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Molecular structures and spectroscopic characterization of cobalt(III) and nickel(II) complexes of *N*-(2-hydroxyethyl)-2-(thiophene-2-ylmethylene)-hydrazinecarbothioamide

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Abstract Two complexes of a thiosemicarbazone ligand, namely *N*-(2-hydroxyethyl)-2-(thiophene-2-ylmethylene)-hydrazinecarbothioamide (HL), have been synthesized. The complexes have been characterized by physico-chemical and spectroscopic methods. The crystal and molecular structures of $[CoL_3]\cdot 2MeOH$ (**1**) and $[NiL_2]$ (**2**) have been determined by X-ray diffraction studies. For both complexes, the metal is coordinated through the sulfur and azomethine nitrogen atoms of the thiosemicarbazone. The ligand exists in its thiolate tautomeric form, and the central Co(III) and Ni(II) atoms have distorted octahedral and square planar geometries, respectively, with five-membered chelate rings formed by the ligand. The lattice of **1** shows infinite oxygen donor/acceptor hydrogen bonds in the *ab* plane and weak interactions between rings along the *c* axis, respectively, giving a supramolecular network. The molecular units in **2** are linked together by hydrogen bonds between the hydroxyl oxygen and hydrazone N proton, giving rise to an infinite ribbon extended along the *c*-axis. These chains are connected by N3–H3···O1 interactions that form a sheet within the *ac* plane.

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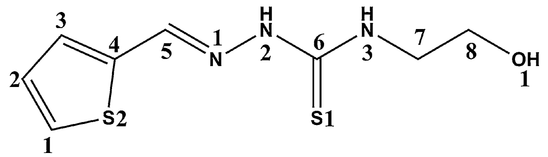
Introduction

Thiosemicarbazones with nitrogen and sulfur as hard and soft donor atoms, respectively, show reasonable ability to form coordination compounds with main and transition metals as multidentate ligands [1–3]. Furthermore, the presence of sulfur in these compounds often donates considerable pharmacological properties that include insulin-like activity [4], antineoplasic [5, 6], tuberculosis drugs [7, 8], anticancer [9], antibacterial [10], antifungal activity [11] and anti-HIV activity [12, 13].

The activity of thiosemicarbazones depends very much on the parent aldehyde or ketone and is also affected by the presence of *N* substitution [14]. In recent years, some structural and spectral studies on thiophene-derived thiosemicarbazones have been undertaken [15–20].

Crystal engineering is concerned with the synthesis of functional solid-state structures, based on a bottom-up approach from smaller building blocks. Typical design strategies use hydrogen bonds and coordinate bonds, which define substructural units that are called respectively, supramolecular synthons and secondary building units. For this purpose, we need appropriate functional groups in order to create suitable intra- and intermolecular interactions for supramolecular networks.

In order to achieve as appropriate structure for supramolecular synthons, we have designed a new ligand containing a hydroxyl group in the tail end. The new bidentate NS donor ligand *N*-(2-hydroxyethyl)-2-(thiophene-2-ylmethylene)-hydrazinecarbothioamide (HL) (Scheme 1) and its Co(III) and Ni(II) complexes have been synthesized



Scheme 1 The thione and thiol form of free thiosemicarbazone ligand

and characterized with the usual spectroscopic methods. In addition, the crystal structures of the complexes $[CoL_3]\cdot 2MeOH$ (**1**) and $[NiL_2]$ (**2**) are described.

Experimental

All chemicals were analytical grade and unless otherwise specified, were used as received. Elemental analyses (CHNS) were carried out with a Thermo Finnigan Flash Elemental Analyzer 1112EA. The molar conductance values of 10^{-3} M solutions of the complexes were measured in DMF with a Metrohm 712 Conductometer. IR spectra (KBr pellets) were recorded with a FT-IR 8400-SHIMADZU spectrophotometer (4,000–400 cm^{-1}). ^{1}H and ^{13}C NMR spectra were recorded at 25 °C with Bruker BRX 100 AVANCE and Bruker BRX-300 AVANCE spectrometers, respectively. The electronic spectra were recorded in DMF with a SHIMADZU model 2550 UV–Vis spectrophotometer (260–900 nm). Diffraction data were measured using an Oxford Diffraction Gemini Ultra diffractometer.

Synthesis of *N*-(2-hydroxyethyl)-2-(thiophene-2-ylmethylene)-hydrazinecarbothioamide, HL

Methyl 1-(thiophene-2-ylmethylene)-hydrazinecarbodithioate was prepared using a reported procedure [21]. For preparation of HL, a solution of methyl 1-(thiophene-2-ylmethylene)-hydrazinecarbodithioate (1.7 g, 7.86 mmol) in ethanol (10 ml) was treated with 2-aminoethanol (0.5 ml, 7.86 mmol) and refluxed for 72 h. The solution was chilled (overnight), and the pale yellow solid precipitate was collected by filtration and washed well with cold ethanol. The compound was recrystallized from ethanol and dried in vacuum over silica gel.

HL: pale yellow, Yield: 0.93 g (52%). m.p.: 147.5 °C. Anal. Found for $C_8H_{11}N_3OS_2$ (229.3 g mol^{-1}): C, 41.6; H, 4.8; N, 19.1; S, 27.1%. Calcd.: C, 41.9; H, 4.8; N, 18.3; S, 28.0%. IR spectrum in KBr, cm^{-1}: ν(OH) 3358w, ν(NH) 3165, 3,053 m, ν(C=N) + ν(C=C) + δ(N–H) 1547 s, ν(C=S) 1,277 m, ν(C–O) 1,225 m, ν(C–N) 1,128 m, ν(N–N) 1051 s, δ(C–S) 869w, ρ(ring) 623 s. UV/Vis (DMF), λ_{max}, nm (logε, L mol^{-1} cm^{-1}): 269 (4.70), 334 (4.71), 350 (4.59). ^{1}H NMR (300 MHz, DMSO-d_6): δ = 11.54 (s, 1H, N^2H; exchangable with D_2O), 8.25 (s, 1H, C^5H), 7.65 (d, 1H, C^1H), 7.43 (d, 1H, C^3H), 7.11 (t, 1H, C^2H), 4.85 (s, 1H, N^3H; exchangable with D_2O), 3.58 (s, 5H, $C^7H_2C^8H_2O^1H$; OH exchangable with D_2O). ^{13}C NMR (300 MHz, DMSO-d_6): δ = 177.16 (C^6), 139.01 (C^4), 137.89 (C^3), 131.18 (C^1), 129.23 (C^2), 128.44 (C^5), 59.69 (C^8), 46.41 (C^7).

tris(*N*-(2-hydroxyethyl)-2-(thiophene-2-ylmethylene)-hydrazinecarbothioamido) cobalt(III)

A solution of HL (0.46 g, 3 mmol) was mixed with $Co(OAc)_2$. $4H_2O$ (0.25 g, 1 mmol) in ethanol (10 mL). The mixture was stirred at room temperature for 4 h. To prevent the formation of a sticky product, the solution was kept at 60 °C for a week and the precipitate was then filtered off, washed with ethanol and dried in vacuum.

Dark brown, Yield: 0.48 g (64% based on HL). m.p.: 210 °C. molar conductance (10^{-3} M, DMF) 10 ohm^{-1} cm^2 mol^{-1}. Anal. Found for $C_{24}H_{30}CoN_9O_3S_6$ (746.90 g mol^{-1}): C, 37.6; H, 4.4; N, 16.7; S, 25.0%. Calcd.: C, 38.8; H, 4.1; N, 16.9; S, 25.9%. IR spectrum in KBr, cm^{-1}: ν(OH) 3,319 m, ν(NH) 3070w, ν(C=N) 1566 s, ν(C=N) + ν(C=C) + δ(N–H) 1500 s, ν(C=S) 1,251 m, ν(C–O) 1,251 m, ν(C–N) 1220w, ν(N–N) 1,057 m, δ(C=S) 833w, ρ(ring) 675 m. UV/Vis (DMF), λ_{max}, nm (logε, L mol^{-1} cm^{-1}): 270 (4.57), 334 (4.51), 368 (4.49)sh, 591 (2.61). NMR (100 MHz, DMSO-d_6): δ = 8.3 (s, 1H, C^5H), 7.85 (d, 1H, C^1H), 7.1 (d, 1H, C^3H), 7.5 (t, 1H, C^2H), 4.7 (s, 1H, N^3H; exchangable with D_2O), 3.5–3.29 (s, 5H, $C^7H_2C^8H_2O^1H$; OH exchangable with D_2O).

bis(*N*-(2-hydroxyethyl)-2-(thiophene-2-ylmethylene)-hydrazinecarbothioamido)nickel(II)

To a solution of HL (0.46 g, 2 mmol) in 10 mL ethanol, $Ni(OAc)_2$. $4H_2O$ (0.25 g, 1 mmol) was added. The mixture was vigorously stirred and refluxed in water bath for 2 h. After cooling to room temperature, the precipitate was collected by filtration, washed well with cold ethanol and dried in vacuum over silica.

Dark brown, Yield: 0.08 g (66% based on HL). m.p.: 225 °C. molar conductance (10^{-3} M, DMF) 9 ohm^{-1} cm^2 mol^{-1}. Anal. Found for $C_{16}H_{20}N_6NiO_2S_4$ (515.32 g mol^{-1}): C, 37.3; H, 3.9; N, 15.0; S, 20.9%. Calcd.: C, 37.2; H, 3.8; N, 16.3; S, 24.9%. IR spectrum in KBr, cm^{-1}: ν(OH) 3,201 m, ν(NH) 3,030 m, ν(C=N) + ν(C=C) + δ(N–H) 1510 s, ν(C=S) 1,288 m, ν(C–O) 1,244 m, ν(C–N) 1205w, ν(N–N) 1,066 m, δ(C=S) 840w, ρ(ring) 623w. UV/Vis (DMF), λ_{max}, nm (logε, L mol^{-1} cm^{-1}): 267 (4.59), 337 (4.52), 359 (4.50)sh, 382 (4.44)sh, 618 (2.30). ^{1}H NMR (100 MHz, DMSO-d_6): δ = 7.9 (d, 1H, C^1H), 7.72 (s, 1H, C^5H), 7.6 (d, 1H, C^3H), 7.15 (t, 1H, C^2H), 4.7 (s, br, 1H, N^3H; exchangable with D_2O), 3.6–3.3 (s, 5H, $C^7H_2C^8H_2O^1H$; OH exchangable with D_2O).

Crystal structure determination

Single crystals of **1** and **2**, adequate for structural X-ray diffraction work, were obtained after slow diffusion of methanol into a DMF solution of complex **1** and slow evaporation of the solution of **2**, respectively. Data were collected with an Oxford Diffraction Gemini Ultra diffractometer at 150.0 K and graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) in the ω scan mode.

Crystal data, experimental details and refinement results are listed in Table 1. The substantial redundancy in data allows multiscan absorption corrections using CrysAlis Pro [22]. The structure was solved by direct methods using the program SHELXS-97 [23] and refined on F^2 with anisotropic temperature parameters for all non-H atoms using the program SHELXL-97 [24]. The unit cell parameters were obtained by full-matrix least-squares refinements of 2857 and 2357 independent reflections for **1** and **2**, respectively. All non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located in a difference Fourier map, although they were positioned geometrically after each cycle of refinement.

Results and discussion

The elemental analyses data confirm the general empirical formulae. The complexes are insoluble in most common solvents. They are however soluble in DMF and DMSO. Based on elemental analysis, spectral, molar conductivity and X-ray studies, compounds **1** and **2** are found to have distorted octahedral and square planar geometries, respectively.

The numbering scheme used in the ^{1}H NMR spectrum of the free ligand is given in scheme 1, and data for the compounds are given in the "Experimental" section. The spectrum of the free ligand shows well-defined signals that indicate no fluxionality in solution. Signals at 11.54 and

Table 1 Crystal data and structure refinement details for **1** and **2**

Compound	1	2
Empirical formula	$C_{8.42}H_{11}Co_{0.33}N_3O_{1.42}S_2$	$C_8H_{10}ONi_{0.5}S_2N_3$
Formula weight	260.63	257.67
Temperature	150.0 K	150.0 K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Trigonal	Monoclinic
Space group	*R-3*	$P2_1/n$
Unit cell dimensions	$a = 15.3010(7)$ Å	$a = 6.5751(5)$ Å
	$b = 15.3010(7)$ Å	$b = 15.4777(11)$ Å, $\beta = 90.188(7)°$
	$c = 27.0067(15)$ Å	$c = 10.5270(7)$ Å
Volume	5475.7(5) Å^3	1071.31(13) Å^3
Z	18	4
Density (calculated)	1.423 Mg/m^3	1.598 Mg/m^3
Absorption coefficient	0.858 mm^{-1}	1.321 mm^{-1}
F(000)	2427	532
Crystal size	0.09 × 0.05 × 0.03 mm^3	0.14 × 0.05 × 0.04 mm^3
Theta range for data collection	3.16–29.30°	3.27–29.36°
Index ranges	$-19 \le h \le 12$,	$-4 \le h \le 8$
	$-18 \le k \le 20$,	$-7 \le k \le 20$
	$-32 \le l \le 36$	$-13 \le l \le 12$
Reflections collected	6893	3518
Independent reflections	2857 [$R_{(int)} = 0.0669$]	2357 [$R_{(int)} = 0.0201$]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2875/0/142	2357/0/135
Goodness-of-fit on F^2	1.119	0.961
Final R indices [$I >$ 2sigma(I)]	$R_1 = 0.0548$, $wR_2 = 0.1668$	$R_1 = 0.0302$, $wR_2 = 0.0656$
R indices (all data)	$R_1 = 0.0650$, $wR_2 = 0.1790$	$R_1 = 0.0374$, $wR_2 = 0.0671$
Largest diff. peak and hole	1.188 and −0.620 e.Å^{-3}	0.817 and −0.285 e.Å^{-3}

4.85 ppm are assigned to the N^2H and N^3H protons, respectively, which disappear on D_2O exchange. This is consistent with the presence of the thione form in solution. The downfield shift of N^2H may be attributed to hydrogen-bonding interactions in the solvent, suggesting the *Z*-form configuration in solution. The methine proton C^5H is observed at 8.25 ppm as a singlet. For the thiophene ring, a doublet at 7.65 ppm is assigned to the C^1H proton. The electronic effect of the adjacent electronegative thiophene sulfur shifts the C^1H proton downfield. The C^3H and C^2H signals are found at 7.43 and 7.11 ppm, respectively.

In the ^1H NMR spectra of the complexes, the signal of N^2H observed for free HL was absent, indicating coordination of the thiosemicarbazone in the anionic form with deprotonation at N^2. The very small shift of the N^3H resonance relative to the free ligand indicates that this nitrogen atom does not participate in coordination. However, the protons on the CH_2CH_2OH group, which do not take part in coordination, remain more or less unchanged in the complexes.

The ^{13}C NMR spectrum of the free ligand was recorded in DMSO, and the signals are in good agreement with the probable structure. Signals at 177.16 and 128.44 ppm are assigned to C^6 and C^5, respectively. The signals for C^3, C^1 and C^2 of the thiophene ring are at 137.89, 131.18 and 129.23, respectively. Finally, two CH_2 (C^8, C^7) are observed at 59.69 and 46.41 ppm, respectively.

The characteristic IR bands for the free ligand are different from the complexes and provide significant indications regarding the bonding sites of the ligand. IR spectral assignments for the ligand and the complexes are listed in the experimental section. The IR spectrum of HL does not exhibit a υ(S–H) band at around 2,500–2,700 cm^{-1}, suggesting that in the solid state, it remains in the thione form [25]. The IR spectrum of HL exhibits a band at 3,053 cm^{-1} assigned to $\upsilon(N^2\text{–}H)$, which is absent from the spectra of complexes, providing strong evidence for ligand coordination to the metal in the deprotonated thiolate form. The υ(C–S) vibration for the free ligand observed at 1,277 cm^{-1} is moved to 1,251, 1,288 cm^{-1} in the complexes, and these shifts support coordination through the sulfur atom in thiolate form [26]. Further, the absorption of HL at ca. 869 cm^{-1} is attributed to the δ(CS) vibration, and in the spectra of the complexes, it is shifted to lower frequencies (833, 840 cm^{-1}), showing coordination through the sulfur atom. The N–N stretching vibration of free HL at 1,051 cm^{-1} shifts to higher energy (1,057, 1,066 cm^{-1}) after coordination. Finally, a broad band at 3,319 and 3,201 cm^{-1} is assigned to the –OH stretch for complexes **1** and **2,** respectively.

The electronic spectral assignments of the free ligand and its complexes in DMF solution are given in the experimental section. In the spectrum of the free ligand, two bands at 350 and 334 nm are attributed to $n \rightarrow \pi^*$ transitions of thiophene and thioamide moieties, respectively. A band assigned to $\pi \rightarrow \pi^*$ transition at 269 nm in the spectrum of the free ligand shows no considerable shift after coordination. In the spectra of the complexes, a new band at 368 and 382 nm corresponding to S → M(d) LMCT charge transfer confirms that bonding of sulfur to the metal. The tailing of the charge transfer band into the visible region obscures the very weak d–d bands, so only one d–d transition is observed [27].

Single crystal X-ray diffraction analysis allowed structure determinations for both complexes. ORTEP plots of **1** and **2** shown in Figs. 1 and 2, respectively; and Table 2 shows important bond distances and angles.

Crystal structure of $[CoL_3]\cdot 2MeOH$

The brown–red crystals of complex **1** are trigonal, and the space group is R-3. The crystallographic analysis revealed that the asymmetric unit contains three molecules of the Co-complex $[CoL_3]$ and two disordered methanol molecules. $[CoL_3]$ has a slightly distorted octahedral geometry (N1–Co–S1 86.0(1)°, N1–Co–S1^i 91.0(1)°, N1–Co–N1^i 93.5(1)°, S1–Co–S1^i 89.52(5)°), in which the three thiosemicarbazone bidentate NS ligands in their thiol form (L^-) are chelated via their azomethine nitrogen N1 and thiol sulfur S1 donor atoms; thus each one forms a five-membered chelate ring, and the thiophene ring is pendant. The two donor nitrogen atoms N1 and S1 lie *cis* to each other with respect to the C6–N2 bond, and the structure is in *Z* conformation with respect to the C5–N1 bond.

The rms plane of the thiosemicarbazone moiety (N1N2C6S1N3) is approximately planar with a maximum deviation of 0.014 Å for N2. In comparison with this plane, the whole of the ligand is approximately planar with a maximum deviation of 0.026 Å for C5, except for the hydroxyethyl group which is situated out of this plane with 70.27°. The three thiosemicarbazone ligands are nearly perpendicular to each other (88.62°). The five-membered chelate ring Co1N1N2C6S1 is practically planar with a maximum deviation of 0.013 Å for C6.

The C6–S1 bond distance is (1.736(6) Å), with which is shorter than a C–S single bond of 1.82 Å but longer than a C=S double bond of 1.56 Å [28, 29]. This is an indication that there is some electron delocalization in the thiosemicarbazide chain, conferring a partial double bond character [30].

The oxidation state of 3+ for cobalt is shown by its coordination bond distances Co–S and Co–N, which are in the expected ranges of 2.222(1), 1.962(3) Å, respectively, as observed in several Co(III) complexes [31].

The packing of complex **1** shows noteworthy intermolecular O1-H1A···O1 contacts (2.687(4) Å, 156.83°) and vice versa hydrogen bonds that form a one dimensional chain. In Online Resource 1, two different color molecules

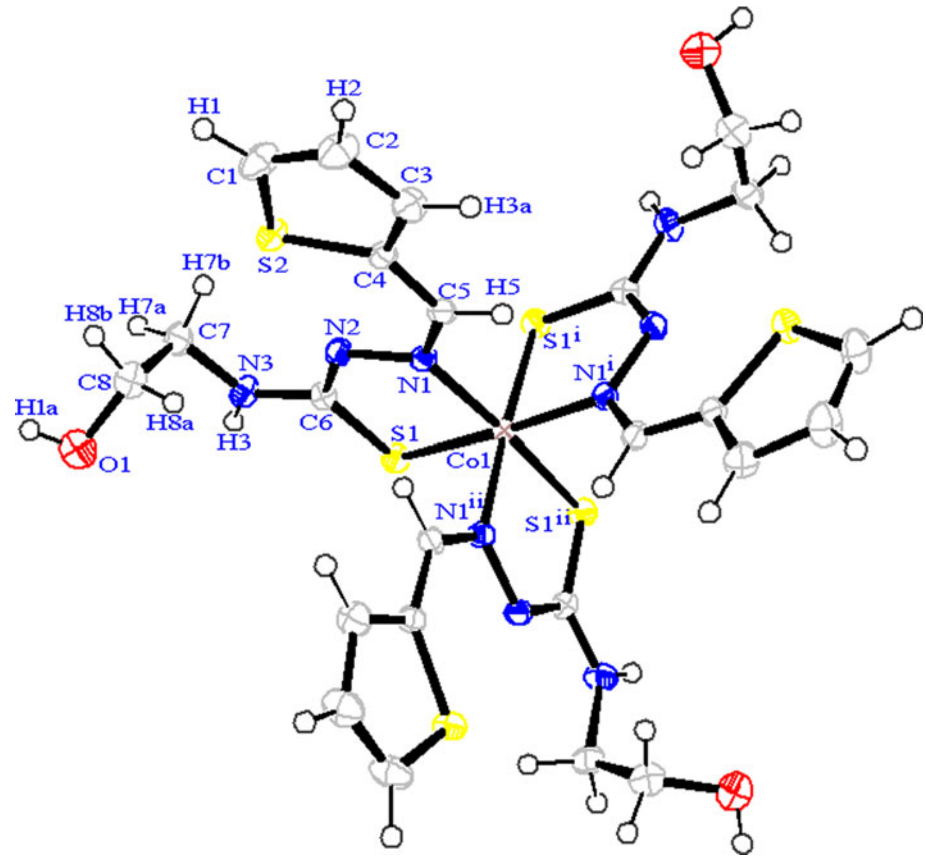


Fig. 1 Thermal ellipsoidal view of $[CoL_3]\cdot 2MeOH$ at 50% probability with atom numbering scheme. Two methanol molecules have been omitted for clarity

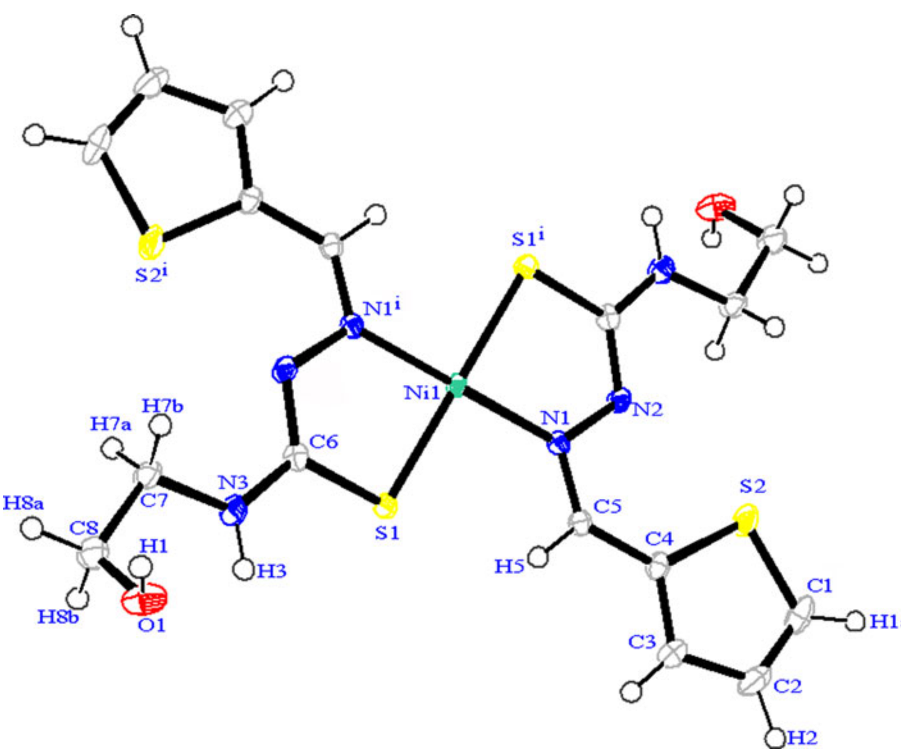


Fig. 2 ORTEP Diagram of $[NiL_2]$ showing the labeling scheme used and ellipsoids at 50% of probability

illustrate sorting molecules along the *b* axis. The 1D chains are held together in the crystal packing through an extended network of intermolecular hydrogen bonds involving the same groups and form a supramolecular two dimensional network in the *ab* plane (Online Resource 1). Six adjacent molecules are situated on hexangular vertices, and

Table 2 Selected bond lengths [Å] and angles [°] for **1** and **2**

	1	**2**
M–N1	1.962(3)	1.906(2)
M–S1	2.222(1)	2.1763(6)
C6–S1	1.736(6)	1.739(2)
C6–N3	1.377(5)	1.346(3)
C6–N2	1.306(5)	1.319(3)
C5–N1	1.299(5)	1.301(3)
N1–N2	1.387(5)	1.398(3)
S2–C1–C2–C3	1.704(5), 1.363(7), 1.403(5)	1.708(3), 1.354(4), 1.404(4)
C3–C4–S2	1.385(6), 1.733(5)	1.384(3), 1.728(2)
C4–C5	1.433(6)	1.431(3)
N3–C7–C8–O1	1.455(5), 1.490(7), 1.421(8)	1.460(3), 1.506(3), 1.424(3)
S1–M–N1^{i}	85.9(1)	85.88(6)
S1–M–S1^{i}	89.52(5)	180.00(2)
N1–M–N1^{i}	93.5(1)	180.00(8)
C5–N1–N2	114.0(3)	113.0(2)
N1–N2–C6	114.2(4)	112.2(2)
N2–C6–N3	117.7(4)	118.8(2)
C6–N3–C7	121.5(3)	122.4(2)
N3–C7–C8	112.9(4)	109.4(2)
C7–C8–O1	113.1(4)	116.6(2)

this sixfold unit repeats in the lattice. Finally, the molecular packing is completed with weak interactions (3.506 Å) between donor C3–H3 groups and the thiophene ring (C2, C3, C4) as acceptors to give a third dimension (Online Resource 2).

Crystal structure of [NiL_2]

The centrosymmetric structure of complex **2** consists of neutral molecules of [NiL_2], with nickel(II) at the centre of symmetry. The coordination environment around the nickel(II) center consists of a square planar of N_2S_2 arrangement. The compound crystallized in the monoclinic space group $P2_1/n$. The ligands are coordinated in their deprotonated imino-thiolate form (via azomethine nitrogen and thiolate sulfur atoms), and the donor atoms are arranged in a *trans*-planar configuration with a *Z* configuration around the C6–N2 bond. The Ni complex shows nonparticipation of the thiophene sulfur in the coordination to the central Ni atom.

As the ligand is deprotonated by loss of the N2-hydrogen atom, the resulting negative charge is delocalized along the thiosemicarbazone moiety, which is indicated by the intermediate C5=N1 (1.301(3) Å), N1–N2 (1.398(3) Å) and C6=N2 (1.319(3) Å) bond distances. The C6-S1 bond length is 1.739(2) Å, which is shorter than 1.82 Å for a C–S bond and longer than 1.56 Å for a C–S bond [28, 29], supporting the suggestion that the complex formation involves the ligand in its thiol form. Further, this bond length is longer than that of a typical C–S double bond found in free thiosemicarbazones e.g., 1.687(3) Å in 3-thiophenealdehyde thiosemicarbazone [20], 1.704(5) Å in ferrocene-1-carbaldehyde thiosemicarbazone [32], 1.704(3) Å 4-methylbenzaldehyde thiosemicarbazone [33] and 1.693(2) Å in (*E*)-4-octyloxybenzaldehyde thiosemicarbazone [34], which is another evidence for the thiolate form in the complex. The C5–N1 and C6-N2 bond distances are typical for double-bonded Schiff base compounds [17]. The mean Ni1–N1 and Ni1–S1 bond distances are 1.906(2) and 2.1763(6) Å, respectively, which agree with those found in the Cambridge Structural Database for square planar thiosemicarbazone nickel(II) complexes (Ni1–N1 1.84–1.93 Å and Ni1-S1 2.09–2.18 Å) and compare well with those of other square planar nickel(II) complexes with similar ligands [17, 18, 20, 35].

The angles S1Ni1S1 and N1Ni1N1 are 180°, but the other four angles (94.12° and 85.88°) that subtended at the nickel(II) atom all deviate from the values expected for an ideal square planar geometry. The thiophene rings are planar with a maximum deviation from the mean least-squares plane of 0.006 Å for C1; they form angles of 14.33° and 9.84° with the plane containing the metal atom, the chelating centers (S1N1Ni1S1N1) and the thiourea group (C5N1N2C6N3S1).

The crystal packing is governed by hydrogen-bonding interactions between the hydrazone hydrogen H3 with O1 and the hydroxyl hydrogen H1 with N2. These hydrogen bonds show distances of 2.807(3) and 2.878(3) Å and bond angles of 171.30° and 168.72°, respectively. In the lattice, O1-H1···N2 (2.878(3) Å, 168.72°) hydrogen bonding connects the hydroxyl group of one molecule to the hydrazone N2 of an adjacent molecule, giving a one dimensional ribbon along the *c* axis (Online Resource 3). These ribbons are linked by other hydrogen bonds, N3-H3···O1 (2.807(3) Å, 171.30°) in the *ac* plane, expanding the lattice into two dimensions (Online Resource 3). The Online Resource 3 shows the eight-membered rings formed by hydrogen bonding to give a supramolecular structure. There is no obvious 3D expansion, but a weak C1-H1A···C5 interaction along the *b* axis has been observed.

Conclusion

Two new complexes [CoL_3]·2MeOH and [NiL_2] of the novel ligand *N*-(2-hydroxyethyl)-2-(thiophene-2-ylmethylene)-hydrazinecarbothioamide (HL) were prepared. The

X-ray crystallography and spectral data show distorted octahedral and square planar geometries for complexes **1** and **2**, respectively. In both complexes, the ligand is coordinated in its thiolato form. Structural studies for compound **1** show that hydrogen bonds and weak C3-H3···ring interactions cause three dimensional supramolecular expansion of the structure. In complex **2**, O1-H1···N2 and N3-H3···O1 hydrogen bonds give rise to a supramolecular network. We are now trying to get high-quality single crystals of other transition metal complexes of this ligand in order to obtain their structural data for comparison with the complexes.

Supplementary materials

CCDC 768928 and 770567 contain the supplementary crystallographic data for complexes **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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