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Synthesis, structural study and X-ray structure determination of transition metal complexes of 4-phenyl-1-(1-(pyridin-2-yl) ethylidene)thiosemicarbazide

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Abstract: *Reaction of 4-phenylthiosemicarbazide and 2-acetylpyridine afforded the ligand 4-phenyl-1-(1-(pyridin-2-yl)ethylidene)thiosemicarbazide (H_2L). Reaction of H_2L and metal transition chloride salt in presence of potassium thiocyanate yield complexes formulated as $[Mn(HL)_2\cdot(SCN)]\cdot(H_2O)$ (**1**), $[Fe(HL)_2]\cdot(SCN)\cdot(H_2O)$ (**2**), $[Co(HL)(H_2L)]\cdot(SCN)\cdot(H_2O)$ (**3**), $[Ni(HL)(SCN)]$ (**4**), $\{[Cu(H_2L)\cdot(SCN))](\mu\text{-}NCS)_2[Cu(H_2L)\cdot(SCN)]\}\cdot(H_2O)_2$ (**5**), $[Zn(H_2L)(SCN)_2]$ (**6**). Elemental analysis, IR, UV, molar conductivity and room temperature magnetic moment measurements were used for characterizing these compounds. The structures of $[Fe(HL)_2]\cdot(SCN)\cdot(H_2O)$ (**2**) and $[Zn(H_2L)(SCN)_2]$ (**6**) were determined by X-ray diffraction technic. The two mononuclear complexes (**2**) and (**6**) crystallize in the monoclinic space group P21/c. In $[Fe(HL)_2]\cdot SCN\cdot H_2O$, the Fe^{3+} is hexacoordinated in an octahedral environment by two molecules ligand of H_2L which acts in tridentate fashion via one imino nitrogen atom, one pyridyl nitrogen atom and one sulfur atom; one SCN^- anion stabilize the complex and one lattice water molecule is present. In $[Zn(H_2L)(SCN)_2]$, the Zn^{2+} is pentacoordinated in a bipyramidal trigonal environment by one ligand molecule of H_2L which acts in tridentate fashion and two SCN^-.*

Keywords: *Iron, Zinc, Thiosemicarbazide, Thiocyanate, IR, UV, Crystal structure.*

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I. Introduction

The chemistry of metal-thiol compounds has attracted attention because of their utility as structural and functional models for metal-cysteine centers in metalloenzymes. Over the last few years, the synthesis of metal complexes containing mixed N/S-donors is engaged. Many complexes with N_2S, N_3S_2 and N_2S_3 donors are synthetized in the optic to get models for bacterial nitrile hydratase enzymes (NHase)[1-3], which catalyse the partial hydration of nitriles to amides. Novel orally active iron chelators with high iron mobilization efficacy and low toxicity suitable for the treatment of iron overload disease are designed and synthesized [4][4]. Thiosemicarbazone derivatives and their complexes have been widely studied due their applications in many fields such as biochemical [5], pharmacological [6] and as structural models for metalloenzymes [7]. In human body, traces of copper(II) and zinc(II) are largely present in many biomolecules and are essential for their biological properties [8-10]. Schiff base synthetized between aldehyde (or ketone) and thiosemicarbazone present a good coordination ability owing to the potential donor atoms (N, S) and the delocalization of the electronic density on the skeleton (R_1R_2)–C=N—NH—C(S)—NH—R_3. The nature of R_3 influence the delocalization and the coordination of the ligand. Aromatic ring extends the delocalization *via* the azomethine atom and can participate to the coordination if additional donor atoms are present as in the pyridyl ring. These kind of Schiff bases have versatile coordination behavior due to the both presence of hard and soft donor atoms. Upon reaction with metal transition different structure topologies [11-13] afforded. According to these considerations, our research group was motivated to design and synthesis of a ligand H_2L ((4-phenyl-1-(1-(pyridin-2-yl)ethylidene)thiosemicarbazide)) using 2-acetylpyridine and thiosemicarbazide (Scheme 1) and its mononuclear transition metal complexes in the presence of thiocyanate anion. The ligand H_2L can coordinate through the azomethine, the hydrazino nitrogen atom and the nitrogen pyridyl ring. The thiocyanate moiety can acts as conter-ion or as unidentate or bridged coordinated unit through the nitrogen atom and/or the sulphur atom. The spectroscopic properties of the complexes were studied and the X-ray structures of the Fe(II) and the Zn(II) complexes were determined. Considering the aforementioned concepts and as a way to extend our previous studies on the chemistry and magnetic studies in iron (III)-based compounds, we have focused on the study of thiocyanate as a bridging ligand [14]. The simultaneous presence of N and S donor atoms in the thiocyanate ligand would facilitate the development of a rich hetero-polynuclear chemistry when acting as a bridge and also would involve an enhancement of the magnetic coupling due to the diffuse character of the valence orbitals of the sulphur atom. This idea has been materialized in a recent communication where the authors reported a value of the magnetic interaction.

II. Experimental section

2.1. Starting materials and instrumentation

Commercially available 4-phenylthiosemicarbazide, 2-acetylpyridine, $M(NO_3)_2\cdot xH_2O$ (M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) and KSCN were purchased from Aldrich and used without further purification. Solvents were purified according to standard procedures. Elemental analysis of C, H and N was performed by the analytical laboratory of the Department of Inorganic Chemistry (University of Padua, Italy). FTIR spectra were recorded with a Nicolet 5SXC FT-IR spectrophotometer using KBr pellets. The UV-Vis spectra were run on a Perkin Elmer Two Spectrophotometer (1100–200 nm) on 10^{-3} M DMF solutions of the complexes. Molar conductance measurement was made using a WTW LF-330 conductivity meter with a WTW conductivity cell on about 1 mmol dm^{-3} dimethylformamide solution at room temperature. Room temperature magnetic susceptibility measurements were made on solid complex using a Johnson-Mathey Gouy balance with $Hg[Co(SCN)_4]$ as the calibrator. X-ray data were collected using a ENRAF NONIUS Kappa CCD diffractometer with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å) (Centre de Recherche de Gif, France).

2.2. Synthesis of the ligand 4-phenyl-1-(1-(pyridin-2-yl)ethylidene)thiosemicarbazide H_2L.

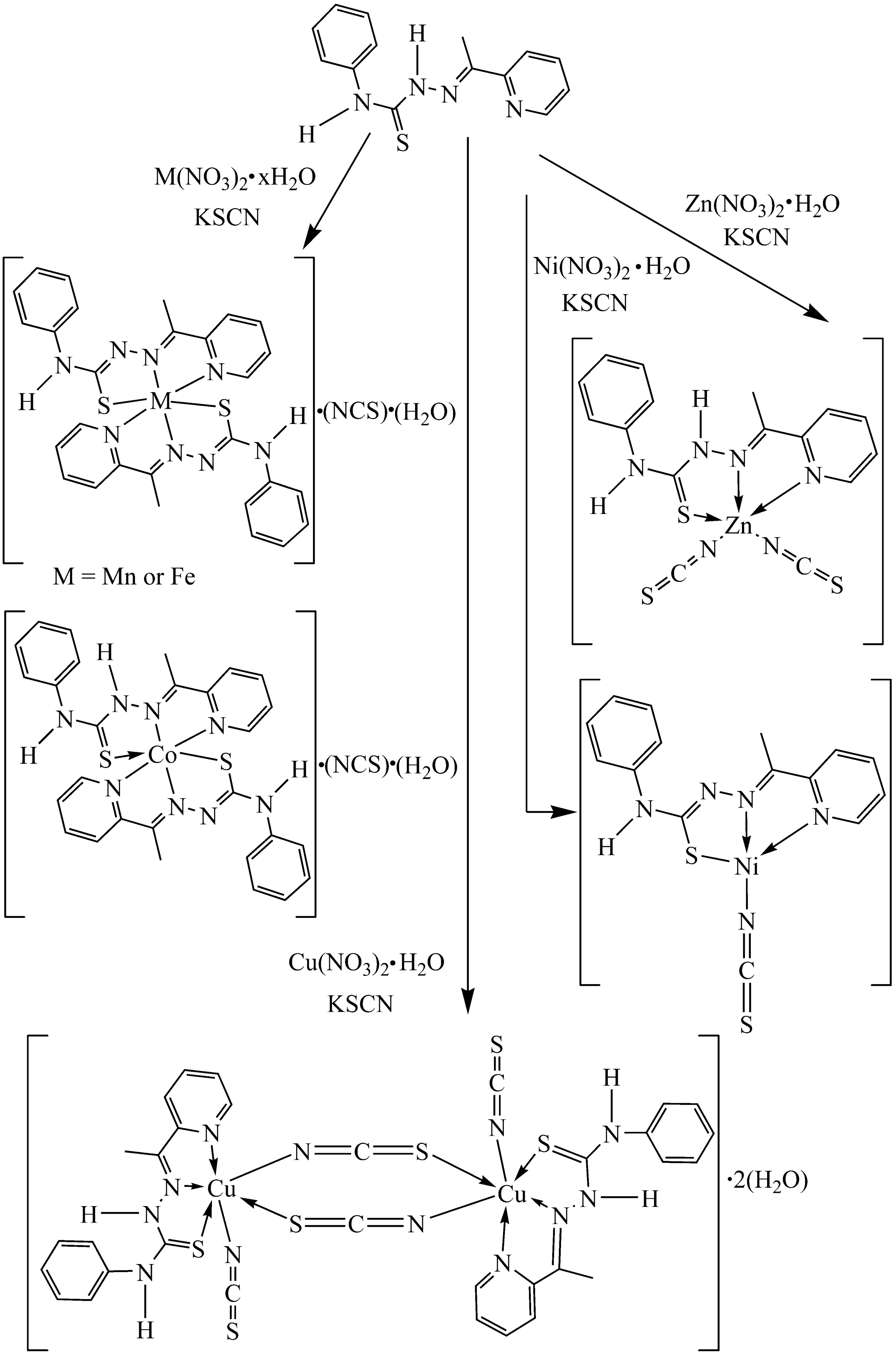
To a mixture of 1 g (5.9 mmol) of 4-phenylthiosemicarbazide in 10 mL of methanol was added a solution of 0.72 g (5.9 mmol) of 2-acetylpyridine and two drops of glacial acetic acid. The resulting mixture was stirred under reflux for 120 min. The resulting yellow (H_2L) solid was isolated by filtration and dried in air. MP 155°C. Yield 60.53 %. Analysis calculated for $C_{14}H_{14}N_4S$: C 62.20, H 5.22, N 20.72, S 11.86; found C 62.16, H 5.19, N 20.62, S 11.80. IR (ν/cm^{-1}): 3255 (N—H); 1596, 1548 (C=N) + (C=C), 1084 (N—N) and 781 (C=S). ^1H NMR (DMSO, 400 MHz, δ(ppm)): 2.71 (s, C**H**$_3$C=N, 3H), 6.78, 6.89 (Ph, 5H), 7.87–7.96 (m, Py 4H), 9.1 (s, N**H**Ph, 1H) and 9.29 (s, N**H**Ph, 1H). UV-Vis (MeOH) λ_{max} (nm): 233; 268.

2.3. Synthesis of the complexes (1-6).

To a suspension of H_2L (0.2 mmol) in MeOH was added a solution of $M(NO_3)_2\cdot xH_2O$ (0.2 mmol) and KSCN (0.6 mmol). The resulting mixture was stirred under reflux for 120 min. After cooling the colored solution was filtered off and left at room temperature. After three weeks crystals suitable for X-ray analyses was isolated by filtration and dried in air in case of the Fe(II) (red) and Zn(II) (yellow) complexes. For Co(II) (deep red), Mn(II) (yellow), Ni(II) (yellowish) and Cu(II) (brown) powder was isolated

$[Mn(HL)_2]\cdot(SCN)\cdot(H_2O)$ (**1**). Yield: 62.69 %. IR (cm^{-1}, KBr): 3400, 2050, 1560, 1540, 1517, 775. Analysis calculated for $C_{29}H_{28}N_9OS_3Mn$: C, 52.01; H, 4.21; N, 18.82; S, 14.36. Found: C, 52.08; H, 4.23; N, 18.29; S, 14.35. UV-Vis (MeOH) λ_{max} (nm): 233; 268; 420. $\mu_{eff} = 4.67\ \mu_B$. Λ_m ($S.m^2.mol^{-1}$): 25-65.

$[Fe(HL)_2]\cdot(SCN)\cdot(H_2O)$ (**2**). Yield: 52.12 %. IR (cm^{-1}, KBr): 3400, 2090, 1570, 1525, 1510; 835. Analysis calculated for $C_{29}H_{28}N_9OS_3Fe$: C, 51.94; H, 4.21; N, 18.80; S 14.34. Found: C, 51.99; H, 4.23; N, 18.76; S, 14.31. UV-Vis (MeOH) λ_{max} (nm): 232; 267; 384; 671. $\mu_{eff} = 5.5\ \mu_B$. Λ_m ($S.m^2.mol^{-1}$): 70-75.



Scheme 1. Synthetic scheme for complexes preparation

$[Co(HL)(H_2L)]\cdot(SCN)\cdot(H_2O)$ (**3**). Yield: 60.15 %. IR (cm^{-1}, KBr): 3400; 2060; 1570; 1525; 1510; 773. Yield: Analysis calculated for $C_{29}H_{29}N_9OS_3Co$: C, 51.62; H, 4.33; N, 18.68; S, 14.26. Found: C, 51.58; H, 4.28; N, 18.65; S, 14.23. UV-Vis (MeOH) λ_{max} (nm): 622, 242; 259; 303; 385. $\mu_{eff} = 6.38\ \mu_B$. Λ_m ($S.m^2.mol^{-1}$): 77-79.

[Ni(HL)(SCN)] (**4**). Yield: 53.94 %. IR (cm^{-1}, KBr): 3400, 2050, 1540, 1515, 775. Analysis calculated for $C_{15}H_{13}N_5S_2Ni$: C, 46.66; H, 3.39; N, 18.14; S, 16.61. Found: C, 46.63; H, 3.41; N, 18.10; S, 16.58. UV-Vis (MeOH) λ_{max} (nm): 232; 266; 339; 403. Diamagnetic. Λ_m ($S.m^2.mol^{-1}$): 11-15.

{$[Cu(H_2L)(SCN)_2]_2$}$\cdot(H_2O)_2$ (**5**). Yield: 42.29 %. IR (cm^{-1}, KBr): 3400, 2150, 2090, 1560, 1525, 1510, 776. Analysis calculated for $C_{32}H_{32}N_{12}O_2S_6Cu$: C, 41.06; H, 3.45; N, 17.95; S 20.55. Found: C, 41.02; H, 3.41; N, 18.00; S, 20.51. UV-Vis (MeOH) λ_{max} (nm): 235; 277; 321; 459; 601. $\mu_{eff} = 1.85\ \mu_B$. Λ_m ($S.m^2.mol^{-1}$): 5-8.

$[Zn(H_2L)(SCN)_2]$ (**6**). Yield: 61.96%. IR (cm^{-1}, KBr): 3308, 2035, 1530, 1510, 720. Analysis calculated for $C_{16}H_{14}N_6S_3Zn$: C, 42.52; H, 3.12; N, 18.60; S, 21.29. Found: C, 42.60; H, 3.09; N, 18.54; S, 21.35. Diamagnetic. UV-Vis (MeOH) λ_{max} (nm): 232; 266. Λ_m ($S.m^2.mol^{-1}$): 65-73.

2.4. X-ray data collection, structure determination and refinement

Details of the X-rays crystal structure solution and refinement are given in Table 1. Diffraction data were collected using an ENRAF NONIUS Kappa CCD diffractometer with graphite monochromatized MoKα radiation ($\lambda = 0.71073$ Å). All data were corrected for Lorentz and polarization effects. No absorption correction was applied. Complex scattering factors were taken from the program package SHELXTL [15]. Structure solution and refinement were performed using SHELXT [16] and SHELXL-2014/7 [17]. All hydrogen atoms were added in calculated positions and refined in riding mode on the parent atom. Molecular graphics were generated using ORTEP-3 [18].

Table -1. Crystallographic data and refinement parameters for the complexes (**2**) and (**6**).

Chemical formula	$C_{29}H_{28}FeN_9OS_3$ (**2**)	$C_{16}H_{14}ZnN_6S_3$ (**6**)
M_r	670.63	451.88
Crystal system,	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Temperature (K)	293	293
a (Å)	9.1324 (4)	12.7292 (7)
b (Å)	23.0081 (10)	9.0500 (4)
c (Å)	14.3600 (6)	16.9350 (8)
β (°)	91.340 (4)	98.144 (4)
V ($Å^3$)	3016.5 (2)	1931.22 (17)
Z	4	4
Radiation type	Mo Kα	Mo Kα
μ (mm^{-1})	0.75	1.61
Crystal size (mm)	0.30 × 0.25 × 0.15	0.30 × 0.20 × 0.15
No. of measured	27966	31994
independent	5480	7805
observed [$I > 2\sigma(I)$] reflections	4556	4286
Rint	0.071	0.032
$R[F^2 > 2\sigma(F^2)]$	0.049	0.045
$wR(F^2)$	0.125	0.152
Gof	1.09	1.04
No. of reflections	5480	7805
No. of parameters	430	236
No. of restraints	361	0
Δρmax, Δρmin (e $Å^{-3}$)	0.48, −0.30	0.46, −0.44

III. Result and discussion

3.1. General study

Reacting 4-phenylthiosemicarbazide and 2-acetylpyridine under reflux in methanol afforded the ligand 4-phenyl-1-(1-(pyridin-2-yl)ethylidene)thiosemicarbazide (H_2L). The reaction of H_2L and $M(NO_3)_2{\cdot}xH_2O$ in presence of KSCN in a 1:1:2 ratio in methanol produce pure precipitate ($M^{2+} = Mn^{2+}$, Co^{2+}, Ni^{2+}, Cu^{2+}) or crystal ($M^{3+} = Fe^{2+}$and $M^{2+} = Zn^{2+}$) suitable for X-ray analysis of metal complexes. These complexes are soluble in DMSO and DMF solvent. Elemental analysis are in accordance with theorical values calculated from the following formulation: $[Mn(HL)_2{\cdot}(SCN)]{\cdot}(H_2O)$ (**1**), $[Fe(HL)_2]{\cdot}(SCN){\cdot}(H_2O)$ (**2**), $[Co(HL)(H_2L)]{\cdot}(SCN){\cdot}(H_2O)$ (**3**), $[Ni(HL)(SCN)]$ (**4**), {$[Cu(H_2L){\cdot}(SCN))](\mu\text{-}NCS)_2[Cu(H_2L){\cdot}(SCN)]$}$\cdot(H_2O)_2$ (**5**), $[Zn(H_2L)(SCN)_2]$ (**6**). In complexes **1**, **2** and **3** the ligand acts as monoanionic tridentate ligand and in complexes **4**, **5** and **6** it acts as neutral tridentate ligand.

The infrared spectrum of the ligand H_2L reveals two bands at 3300 cm^{-1} and 3200 cm^{-1} attributed to the two H—N stretching vibrations. The bands in the range 1560-1520 cm^{-1} represent the combination of ν(C=C) +

ν(C=N). The band at 1280 cm^{-1} is assigned to ν(C=S) of the thiosemicarbazide moiety. Upon coordination some of these bands are shifted to low frequencies. For the complex **6** the band attributed to the H—N vibration is pointed at 3308 cm^{-1}. For all the others complexes an intense band appearing near 3400 cm^{-1} hide the bands of the N—H. This large band is due to the ν(O—H) + ν(N—H) vibrations. Additional band at 1560 cm^{-1} attributed to δ(O—H) confirms the presence of water molecule in complex (**1-3** and **5**). The absence of the bands and at 1560 cm^{-1} and 3400 cm^{-1} in the spectra of **4** are indicative of the absence of water molecule in the structure of the complex **4**. The band in the range 1050-1025 cm^{-1} are due to the vibration of the N—N bond. In all spectra (**1**-**6**) the stretching frequency of the C—S moiety is pointed in the range 835-720 cm^{-1}. Bands due to C=N groups are shifted to low frequency [1540-1510 cm^{-1}] indicating the involvement of the azomethine and the pyridine nitrogen in the coordination to the metal center. A strong and sharp band pointed in the region [2035-2090 cm^{-1}] in the spectra of the whole complexes is attributed to the thiocyanate moiety. Additional band at 2150 cm^{-1} is probably due to the presence of two modes of coordination of the SCN group in the complex **5**.

According to *Geary* [19], molar conductance of 10^{-3} M solutions in DMF at room temperature are in the range 65-90 ohm^{-1} cm mol^{-1} for 1:1 electrolyte, 130-170 ohm^{-1} cm mol^{-1} for 1:2 electrolyte and 200-240 ohm^{-1} cm mol^{-1} for 3:1 electrolyte. The complexes **2** and **3** are 2:1 electrolyte with conductance values respectively of 70 and 77 ohm^{-1} cm mol^{-1}. The complexes **1**, **4** and **5** are non-electrolytic nature with conductance values of 25, 11 and 5 ohm^{-1} cm mol^{-1} respectively. These complexes are stable in solution as indicated by the slight variation of the conductance values after two weeks. For the complex **6** the X-ray structure determination shows a neutral complex. In DMF solution, complex **6** is 1:1 electrolytic with conductance value of 65 ohm^{-1} cm mol^{-1} and remains unchanged after two weeks indicating a mono ionisation of the complex in solution. These observations are in accordance with the formulae suggested by analytical data and spectral studies.

Information on the geometry environment of the central metals in complexes can be obtained from the values of the magnetic moment. For the complex (**1**) an effective magnetic moment of 4.67 μ_B was obtained using the Gouy's balance method. This magnetic moment value is in good accordance with the expected value of 4.90 μ_B for a high spin d^4 configuration [20]. The formulation of the complex using spectroscopic methods and conductance measurement assume the complete oxidation of the Mn(II) into Mn(III) species indicating a passage of d^5 to d^4 configuration after complexation of manganese ion. The complex **2** showed magnetic moments of 5.5 μ_B. Fe^{3+} which is indicative of the presence of five unpaired electrons. In fact, iron complex in high-spin d^5 octahedral configuration give generally a magnetic moment value [21] close to the spin-only value of 5.90 μ_B. This observation is in accordance with the X-ray structure determination which show a d^5 configuration in octahedral environment. The room temperature magnetic moment of the cobalt complex (**3**) is 5.38 μ_B. This value is slightly higher than the value of 5.02 μ_B which is characteristic of high-spin octahedral Co(II) complex [22]. The nickel(II) complex (**4**) shows diamagnetism assuming the absence of unpaired electron. The complex is a low spin square planar geometry around the d^8 Ni(II) ion [23]. The copper(II) complex (**5**) exhibits magnetic moment value of 1.85 μ_B corresponding to one unpaired electron [21].

The electronic absorption spectra of the ligand and the complexes were recorded in methanol in the region 200–900 nm. The spectrum of the ligand shows two bands at 233 and 268 nm which are attributed to $\pi \rightarrow \pi^*$ transitions. In the electronic spectra of the complexes, intra-ligand $\pi \rightarrow \pi^*$ transitions appear in the region 233—267 nm [24]. In complexes **2**, **3**, **4** and **5**, the band observed respectively at 384, 385, 339 and 321 nm are attributed to the $n \rightarrow \pi^*$ transition thiosemicarbazide moiety [24]. Bands appearing at 420 nm for **1**, 403 nm for **4** and 459 nm for **5** are assigned to the ligand to metal charge transfer transitions [24]. The spectrum of **2** shows a low intensity d→d band at 671 nm which is characteristic of octahedral Fe(III) complex with a d^5 configuration [24]. The d→d band at 622 nm in the spectrum of **3** is indicative of a cobalt complex with distorted octahedral geometry [25]. In complex **5** a low intensity band pointed at 641 nm is attributed to the d→d transition of the copper(II) complex with a d^9 configuration in distorted octahedral environment [26].

Table-2: Selected bonds lengths (Å) and angles (°).

Fe1—N3	1.918 (2)	Zn1—N5	1.939 (2)
Fe1—N8	1.924 (2)	Zn1—N6	1.996 (2)
Fe1—N4	1.987 (2)	Zn1—N2	2.1287 (19)
Fe1—N9	1.988 (2)	Zn1—N1	2.149 (2)
Fe1—S2	2.2119 (9)	Zn1—S1	2.4707 (7)
Fe1—S1	2.2183 (9)	S1—C8	1.669 (2)
S1—C7	1.745 (3)	S3—C15	1.627 (3)
S2—C21	1.748 (3)	S2—C16	1.597 (3)
N3—Fe1—N8	174.96 (10)	N5—Zn1—N6	113.42 (11)

N3—Fe1—N4	80.25 (10)	N5—Zn1—N2	114.94 (10)
N8—Fe1—N4	104.64 (10)	N6—Zn1—N2	131.02 (9)
N3—Fe1—N9	101.58 (10)	N5—Zn1—N1	97.94 (10)
N8—Fe1—N9	80.34 (10)	N6—Zn1—N1	92.70 (10)
N4—Fe1—N9	84.34 (10)	N2—Zn1—N1	73.61 (8)
N3—Fe1—S2	94.33 (7)	N5—Zn1—S1	104.31 (8)
N8—Fe1—S2	84.51 (7)	N6—Zn1—S1	96.50 (8)
N4—Fe1—S2	90.25 (7)	N2—Zn1—S1	78.90 (5)
N9—Fe1—S2	162.03 (8)	N1—Zn1—S1	150.05 (6)
N3—Fe1—S1	84.80 (7)	N5—C16—S2	178.3 (3)
N8—Fe1—S1	90.50 (7)	N6—C15—S3	176.8 (3)
N4—Fe1—S1	163.46 (7)		
N9—Fe1—S1	91.82 (7)		
S2—Fe1—S1	97.93 (4)		

Table-3: Hydrogen bonds

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
Fer				
N1—H1N···O1W	0.844(18)	2.19(2)	3.013(5)	166(3)
N5—H5N···S3a^{i}	0.848 (18)	2.68(2)	3.494(4)	162(3)
N5—H5N···N6Bb^{i}	0.848(18)	1.96(4)	2.78(3)	161(4)
C6—H6···N2	0.93	2.30	2.906(4)	122.0
C9—H9A···S3Bb^{ii}	0.96	2.69	3.433(10)	134.5
C14—H14···S3a	0.93	2.98	3.743(4)	140.3
C28—H28···S3Bb^{ii}	0.93	2.98	3.757(9)	141.9
C27—H27···S3a^{ii}	0.93	2.93	3.693(4)	139.9
C23—H23C···N7^{iii}	0.96	2.49	3.437(4)	170.0
C20—H20···N7	0.93	2.34	2.919(4)	119.7
O1W—H1W1···N6a^{iii}	0.83(2)	1.80(2)	2.630(14)	176(13)
O1W—H1W1···S3Bb^{iii}	0.83(2)	2.84(3)	3.661(13)	174(12)
Zn				
N3—H0AA···S3^{iv}	0.86	2.62	3.398(2)	151.0
N4—H3AA···S3^{iv}	0.86	2.49	3.311(2)	158.9
C14—H1AA···S1	0.93	2.56	3.207(3)	127.3
C7—H8AA···S3^{v}	0.96	2.93	3.653(3)	133.1
C4—H1BA···S2^{vi}	0.93	3.00	3.732(4)	137.0

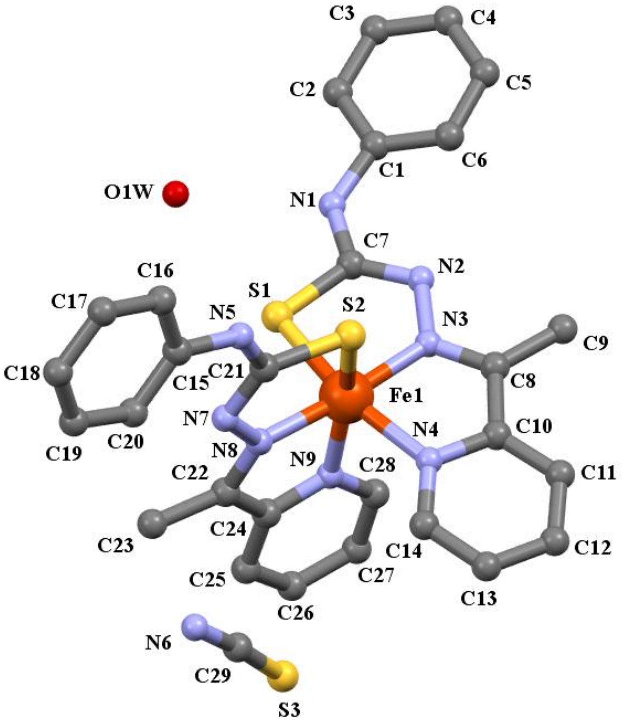
Symmetry codes: (i) x−1, y, z; (ii) x, −y+1/2, z+1/2; (iii) −x+1, −y+1, −z+1; (iv) −x+1, −y, −z+1; (v) x, −y−1/2, z−1/2; (vi) x, −y+1/2, z−1/2.

3.2. X-ray structures

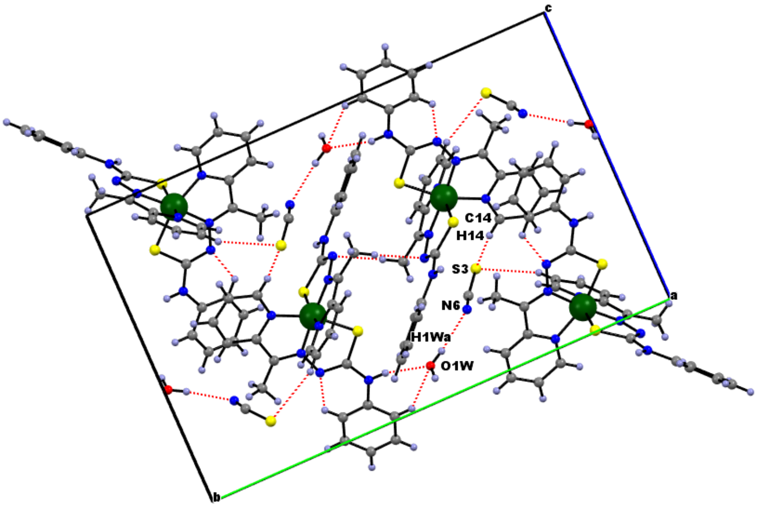
3.2.1. Complex 2

The title compound $[Fe(HL)_2]\cdot SCN\cdot H_2O$ (**2**) crystallizes in the monoclinic space group $P2_1/c$ with cell parameters a = 9.1324(4) Å, b = 23.0081(10) Å, c = 14.3600(6) Å, β = 91.340(4)°, Z =4 and V = 3016.5(2) Å^3 (Table 1). The *ORTEP* diagram of the complex with the atomic labelling is shown in Fig 1. The asymmetric unit contains an mononuclear mono-cationic unit $[Fe(HL)_2]^+$, one anionic SCN$^-$ and one water molecule. Each molecule mono-deprotonated ligand acts in tridentate fashion in his thiolate form. The Fe^{3+} cation is coordinated to two ligand molecules through one sulfur atom, one azomethine atom and one hydrazino nitrogen atom resulting in a N_4S_2 core. The geometry around the iron(III) atom is best described as a distorted square pyramidal. The basal plane is occupied by two hydrazino nitrogen atoms (N3 and N8) one imino nitrogen atom (N4) and one thiolate sulfur atom (S1). The angles in the basal plane of the octahedral complex are severely deviated from the ideal angle values of 90° and 180° for this type of environment: N3—Fe1—N4 = 80.26(10)° ;

N8—Fe1—N4 = 104.64(10)°; N3—Fe1—S1 = 84.79(7)° ; N8—Fe1—S1 = 90.50(7)° ; N4—Fe1—S1 = 163.46(7)° ; and N3—Fe1—N8 = 174.96(10)°. The angle formed by the imino nitrogen atom (N9) and the thiolate sulfur atom (S2) atoms occupying the apical positions is N9—Fe1—S2 = 162.03(8)° which is severely different to the ideal value of 180°. In the equatorial plane, there two type of bond distances Fe1: Fe1—N are similar [1.918(2)—1.987(2) Å] and are shorter than the distance Fe1—S1 = 2.2183(9) Å owing to the hard character of the nitrogen atom and the soft character of the sulphur atom. The two distances from the central atom and the atoms in apical positions are also different: Fe1—S(2)= 2.2119(9) Å and Fe1—N9 =1.988(3) Å. The distances Fe—S [2.2119(9) Å—2.2183(9) Å] and C—S [1.745(3) Å —1.748(3) Å] are consistence with a mono-deprotonated form of the ligand. These facts are in accordance with the observations for similar complexes [27]. The uncoordinated thiocyanate anion is (SCN^-) is disordered with two sites having occupancies of 0.238(7) and 0.762(7). This free thiocyanate group is quasi-linear [28] with S—C—N angle of 172.2(8)°. The crystal structure is stabilized by hydrogen bonds giving rise to a three-dimensional network. There is some intramolecular hydrogen bond interactions involving amino nitrogen atoms, water molecule and sulphur and nitrogen thiocyanate atoms: N(1)—H(1N)...O(1W), C(14)—H(14)...S(3a) and C(6)—H(6)...N(2) (Fig. 2, Table 2). The complex exhibits also intermolecular hydrogen bonds (Fig. table) which consolidate the three-dimensional network. Molecular layers running almost parallel to the a axis are formed by intermolecular hydrogen bonds N(1)-H(1N)...O(1W), O(1W)-H(1W1)...N(6a)#3 , N(5)-H(5N)...S(3a)#1 and allow to develop a three-dimensional network supramolecular between three asymmetric units.



(**a**)

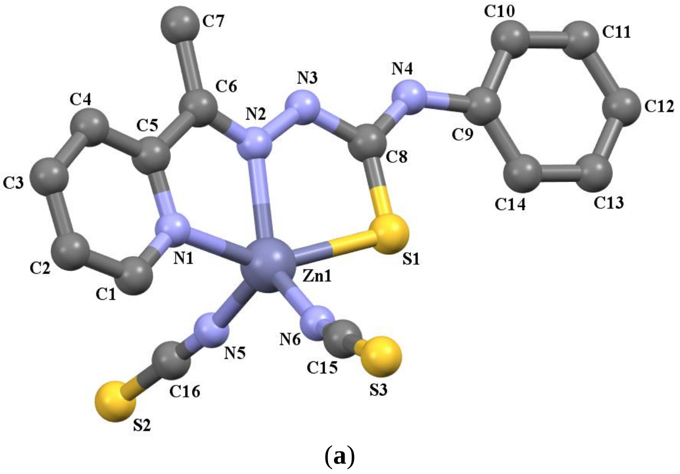


(**b**)

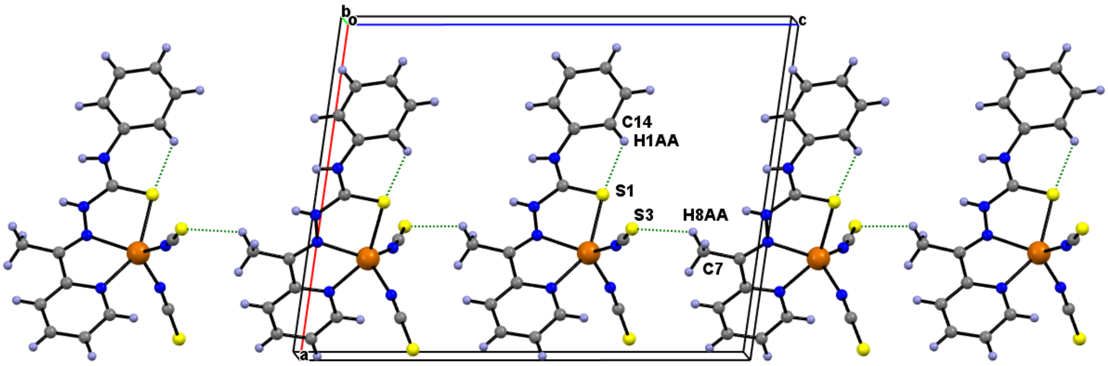
Figure 1*: ORTEP* plot (30% probability ellipsoids) showing the molecule structure of the Fe(III) complex (H atoms are omitted for clarity) (**a**) and the hydrogen bonds (**b**) in the complex.

3.2.2. Complex 6

The title compound [Zn(H_2L)($SCN)_2$] (**6**) crystallizes in the monoclinic space group P2_1/c with cell parameters a = 12.7292 (7) Å, b = 9.0500 (4) Å, c = 16.9350 (8) Å, β = 98.144 (4), V = 1931.22 (17) Å^3, Z = 4 (Table 1). The *ORTEP* diagram of the complex with the atomic labelling is shown in Fig 3. The asymmetric unit of **6** consists of one unique unit containing one non-deprotonated ligand molecule acting in tridentate manner, on Zn^{2+} ion as central atom and two thiocyanate anions acting in unidentate fashion through his nitrogen hard site. The Zn(II) is penta-coordinated and the environment around the metal center can be discussed using the Addison [29] parameter and the modifier parameter of Konno [30]. The Addison parameter is calculated using the two largest angles around the metal center ($\tau = (\beta - \alpha) / 60$) while the Konno parameter use the two largest angles, γ and δ being the other angles around the metal centers without the donor atoms defining β ($\chi = (\beta + \gamma + \delta - 2\alpha) / 180$). The τ (or χ) value of 0 defined a perfect square-pyramidal environment while a τ (or χ) value of 1 defined a perfect square pyramidal geometry.



(**a**)



(**b**)

Figure 2*: ORTEP* plot (30% probability ellipsoids) showing the molecule structure of the Zn(II) complex (H atoms are omitted for clarity) (**a**) and the hydrogen bonds (**b**) in the complex.

In the case of our complex the τ value of 0.317 is indicative of a distorted square-pyramidal geometry while the χ value of 0.641 suggests that the geometry around the Zn center is a distorted trigonal bipyramid. The azomethine atom (N2) and the nitrogen atoms (N5 and N6) the thiocyanate groups defined the equatorial plane. The axial positions are occupied by the sulphur atom S1 and the pyridyl nitrogen atom (N1) of the other cyanate group. The angles values in the equatorial plane deviated severely from the ideal value of 120° in trigonal plane and are: N2—Zn—N5 = 114.94(10)°, N2—Zn—N6 = 131.02 (9)° and N5—Zn—N6 = 113.42 (11)°. The value of the sum of the subtended angles is 359.38°. The value of the angle subtended by the atoms in apical positions is S1—Zn—N1 = 150.05 (6)° which is far from the ideal value of 180°. These facts confirm the severely distortion of the geometry around the central zinc(II). The two coordinated thiocyanate are quasi-linear with angle S—C—N of 178.3(3)° and 176.8(3)° as observed in the literature [28]. Because of their hard character, the nitrogen atoms of the thiocyanate group are strongly linked to the zinc(II) center with the shortest distances Zn1—N5 = 1.939 (2) Å and Zn1—N6 = 1.996 (2) Å. These distances are longer than those found in the complex $[Zn(Dach)(NCS)_2]$ (Dach is *cis*-1,2-diaminocyclohexane) reported in the literature [31]. The pyridyl nitrogen atom and the azomethine atom which are less hard than the previous nitrogen atoms are moderately linked to Zn(II) with distances: Zn1—N1 = 2.149 (2) Å and Zn1—N2 = 2.1287 (19) Å as observed in the complex . The bond length of the Zn(II) to the sulphur atom which have the soften character, is the longest distance Zn1—S1 = 2.4707 (7) Å. The double bond character of the C8—S1 = 1.669(2) Å combined to the larger distance Zn1—S1 are indicative of the non-deprotonation of the ligand. These observations are in accordance with those found in similar complexes [32, 33]. When the ligand H_2L react with $ZnCl_2$ in the presence of Et_3N a yellow complex formulated as $[Zn(HL)_2]$, in which the ligand acts in this deprotonated form, was reported [34]. The coordination capacity of the chloride anion is weaker than those of the thiocyanate anion. For all the intermolecular hydrogen bonds the sulphur atoms play the role of acceptor. The CH and the NH groups play the role of donors: N3—H…S3, N4—H…S3, C4—H…S2, C7—H…S3 and C14—H…S1 (Fig. 4, Table 2).

IV. Conclusion

Six Schiff base complexes of the tridentate ligand H_2L (4-phenyl-1-(1-(pyridin-2-yl)ethylidene)thiosemicarbazide) derived from 2-phenylsemicarbazide and 2-acerylpyridine have been prepared and characterized by NMR, IR, UV, conductance measurement and room temperature magnetic moment determination. In addition to the spectroscopic studies, the structure of two complexes **2** and **6** were determined by X-ray diffraction. The IR spectral data showed that the ligand is coordinated with the metal center through the imino and pyridyl nitrogen atoms and the sulphur atom. The electronic spectral show bands due to the ligand and the MLCT for all complexes. The d—d bands for **2** and **5** complexes are in accordance with octahedral structure. Room temperature magnetic susceptibility measurement indicated that the Ni(II) and Zn(II) complexes are diamagnetic and the Mn(III), Fe(III), Co(II) and Cu(II) are paramagnetic. Conductance measurement show that the complexes **1**, **4** and **5** are non-electrolyte in nature while the complexes **2** and **3** are 2:1 electrolyte and the complex **6** is 1:1 electrolyte. The X-ray structure determination show an octahedral geometry for the complex **2** and a distorted trigonal bipyramidal for **6**.

V. Supporting information

CCDC-1936459 and 1936460 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

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