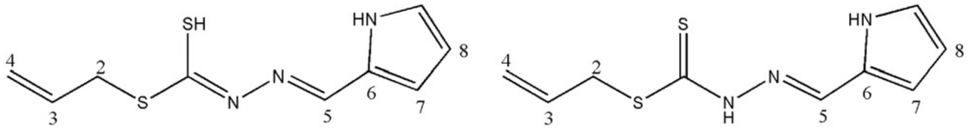
30 mL of ethanol at 5°C, with continuous stirring. The ethanolic solution (25 mL) of pyrrole-2-carboxaldehyde (9.51 g, 0.1 mol) was added to this mixture while heating. The brown product was separated by filtration, washed with water, and dried in a vacuum. HL was recrystallized from ethanol. Yield: 42% (based on aldehyde); m.p. 115°C. $C_9H_{11}N_3S_2$ (225.33 g mol^{-1}) (%), Anal. Calcd: C, 47.97; H, 4.92; N, 18.65; S, 28.46. Found: C, 47.11; H, 4.81; N, 18.25; S, 28.56. Mass spectrometry: $m/z = 225$, 184, 108, 93, 66, 41, and 28. ^{1}H NMR (100 MHz, $CDCl_3$, 25°C, TMS): $\delta = 3.98$ (d, 2H; C2), 5.28 (dd, 2H; C4), 5.8–6.2 (m, H; C3), 7.25 (d, H; C8), 7.55 (dd, H; C9), 7.95 (d, H; C7), 7.83 (s, H; C5), 9.05 (bs, H; NH), 10.99 (bs, H; pyrrole-NH).

2.4. *Preparation of bis[allyl-2-[1H-pyrrol-2-ylmethylidene]-1-hydrazinecarbodithioatonickel(II) ([Ni(L)$_2$], 2)*

An ethanolic solution (20 ml) of the ligand (0.225 g, 1 mmol) was mixed with a solution of $Ni(NO_3)_2 \cdot 6H_2O$ (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% (based on ligand); m.p. 139.5°C. $C_{18}H_{20}N_6NiS_4$ (507.35 g mol^{-1}) (%), Anal. Calcd: C, 42.61; H, 3.97; N, 16.56; S, 25.28. Found: C, 41.88; H, 3.87; N, 16.38; S, 24.79. Mass spectrometry: $m/z = 507$, 283, 224, 182, 151, 93, 79, 66, 41, and 28. ^{1}H NMR (100 MHz, $CDCl_3$, 25°C, TMS): $\delta = 3.65$ (d, 2H; C2), 5.3 (dd, 2H; C4), 5.7–6.3 (m, H; C3), 7.25 (d, H; C8), 7.75 (dd, H; C9), 7.94 (d, H; C7), 7.42 (s, H; C5), 10.70 (bs, H; pyrrole-NH). $\Lambda_m = 1.07\ \Omega^{-1}\,cm^2\,mol^{-1}$ in acetonitrile.

3. Results and discussion

As noted above, many studies have been reported on Schiff bases of S-methyl- and S-benzyl dithiocarbazate and their metal complexes, but S-allyl dithiocarbazate is a new series. A new bidentate Schiff base (**1**) having an NS donor atom set was synthesized from the condensation (1 : 1) of pyrrole-2-carbaldehyde and S-allyl hydrazinecarbodithioic acid. This Schiff base can also exhibit thione (**1a**) and thiol (**1b**) tautomerism since it contains the thioamide, –NH–C(=S)S functional group (scheme 1). For **1** and **2** the melting points, elemental analyses, ^{1}H NMR, mass, and percentage yields have been given in section 2. All the compounds are stable in air and are moderately soluble in organic solvents. The molar conductance value for **2** ($\Lambda_m = 1.07\ \Omega^{-1}\,cm^2\,mol^{-1}$) in CH_3CN solution shows neutral behavior. The analytical data for **2** indicate a metal:ligand molar ratio of 1 : 2. The mass spectrometric data of **1** and **2** have been



1a **1b**

Scheme 1. The thione (**1a**) and thiol (**1b**) forms of **1**.

given in section 2. Both mass spectra exhibit parent ions at 225 and 507 m/z, respectively. For **1**, the main fragments at m/z 184, 108, 93, 66, 41, and 28 are attributed to $[\mathrm{C_4H_4N{-}CH{=}NN(H)CS_2}]^+$, $[\mathrm{C_4H_4N{-}CH{=}N_2H}]^+$, $[\mathrm{C_4H_4N{-}CH{=}N}]^+$, pyrrole$^+$, allyl$^+$, and $\mathrm{N_2}^+$, respectively. Complex **2** has main fragments at m/z 283, 224, 182, 151, 93, 79, 66, 41, and 28 that can be assigned for $[\mathbf{1}+\mathrm{Ni}]^+$, $[\mathbf{1}-1]^+$, $[\mathrm{C_4H_4N{-}CH{=}N{-}N(H)CSS}]^+$, $[\mathrm{C_4H_4N{-}CH{=}N{-}N(H)CS}]^+$, $[\mathrm{C_4H_4N{-}CH{=}N}]^+$, $[\mathrm{C_4H_4N{-}CH}]^+$, pyrrole$^+$, allyl$^+$, and $\mathrm{N_2^+}$, respectively.

3.1. *Infrared spectra*

IR spectra of **1** (table 2) show bands at 3108 and 3390 cm^{-1} attributed to the *sec* NH group of the thione form and pyrrole ring, respectively. The spectra in the solid state display the ν(NH) band at 3108 cm^{-1} but do not show ν(SH) at 2700 cm^{-1}, indicating that in the solid state they remain as the thioketo tautomer (**1b**) [16]. On metal complexation, the ligand is uninegatively thiol, involving deprotonation of NH (**1a**). The compound **1** also showed ν(C=S) mode at 1103 cm^{-1}. The ν(C=S) is observed in the free ligand and disappears in the complex, supporting the coordination of a thiolate S to the metal. Coordination of the azomethine nitrogen to Ni(II) is apparent by the red-shift of the ν(C=N) band (*ca* 17 cm^{-1}). The ν(NN) band shows a red shift (*ca* 11 cm^{-1}) in the complex, which provides further evidence for involving the azomethine nitrogen in the coordination.

The ν(NH) band (3108 cm^{-1}) disappears in the IR spectra of **2**, suggesting that the proton attached to the α-nitrogen atom is lost upon complexation [17]. This coordination is confirmed by the presence of two bands at 347 and 432 cm^{-1}, which can be assigned to metal-sulfur and metal-nitrogen stretching modes, respectively [18]. The pyrrole ν(NH) band at 3368 cm^{-1} indicates that the pyrrole nitrogen is not involved in coordination in **2**.

3.2. *Electronic spectra*

The electronic spectra of **1** and **2** recorded in $\mathrm{CHCl_3}$ are summarized in table 2. The higher energy $\pi \rightarrow \pi^*$ band at 240 nm may be related to the pyrrole ring, which is not affected by complexation. The electronic spectra of **1** exhibit two intra-ligand $n \rightarrow \pi^*$ bands at *ca* 357 and *ca* 426 nm. The band at 357 nm is for both the pyrrole ring and imine function of the dithiocarbazate moiety. The lower energy band at 426 nm results from the thioamide portion of the dithiocarbazate moiety. The thioamide

Table 2. Main IR spectral vibrations (cm^{-1}) and electronic spectral data.

	IR bands[a]							Electronic spectra
Compound	NH ring	NH	C=N	C=S	NN	Ni–N	Ni–S	$\lambda_{\max}$ ($\log \varepsilon$)[b]
1	3390	3108	1606	1103	1021	–	–	241(5.23), 357(5.84), 426(3.76)
2	3368	–	1589	–	1010	432	326	240(5.81), 236(5.87), 386(4.47), 439(4.39)

[a] Wavenumbers are in units cm^{-1}.

[b] Units of $\lambda_{\max}$ are in nm and $\log \varepsilon$ (L mol^{-1}cm^{-1}) are given in parentheses.

$n \rightarrow \pi^*$ intra-ligand bands are shifted to high energy (blue shift) on the coordination of the thiol sulfur [19].

The band at approximately 439 nm can be assigned to the $S \rightarrow M^{II}$ charge transfer. The appearance of this LMCT band in Ni(II) complexes is also strong evidence that Ni(II) is coordinated to sulfur through the thiol sulfur. The d^8 square planar complexes are expected to exhibit three spin-allowed d–d bands in their electronic spectra, corresponding to $^1A_{1g} \rightarrow {}^1A_{2g}$, $^1A_{1g} \rightarrow {}^1B_{1g}$, and $^1A_{1g} \rightarrow {}^1E_g$ transitions. But, the presence of chalcogen donor in **1** brings about strong CT band in the complex, the tail of which generally extends up to the visible portion of the spectrum with the result that no d–d bands are generally observed in the electronic spectra of **2** [20].

3.3. *NMR studies*

The main parameters of ^1H NMR spectra are explained in section 2. The spectra of **1** and **2** were recorded in $CDCl_3$. The assignments are based on those for similar Schiff bases [21]. The ^1H NMR spectrum of **1** does not show a signal at *ca* δ 4.00 ppm attributed to the S–H proton, confirming that the thiolo tautomer (**1a**) is not present in solution [22].

The ^1H NMR of **1** shows peaks at 10.99 and 9.05 ppm attributed to the resonance of NH of pyrrole ring and thioamide, respectively. These peaks disappear upon deuteration. In the ^1H NMR spectrum of **2**, the absence of a signal of –NH (thioamide), found at 9.05 ppm for **1**, confirms deprotonation, followed by coordination to Ni center as a uninegative ligand. The pyrrole shows three peaks C(9) at 6.95, C(8) at 6.25, and C(7) at 6.55 ppm in **1** which are not affected by complexation. Similarly, the allyl group has three peaks C(2) at 3.98, C(3) at 5.8–6.2, and C(4) at 5.3 ppm in **1** and only C(2) undergoes upfield shift.

The narrow ^1H NMR spectra of **2** indicate that the nickel complexes are diamagnetic, with square-planar N2S2 coordination [23].

3.4. *Crystal structures of 1 and 2*

The molecular structures in the crystal were determined by single crystal X-ray diffraction for both compounds and ORTEP drawings are shown in figures 1 and 2.

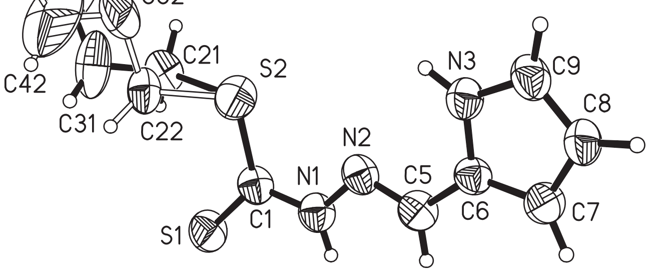


Figure 1. ORTEP diagram of **1** showing the atom labeling scheme and displacement ellipsoids are drawn at the 30% probability level. Note the one-to-one disorder of the S-allyl groups.

A list of the main interatomic distances and angles is reported in table 3. Compounds **1** and **2** crystallize in the tetragonal space group *$P4_2/n$* and the monoclinic space group *$P2_1/c$*, respectively. In **1**, the β-nitrogen and the thioketo S are in the *trans* configuration, namely in E form around C(1)–N(1). The charge delocalization in the C6=N2–N3=C1–S1 moiety can be recognized from the bond lengths of the S1–C1, N3–C1, N2–C6 and the planarity of the fragment. Intermolecular hydrogen bonds, which link two molecules as a dimer in the solid state of free ligand, are shown in figure 3.

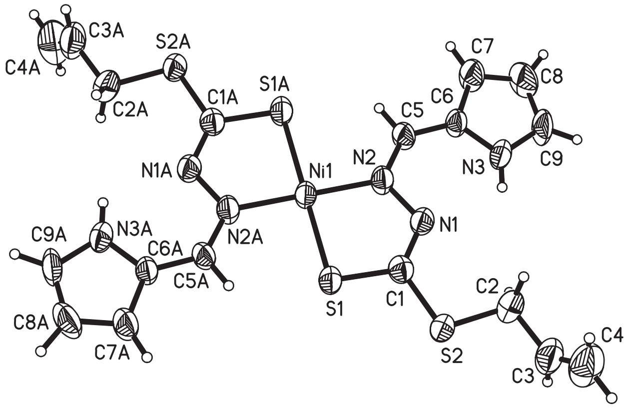


Figure 2. ORTEP diagram of **2** showing the atom labeling scheme and displacement ellipsoids are drawn at the 30% probability level; symmetry code: $A = -x, -y+1, -z+1$.

Table 3. Selected bond lengths (Å) and angles (°) for **1** and **2**.

Bond length	1	2	Bond angle	1	2
S(1)–C(1)	1.637(3)	1.720(14)	C(1)–S(2)–C(21/22)	104.3(5)	105.3(7)
S(2)–C(1)	1.725(3)	1.723(15)	C(1)–S(2)–C(22)	98.6(3)	
S(2)–C(21/22)	1.777(11)	1.750(16)	C(1)–N(1)–N(2)	122.3(3)	113.0(10)
S(2)–C(22)	1.831(10)		C(5)–N(2)–N(1)	115.6(3)	111.7(11)
N(1)–C(1)	1.329(3)	1.306(16)	C(9)–N(3)–C(6)	109.2(3)	109.3(13)
N(1)–N(2)	1.362(3)	1.409(14)	N(1)–C(1)–S(1)	121.4(3)	122.6(11)
N(2)–C(5)	1.258(3)	1.299(15)	N(1)–C(1)–S(2)	112.5(2)	122.0(10)
N(3)–C(9)	1.338(3)	1.350(17)	S(1)–C(1)–S(2)	126.1(2)	115.3(9)
N(3)–C(6)	1.360(3)	1.356(16)	C(31/32)–C(21/22)–S(2)	108.9(8)	108.1(11)
C(21/22)–C(31/32)	1.500(4)	1.487(9)	C(41/42)–C(31/32)–C(21/22)	106.0(9)	121.6(19)
C(31/32)–C(41/42)	1.300(4)	1.271(10)	C(32)–C(22)–S(2)	104.3(7)	
C(22)–C(32)	1.500(4)		C(42)–C(32)–C(22)	106.6(8)	
C(32)–C(42)	1.300(4)		N(2)–C(5)–C(6)	121.1(3)	132.3(14)
C(5)–C(6)	1.403(4)	1.400(17)	C(7)–C(6)–N(3)	105.3(3)	106.7(13)
C(6)–C(7)	1.349(4)	1.379(19)	C(7)–C(6)–C(5)	132.1(4)	125.8(14)
C(7)–C(8)	1.368(4)	1.34(2)	N(3)–C(6)–C(5)	122.6(3)	127.5(13)
C(8)–C(9)	1.326(4)	1.33(2)	C(6)–C(7)–C(8)	109.9(3)	106.8(15)
Ni(1)–N(2)		1.919(10)	C(9)–C(8)–C(7)	106.4(3)	110.3(14)
Ni(1)–S(1A)		2.169(4)	C(8)–C(9)–N(3)	109.2(3)	106.9(14)
			S(1A)–Ni(1)–N(2A)		85.8(3)
			S(1)–Ni(1)–N(2A)		94.2(3)
			C(1)–S(1)–Ni(1)		97.3(6)
			C(5)–N(2)–Ni(1)		127.7(9)
			N(1)–N(2)–Ni(1)		120.6(8)

Symmetry code: $A = -x, -y+1, -z+1$.

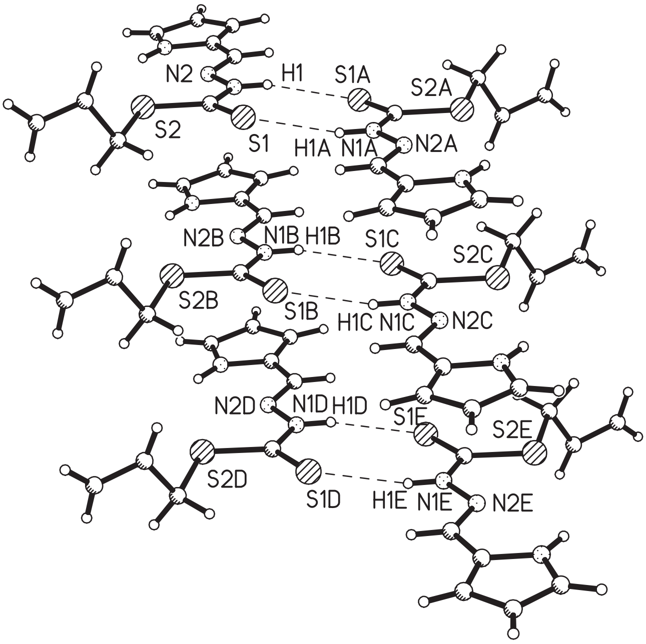


Figure 3. Stacking of the hydrogen bonded dimers of **1** in the crystal; symmetry code: $A = -x+1, -y, -z+1$; molecules having the codes B and C, and D and E, respectively, are generated by subsequent translations along the [0 0 1]; hydrogen bond parameters: N1–H1 0.86 Å, H1 $\cdots$ S1A 2.51 Å, N $\cdots$ S1A 3.338(3) Å, N1–H1 $\cdots$ S1A 162.3°; selected distances to the best plane defined by S1, S1A, N1 and N1A: S1B 3.451 Å, N1B 3.451 Å, N2B 3.535 Å, N3B 3.670 Å, S2C 2.885 Å, S1C 3.453 Å, N3C 3.233 Å, N1C 3.451 Å, N2C 3.367 Å.

Complex **2** has crystallographically imposed centrosymmetry with the metal at the inversion center. The monodeprotonated bidentate ligand shows a *cis*-configuration for its coordinating nitrogen (N2) and sulfur (S1) to make the four-coordinate nickel(II) square planar. In the free Schiff base, however, these centers have a *trans*-configuration (*Z* form), which indicates that complexation occurs after rotation around the C1–N1 and N2–C5 bonds by 180° [24]. As the ligand is deprotonated at N1, a negative charge is delocalized along the dithiocarbazate moiety, confirmed by differences between bond lengths in the deprotonated ligand of **2**: S1–C1 1.720(1) Å (thiolato form); C1–N1 1.306(2) Å and C5–N2 1.299(2) Å, and the respective bond lengths in the free Schiff base **1**: S1–C1 1.637(3) Å (thione form); C1–N1 1.329(3) Å and C5–N2 1.258(3) Å.

The nickel(II) coordination in **2** is almost square planar with S1A–Ni1–S1 and N2A–Ni1–N2 angles of 180° (*trans* configuration). The Ni–N bond in **2**, as expected, is significantly shorter than the Ni–S bond so that the coordination geometry of the metal is more rectangular than square. The *cis* bond angles in **2** are 85.8(3) and 94.2(3)°. The loss of the proton bound to N(1) in **1** produces a negative charge, which is delocalized on the C(1)–N(1)–N(2) system showing an elongation on S(1)–C(1) in **2**. The important difference may be due to the distance around C(1). In the free Schiff base (**1**), the C(1)–N(1) 1.329(3) and C(1)–S(1) 1.637(3) Å distances suggest that C(1)–N(1) is a single bond and C(1)–S(1) a double bond. In the complex, the distances C(1)–N(1) 1.306(2) and C(1)–S(1) 1.720(14) Å suggest that C(1)–N(1) is the double bond and C(1)–S(1) is the single bond. The decrease in the bond length of C(1)–N(1) and increase in the bond length of C(1)–S(1) in **2** confirm that the ligand coordinates to the metal through the sulfur after deprotonation. The bond lengths S(2)–C(1) (1.725(3) Å), N(3)–C(6) (1.356(2) Å), C(21)–C(31) (1.500(1) Å), C(22)–C(32) (1.500(1) Å), C(5)–C(6) (1.403(4) Å), and C(8)–C(9) (1.326(4) Å) in **1** and S(2)–C(1) (1.723(2) Å), N(3)–C(6) (1.356(2) Å), C(2)–C(3) (1.487(9) Å), C(2)–C(3) (1.487(9) Å), C(5)–C(6) (1.400(2) Å), and C(8)-C(9) (1.330(2) Å) in **2** are almost identical.

4. Conclusion

A new S-allyldithiocarbazate Schiff base as a NS bidentate donor (**1**) and its Ni(II) complex (**2**) with a square planar geometry were prepared and their structures were determined by crystal X-ray analysis. The spectroscopic characterization (IR, ^{1}H NMR, UV-Vis, and Mass) showed that the Schiff base is in the thione form in solid state. In case of **2**, both ligand molecules are in deprotonated thiol form functioning as a uninegative bidentate agent. In the free ligand, the β-nitrogen and the thioketo S are in the *trans* configuration, namely in E form around C(1)–N(1), but in the NiL_2 complex in Z form after a 180° rotation around the C1–N1 and N2–C5 bonds during complexation.

Supplementary material

Crystallographic data have been deposited with the CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (Fax: +44-1223-366033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) and are available on request, quoting the deposition number 695637 and 695638 for the ligand **1** and complex **2**, respectively.

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