

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa



Synthesis, spectral, electrochemical and X-ray single crystal studies on Ni(II) and Co(II) complexes derived from 1-benzoyl-3-(4-methylpyridin-2-yl) thiourea



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HIGHLIGHTS

- New complexes were prepared using Ni(II) and Co(II) metal ions with a new derivative of thiourea.
- The complexes were investigated using all valuable spectral.
- X-ray single crystal study was carried out to verify the proposed geometry of the complexes.

G R A P H I C A L A B S T R A C T

ORTEP diagram of Ni(II) complex showing some atomic numbering scheme.



ARTICLE INFO

Article history: Received 4 January 2014 Received in revised form 22 February 2014 Accepted 25 February 2014 Available online 12 March 2014

Keywords: X-ray single crystal Cyclic voltammetry Spectra Thiourea

ABSTRACT

1-Benzoyl-3-(4-methylpyridin-2-yl) thiourea ligand was coordinated with Ni(II) and Co(II) perchlorate salts to isolate complexes. All the prepared compounds are deliberately investigated by all possible spectral tools. A comparative study for IR spectra reveals the neutral bidentate coordinating nature of the ligand towards the two metal ions. The UV/Vis spectra of the complexes display d-d transition bands proposed an octahedral geometry for the complexes. MS analysis data are concerned especially with the base peak which is corresponding to $C_{28}H_{25}N_6O_2S_2$ M ion. The fragmentation patterns are relatively matched with each others. Electrochemical studies were carried out using platinum wire and Ag/AgNO₃ as counter and reference electrodes, respectively. The data reflect the irreversible nature of the electrode couple and showed two successive one electron transfer process. X-ray single crystal studies are used to verifying the octahedral geometry proposed as well as calculating crystal parameters beside the structural refinements.

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Introduction

Organic compounds containing oxygen, nitrogen and sulfur as donors are extensively studied [1]. Recently, their complexes cover several areas ranging from general considerations of the effect of sulfur and electron delocalization in metal complexes behavior

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which elaborate their applications [2]. Chelating ligands with conjugated oxygen or nitrogen donor sites represent some of the most important ligands in coordination chemistry and their metal complexes are useful for homogenous catalysis, chemical vapor deposition, supramolecular chemistry, redox sensing, photophysics, magnetic materials, and so on [3]. A distinguish biological activity was recorded for most investigated complexes especially with the presence of N, S and O heteroatom's [4-14]. This research is considered a continuation of my work, previously, I have contributed in works nearby this research point [15,16]. The aim of the work is based on view of the significant role played by the metal complexes of pyridine moiety. I have motivated to prepare new complexes derived from pyridine nucleus, which may serve in different fields. The chemistry of the complexes are elaborately investigated by all possible tools. Concerning with the crystal structures of the complexes have been reported by single crystal X-ray diffraction to justify on the geometry isolated. Moreover, I have studied the electrochemical behavior of these complexes.

Experimental

General and instrumentation

All reagents and solvents were purchased from commercial sources and used as it is without previous purification. Single crystal X-ray data was collected on a Bruker/Nonius Kappa CCD diffractometer using graphite monochromated Mo Ka radiation $(\lambda = 0.71073 \text{ Å})$, equipped with an Oxford Cryostream cooling apparatus. NMR spectra were measured on a Bruker AM 250-400 or Bruker Av-500 Plus FT-NMR spectrometer. Residual signals of solvent were used for reference for ¹H and ¹³C NMR. For infrared spectra, each compound was pressed into a disk with an excess of dried KBr and measured on a Jasco 660 FT-IR spectrophotometer at the range 400–4000 cm⁻¹. Electrospray (ES) and high-resolution (HR) mass spectra were measured on a Waters LCT Premier XE (oa-TOF) mass spectrometer. UV-Vis absorption spectra were run in HPLC grade acetonitrile (Fisher) and measured on a Jasco V-570 spectrophotometer from 230 to 1100 nm (optical path length 1.0 cm). The cyclic voltammetry experiments were carried out with an AUTOLAB PGSTAT12 potentiostat in conjunction with General Purpose Electrochemical System software (GPES version 4.7 for Windows) in a specially designed three-electrode glass cell with a Teflon-coated cell cap. A Bioanalytical platinum working electrode (model no. MF2013) with a 1.6 mm disk was used for all experiments. The counter electrode was a platinum wire and the reference electrode an Ag/AgNO₃ electrode. To regain electrochemical sensitivity and reproducibility the working electrode was polished, with 600 grid emery paper, to a mirror surface and then ultrasonicated. Prior to each experiment, the electrode was washed with high performance liquid chromatography (HPLC) grade, CH₃CN and dried in air for about 15 min. A 0.1 M [Bu₄N·BF₆] (TBATFB) solution in CH₃CN was used as supporting electrolyte. In all cases, ferrocene was used as an internal reference. Solutions were degassed with nitrogen and a nitrogen atmosphere was maintained over the solution during the experiment.

Synthesis of 1-benzoyl-3-(4-methylpyridin-2-yl) thiourea, H₂L

2.0 g, 18.49 mmol of 4-methylpyridin-2-amine dissolved in acetone (50 ml) and benzoyl isothiocyanate (2.48 ml, 18.49 mmol) was added drop-wise. The mixture was heated up to 40 °C for 10 min then allowed to cool at room temperature. The solvent was removed under reduced pressure. Ether was used to precipitate the product as a yellow powder (4.563 g, 91.07%, 16.83 mmol).



Fig. 1. 1-Benzoyl-3-(4-methylpyridin-2-yl) thiourea, H₂L ligand.

Recrystallisation from hot acetonitrile yielded monoclinic crystals (Fig. 1).

Characterization of H₂L ligand

Significant IR data as fellow: vNH at 3285 cm⁻¹; vC=O at 1677; $\delta(NH)^1$ at 1606; $\delta(NH)^2$ at 1556; vC=N at 1519 and v^{IV}C=S at 831 cm⁻¹. ¹H NMR (Fig. 2) δ_H (400 MHz,CDCl₃): 13.0(1H,s,NH²); 9.04(1H,s,NH¹); 8.57(2H,d,Py); 7.86(2H,d,Py); 6.93–7.49(5H,m,Ar); 3.66(3H,s,CH₃); 2.36(H₂O of solvent). ¹³C NMR δ_C (250 MHz, CDCl₃): 177.0, 166.6, 151.2–148.2, 133–116, 77.2 and 21.5 for pyridine, benzene and CH₃ group. Accurate MS (Fig. 3) (*m*/*z*) = M⁺ 271.0776 (calcd. 271.34) of C₁₄H₁₃N₃OS and the base peak (100% intensity), 82.95 for an organic part fragment. UV/Vis from 230 to 1100 nm in CH₃CN, λ_{max} , nm (ϵ M, M⁻¹ cm⁻¹): CT bands are, 308(171433.4) and 267 (292016.5).

Procedure for the synthesis of complexes H

According to this equation; $2H_2L + M(ClO_4)_2 \cdot 6H_2O \stackrel{olvent}{\to} [M(H_2L)_2(AcN)_2](ClO_4)_2$, the ligand (1 equivalent, typically, 50 mg (0.1845 mmol) was dissolved in a minimum amount of acetonitrile (3 ml). The solutions were warmed to 60 °C to ensure that the ligand fully dissolved. To this stirring solution, the metal perchlorate (1 equivalent, 0.0225 and 0.0225 g of Ni and Co(II) salts, respectively) dissolved in the same solvent and was added drop wise. Recrystallisation of the complexes was carried out by using diethyl ether, the yields are 89.97% and 67.30% for Ni and Co(II) complexes, respectively.

Warning, perchlorate salts are potentially explosive. Care should be taken while handling such complexes.

Characterization of [Ni(C₁₄H₁₃N₃OS)₂(CH₃CN)₂](ClO₄)₂ complex

Green triclinic crystals of the complex were investigated: IR data are; υ NH at 3433 cm⁻¹; υ C=O at 1662; δ (NH)¹ at 1623; δ (NH)² at 1532; υ C=N at 1491 and υ ^{IV}C=S at 759 cm⁻¹. υ Cl–O at 1022(m) and 624(s) cm⁻¹; υ M–N and υ M–S at 463 and 357 cm⁻¹, respectively. Accurate MS (Fig. 4) (*m*/*z*) = 629.55(10), base peak at 599.08(100%) for C₂₈H₂₅N₆O₂S₂Ni. UV/Vis in CH₃CN, λ_{max} , nm (ε M, M⁻¹ cm⁻¹), d–d transitions at; 589(2657.4) and 947.9 (3070.4). Dq, *B* and β are 1054.9 cm⁻¹, 876.52 cm⁻¹ and 0.842, respectively.

Characterization of $[Co(C_{14}H_{13}N_3OS)_2(CH_3CN)_2](ClO_4)_2$

Brown triclinic crystals of the complex (Fig. 5) were investigated: IR data are; vNH at 3431 cm⁻¹; vC=O at 1663; δ (NH)¹ at 1624; δ (NH)² at 1578; vC=N at 1489 and v^{IV}C=S at 757 cm⁻¹. vCl-O at 1020(m) and 624(s) cm⁻¹; vM-N and vM-S at 470 and 360 cm⁻¹, respectively. Accurate MS (Fig. 6) (*m*/ *z*) = 690.16(10), base peak at 600.083(100%) for C₂₈H₂₅N₆O₂S₂Co. UV/Vis in CH₃CN, λ_{max} , nm (ε M, M⁻¹ cm⁻¹), d-d transitions at; 380(26526.5), 520(8122.4) and 1163(1126902). Dq, *B* and β are 859.8 cm⁻¹, 794.96 cm⁻¹ and 0.819, respectively.



Results and discussion

The complexes are stable in air and not soluble in water and common organic solvents but are completely soluble in acetonitrile.

IR spectra

The ligand $\upsilon C=0$ and δNH^2 bands appeared by a relatively lower wave no. (1677 and 1556 cm⁻¹) (Table 1) this is referring to the presence of intraligand H-bonding but $\upsilon C=N$ has a normal appearance. Moreover, the band at 831 cm⁻¹ is assigned to another significant contributed group ($\upsilon^{IV}C=S$). The spectra of the complexes display an observable blue shift with $\upsilon C=N$ and $\upsilon^{IV}C=S$ bands. These bands are attributed to the coordination sites contribute by arms with the central atom in the chelate ring. An observable lower shift with $\upsilon C=O$ band is referring to the remaining of intraligand H-bonding inside the complex and such a general affect is found over a hall molecule significant bands due to LMCT. The complexes spectra reveal characteristic bands at \approx 1100 and \approx 620 cm⁻¹ indicative for ionic perchlorate [17,18]. Also, two bands at \approx 470 and \approx 350 cm⁻¹ are assigned for ν M–N and ν M–S transitions. These features are confirmed by X-ray diffraction studies.

Electronic spectra

The UV/Vis spectra of the ligand and its complexes were recorded from acetonitrile solution and the data represented in Table 2. The ligand shows $\pi \to \pi^*$ and $n \to \pi^*$ transitions at 267 and 308 nm, respectively. The spectrum of Ni(II) complex reflects a six-coordinate environment around the central ion. The transitions appeared at 16,978 and 10,549 cm^{-1} are assigned to the ${}^{3}\text{A}_{2\text{-}}$ $g \rightarrow {}^{3}T_{1}g(F)(\upsilon_{2})$ and ${}^{3}A_{2}g \rightarrow {}^{3}T_{2}g(\upsilon_{1})$, respectively and the third one ${}^{3}A_{2}g \rightarrow {}^{3}T_{1}g(P)(\upsilon_{3})$ being obscured by MLCT band at 27,777 cm⁻¹. Using these assignments yields spectrochemical parameters (Dq, *B* and β), their values are 1054.9 cm⁻¹, 876.5 cm⁻¹ and 0.842. These values are in a good agreement with the related mononuclear compound, [Ni(TPA)(NSC)₂]H₂O, which has a similar absorption profile, containing bands at 11,390, 17,540 and 26,900 cm⁻¹ [19]. The β value (0.842) reports the ionic character of the new coordinate bonds [20]. The Co(II) complex spectrum reveals bands at 8598 and 19,230 cm⁻¹ attributed to ${}^{4}T_{1}g \rightarrow {}^{3}T_{2}g(\upsilon_{1})$ and ${}^{4}T_{1}g \rightarrow {}^{4}A_{2}g(P)(\upsilon_{3})$



Fig. 4. MS spectrum of [Ni(C₁₄H₁₃N₃OS)₂(CH₃CN)₂](ClO₄)₂ complex.



Fig. 5. The structural formula of the investigated complexes, where M = Ni(II) or Co(II) ions.

transitions, respectively. These bands are coincide with an octahedral geometry, which verified by X-ray single crystal diffraction studies. These assignments yield spectrochemical parameters (Dq, *B* and β) calculated [20] their values (859.8 cm⁻¹, 794.96 cm⁻¹ and 0.819) are found within the normal range. The β value (0.819) reflects the same insight of the Ni(II) complex. This feature is expected with introducing of best donor sites (S and N) in coordination [21].

Mass spectral analysis

The mass spectral analysis of the free ligand and its complexes were recorded in CH₃CN. The ligand spectrum displays an accurate molecular ion peak (m/z = 271.077) matched with the theoretical.

The spectra of the complexes display a notable difference with the molecular ion peak in between the found and the calculated. This is may refer to the probability a sudden fragmentation happened during the vaporization process which is considered an introductory step in MS analysis. This is the main cause for the difference between the calculated and found m/z value. The molecular ion may loss ClO₄ groups during the evaporization process although this proposal is not fitted with the results and no possible fragmentation can explain the observed mass spectra. I am satisfying with obtaining of the base peak which displays $C_{28}H_{25}N_6O_2S_2M$ formula. A matching appeared inbetween the two fragmentation patterns as well as the base peak (100) may reflect the same degradation behavior of the two investigated complexes.

Electrochemical measurements

The redox potential is an important parameter as it characterizes the ability of the redox centre to transfer electrons and also to act as a redox catalyst. The electrochemical process is essential with the complexes to assert on the metal ion oxidation state which may be affected during the complexation process through the degree of ligand basicity. The effectiveness of CV results from its capability for rapidly observing the redox behavior over a wide potential range. In metal complexes, the redox behavior of a metal centre is also influenced by the nature of the ligand bonded to the metal. The electrochemical behavior of the Ni(II) and Co(II) complexes was investigated (Table 3) using the cyclic voltammetric (CV) technique in CH₃CN solution containing 0.1 M tetra (n-butyl)ammonium perchlorate as the supporting electrolyte.

The complexes showed similar features in the investigated potential range -3.0 to +2.0 V, and displayed two well-defined electrode couples. The Co(II) complex showed two successive one electron transfer process. The first reduction wave of the complexes is safely assigned to the irreversible couple Co(II)/ Co(I) with $E_{1/2} = -1.65$ V, $\Delta E_p = -1.2$ V and represented as follows:



Fig. 6. MS spectrum of $[Co(C_{14}H_{13}N_3OS)_2(CH_3CN)_2](CIO_4)_2$ complex.

Table 1

Assignments of the IR Spectral bands (cm⁻¹) of H₂L and its metal complexes.

Compound	ν_{NH}^1	$\nu_{c=N}$	$\nu_{c=0}$	δ^2_{NH}	δ^1_{NH}	v_{cl-o}	$\nu_{C=S}^{IV}$	ν_{M-N}	ν_{M-S}
(1) [C ₁₄ H ₁₃ N ₃ SO]	3285	1516	1677	1556	1606	_	831	-	-
						1022			
(2) [Ni(C ₁₄ H ₁₃ N ₃ SO) ₂ (CH ₃ CN) ₂](ClO ₄) ₂	3433	1491	1662	1532	1623	624	759	463	357
(3) [Co(C ₁₄ H ₁₃ N ₃ SO) ₂ (CH ₃ CN) ₂](ClO ₄) ₂	3431	1489	1663	1578	1624	1020624	757	470	360

Table 2

The electronic spectral bands (cm⁻¹) of the complexes and the ligand field parameters.

Compounds	d-d transition (cm ⁻¹)	Intraligand and charge transfer (cm^{-1})	Ligand field parame	Ligand field parameters	
			10Dq (cm ⁻¹)	<i>B</i> (cm ⁻¹)	β
(1)	-	37,453; 32,467	-	-	-
(2)	16,978; 10,549	35,511; 32,790; 27,777	1054.9	876.5	0.842
(3)	26,316; 19,230; 8598	37,878; 32,573; 31,056	859.8	795.0	0.819

Table 3

Cyclic voltammetric data of the prepared complexes in DMF-TBA⁺BF₄^{-a}.

Complex	First electrode couple			Second electrode couple				
	E _{p,a}	$E_{\rm p,c}$	$\Delta E_{\rm p}$	E _{1/2}	E _{p,a}	$E_{\rm p,c}$	$\Delta E_{\rm p}$	E _{1/2}
$\label{eq:constraint} \begin{split} &[\text{Ni}(\text{C}_{14}\text{H}_{13}\text{N}_3\text{SO})_2(\text{CH}_3\text{CN})_2](\text{CIO}_4)_2 \\ &[\text{Co}(\text{C}_{14}\text{H}_{13}\text{N}_3\text{SO})_2(\text{CH}_3\text{CN})_2](\text{CIO}_4)_2 \end{split}$	-1.5 -2.3	0.5 -1.0	-2.0 -1.2	-0.5 -1.65	-1.5 -2.2	0.8 -1.25	-2.3 -0.95	-0.35 -1.73

^a Scan rate = 100 mV s⁻¹; $E_{1/2} = (E_{p,c} + E_{p,a})/2$.

Table 4

Crystallographic data for H₂L, [Ni(H₂L)₂(CH₃CN)₂](ClO₄)₂ and [Co(H₂L)₂(CH₃CN)₂](ClO₄)₂ complexes.

Empirical formula	C ₂₈ H ₂₆ N ₆ O ₂ S ₂	C ₁₈ H ₁₉ Cl N ₅ Ni _{0.50} O ₅ S	C ₃₆ H ₃₈ Cl ₂ Co N ₁₀ O ₁₀ S ₂
Formula weight	542.67	482.25	964.71
T (K)	150(2)	150(2)	150(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	p21/c	p-1	p-1
a (Å)	11.9590(4)	8.7700(2)	8.7520(3
b (Å)	5.2260(2)	10.0480(3)	10.0610(4)
<i>c</i> (Å)	21.6520(9)	13.2650(4)	13.2480(7)
β (°)	96.9930(10)°	83.8990(10)	83.721(2)
v (Å ³)	1343.13(9)	1056.73(5)	1061.11(8)
Z	2	2	1
$ ho_{ m cak.}$ (Mg cm ⁻³)	1.342	1.516	1.510
μ (mm ⁻¹)	0.236	0.752	0.696
F(000)	568	498	497
Crystal size (mm)	$0.40 \times 0.10 \times 0.10$	$0.35 \times 0.30 \times 0.10$	$0.30 \times 0.25 \times 0.04$
Range for data collection (°)	2.40-27.51	2.49-27.51	2.49-27.48
Index ranges	$-15\leqslant h\leqslant 15$, $-6\leqslant k\leqslant 6$,	$-11 \leqslant h \leqslant 11, -13 \leqslant k \leqslant 11,$	$-11\leqslant h\leqslant 11,-13\leqslant k\leqslant 13,$
	$-28 \leqslant l \leqslant 27$	$-17 \leq l \leq 13$	$-15 \leqslant l \leqslant 17$
No. of reflections collected	5410	7293	6838
N0. Of independent reflections (R_{int})	3045(-0.0470)	4785(0.0280)	4797(0.0335)
No. of data/restraints/parameters	3045/0/173	4785/0/280	4797/84/317
Goodness-of-fit (GOF) on F ²	1.045	1.039	1.052
$R_1, w R_2^{ab}[I > 2\sigma(I)]$	0.0527, 0.1204	0.0391, 0.0913	0.0587, 0.12954
$R_1, w R_2^{ab}$ [all data]	0.0837, 0.1338	0.0496, 0.0973	0.0787, 0.1398
Largest difference in peak and hole $(e \text{ Å}^{-3})$	0.292 and -0.358	0.358, 0.349 and -0.490	0.673 and -0.737

Co^{II}L + e[−] ↔ Co^IL. The second couple with $E_{1/2} = -1.73$ V is assigned to irreversible electrode couple Co^{II}/Co^{III} by comparison with analogous Co(II) complexes [22]. The Ni(II) complex voltammogram showed a successive electron process in the same potential range. The first reduction wave of the complexes is assigned to the irreversible couple Ni^{II}/Ni^I with $E_{1/2} = -0.5$ V, $\Delta E_p = -2.0$ V and represented as follows: Ni^{II}L + e[−] ↔ Ni^IL. The second couple with $E_{1/2} = -0.35$ V is assigned to irreversible Ni^{II}/Ni^{III}. The ratio

ip,c/ip,a > 1 confirms the irreversible nature of the electrode couple [23]. The dependence of the cathodic peak current (ip.c) of the electrode couple on the square rote of the sweep rate suggests diffusion-controlled electrochemical process. The peak–peak potential separation (ΔE_p) of the electrode couple increased with increasing the scan rate is confirming the occurrence of a slow chemical reaction and a limited mass transfer following the electrode process. Thus, the electron transfer process is irreversible

Table 5

Selected bond lengths (Å) and angles (°) for the Co(II) complex.

Bond lengths			
C(5)—N(1)	1.341(4)	S(1)-Co(1)	2.4333(9)
C(6) - S(1)	1.655(3)	Co(1)-N(4)#1	2.122(3)
N(1)-Co(1)	2.134(3)	Co(1)-N(1)#1	2.134(3)
N(4)-Co(1)	2.122(3)	Co(1)—S(1)#1	2.4333(9)
Bond angles			
C(5)-N(1)-Co(1)	126.3(2)	N(4)#1-Co(1)-S(1)	86.19(8)
C(1) - N(1) - Co(1)	117.7(2)	N(4) - Co(1) - S(1)	93.81(8)
C(15)-N(4)-Co(1)	174.3(3)	N(1)#1-Co(1)-S(1)	95.57(7)
C(6) - S(1) - Co(1)	100.57(12)	N(1)-Co(1)-S(1)	84.43(7)
N(4)#1-Co(1)-N(4)	180.000(1)	N(4)#1-Co(1)-S(1)#1	93.81(8)
N(4)#1-Co(1)-N(1)#1	88.10(10)	N(4)-Co(1)-S(1)#1	86.19(8)
N(4)-Co(1)-N(1)#1	91.90(10)	N(1)#1-Co(1)-S(1)#1	84.43(7)
N(4)#1-Co(1)-N(1)	91.90(10)	N(1)-Co(1)-S(1)#1	95.57(7)
N(4)-Co(1)-N(1)	88.10(10)		
N(1)#1-Co(1)-N(1)	180.00(10)		

Selected bond lengths (Å) and angles (°) for Ni(II) complex Rond lengths

$\begin{array}{ccccc} C(5)-N(1) & 1.346(2) & N(4)-Ni(1) & 2.0645(\\ C(6)-S(1) & 1.677(2) & Ni(1)-N(4)\#1 & 2.0645(\\ N(1)-Ni(1) & 2.0937(17) & Ni(1)-N(1)\#1 & 2.0937(\\ Bond angles & & & & \\ C(5)-N(1)-Ni(1) & 125.96(13) & Ni(1)-S(1) & 2.4305(\\ C(1)-N(1)-Ni(1) & 117.87(13) & Ni(1)-S(1)\#1 & 2.4305(\\ C(15)-N(4)-Ni(1) & 174.17(18) & N(4)-Ni(1)-S(1) & 93.14(5) \\ N(4)\#1-Ni(1)-N(4) & 180.0 & N(1)\#1-Ni(1)-S(1) & 94.74(5) \\ N(4)\#1-Ni(1)-N(1)\#1 & 89.62(7) & N(1)-Ni(1)-S(1) & 85.26(5) \\ \end{array}$	17) 17) 17)
$\begin{array}{ccccc} C(6)-S(1) & 1.677(2) & Ni(1)-N(4)\#1 & 2.0645(\\ N(1)-Ni(1) & 2.0937(17) & Ni(1)-N(1)\#1 & 2.0937(17) \\ \hline Bond angles & & & & & & \\ C(5)-N(1)-Ni(1) & 125.96(13) & Ni(1)-S(1) & 2.4305(\\ C(1)-N(1)-Ni(1) & 117.87(13) & Ni(1)-S(1)\#1 & 2.4305(\\ C(15)-N(4)-Ni(1) & 174.17(18) & N(4)-Ni(1)-S(1) & 93.14(5) \\ N(4)\#1-Ni(1)-N(4) & 180.0 & N(1)\#1-Ni(1)-S(1) & 94.74(5) \\ N(4)\#1-Ni(1)-N(1)\#1 & 89.62(7) & N(1)-Ni(1)-S(1) & 85.26(5) \\ \end{array}$	17) 17)
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$\begin{array}{cccc} C(5)-N(1)-Ni(1) & 125.96(13) & Ni(1)-S(1) & 2.4305(1) \\ C(1)-N(1)-Ni(1) & 117.87(13) & Ni(1)-S(1)\#1 & 2.4305(1) \\ C(15)-N(4)-Ni(1) & 174.17(18) & N(4)-Ni(1)-S(1) & 93.14(5) \\ N(4)\#1-Ni(1)-N(4) & 180.0 & N(1)\#1-Ni(1)-S(1) & 94.74(5) \\ N(4)\#1-Ni(1)-N(1)\#1 & 89.62(7) & N(1)-Ni(1)-S(1) & 85.26(5) \\ \end{array}$	
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)
N(4)-Ni(1)-N(1)#1 90.38(7) N(4)#1-Ni(1)-S(1)#1 93.14(5)
N(4)#1-Ni(1)-N(1) 90.38(7) N(4)-Ni(1)-S(1)#1 86.86(5)
N(4)-Ni(1)-N(1) 89.62(7) N(1)#1-Ni(1)-S(1)#1 85.26(5)
N(1)#1-Ni(1)-N(1) 180.000(1) N(1)-Ni(1)-S(1)#1 94.74(5)
N(4)#1-Ni(1)-S(1) 86.86(5) S(1)-Ni(1)-S(1)#1 180.00(2)

and the species that initially formed in the electrode process may also react further to give products that are not reoxidized at the same potential as in the first formed species [24].

Crystallographic studies

Crystal parameters, details of the data collection and structural refinements are presented in Table 4. The data was corrected for Lorentz and polarization effects and for absorption using SORTAV [25]. Structure solution was achieved by direct methods (Sir-92 program system) [26], and refined by full-matrix least-squares on F^2 (SHELXL-97) [27]. Molecular structures in the figures were

Fig. 7. ORTEP diagram of H₂L ligand showing some atomic numbering scheme.



Fig. 8. (a) ORTEP diagram of Ni(II) complex showing some atomic numbering scheme, and (b) the geometrical core of the complex.

drawn with ORTEP-3.0 for Windows (version 2.02) [28]. Relevant crystal data are given for all structures in Table 5 along with relevant bond lengths and angles. Yellow monoclinic crystals of the ligand displays bond lengths of C=N and C=S groups are 1.334(3) and 1.667(2) Å, respectively. A similar structures show C=S bond lengths ranging between 1.655 and 1.679 Å. There are one intramolecular hydrogen bond (Fig. 7) which help establishing the molecular conformation of H₂L. Specifically, this interaction occurs between the carbonyl oxygen atom and the thiourea hydrogen atom immediately adjacent to the pyridyl group in the 2-position. Hydrogen bond length are 2.0 Å, which found in a normal region. The hydrogen bond interactions in these examples range from 1.85 to 2.0 Å [29].

Single crystal X-ray of [Ni(H₂L)₂(CH₃CN)₂](ClO₄)₂ complex

The crystallographic data and structural refinement details are given in Table 4. Selected bond distances and bond angles are given in Table 5. Fig. 8a shows the ORTEP diagram of the complex with atomic numbering scheme for the coordinating sites. The metal center in the complex is coordinated in an N₄S₂ core (Fig. 8b) through bidentate ligands and two solvent molecules (secondary ligand). A pyridyl nitrogen, thione sulfur and acetonitrile nitrogen are the sites contribute N₄S₂. A relatively symmetric octahedral environment is drawn based on bond distances and bond angles. Most of angles with the central atom within the classical regions (180° and 90°) except N(1)–Ni(1)–S(1) 85.26(5)° and N(1)–Ni(1)–S(1)#1 94.74(5)° [30] which, somewhat deviated. The bond lengths of C=S and C=N groups as 1.677(2)° and 1.346(2)° Å, which are longer than those of the corresponding distances in the free ligand. This suggests a considerable



Fig. 9. (a) ORTEP diagram of Co(II) complex showing some atomic numbering scheme, and (b) the geometrical core of the complex.

delocalization of the charge on the chelate ring [31] which elongated the length of the contributed donor group. The bond distances for Ni-N1 and Ni-S1 are 2.0937(17)° and 2.4305(5)° Å, respectively, which are comparable to the bond lengths reported for similar Ni(II) complexes in the literature [32]. The NS donor sites from bidentate ligands coordinates the Ni(II) center to form two six membered C₂N₂SNi rings. The complex is stable in the solid state due to delocalization of π – electrons and the presence of $N-H\cdots O$ and $N-H\cdots Cl$ hydrogen bond interactions inbetween amine hydrogen, carbonyl oxygen and perchlorate anion. The perchlorate counter ion accept H-bond from one NH group by 2.0 Å length. Another one was absent from the diagram and I could not find a suitable discussion. Although, there is no doubt for its necessitates presence especially with the appearance of all ligand hydrogen atoms neighboring to C=S and C=O groups which exclude the elimination of perchloric acid molecule.

Single crystal X-ray of [Co(H₂L)₂(CH₃CN)₂](ClO₄)₂complex

Fig. 9a shows the ORTEP diagram of the complex together with the atomic numbering scheme for the coordinating sites, which includes a pair of bidentate ligands with two solvent molecules taking place in octahedral geometry (Fig. 9b). The binucleus ligands coordinate through pyridyl nitrogen and thione sulfur atoms. The crystallographic data and structural refinement details are given in Table 4. Selected bond distances and bond angles are presented in Table 5. The Co-N(1) and Co-S(1) bonding have distances of 2.134(3)° and 2.433(9)° Å, respectively, which are

comparable to the bond lengths reported elsewhere [33,34]. Two six membered C₂N₂S chelate rings are forming by the two ligands. A small deviation is observed with N(1)—Co(1)—S(1) 84.43(7)°, N(1)—Co(1)—S(1)#1 95.57(7)° Å angles. Represents a slight distortion from an ideal geometry form. The bond lengths of C=S and C=N groups in the complex are $1.655(3)(S)^{\circ}$ and $1.341(4)^{\circ} Å(L)$ (L = longer, S = shorter). Which are longer or shorter than those of the corresponding distances in the free ligand due to the bonding towards the Co(II) center. The bond C(7)–O(1) distance, 1.225(4), shows partial double bond character due to the delocalization of π – electrons throughout the aromatic ring [35]. Also, the Co(II) complex is stable in the solid state due to π – electron delocalization and the presence of N-H···O and N-H···Cl, H-bond interaction inbetween amine hydrogen, carbonyl oxygen and two perchlorate anions. The two perchlorate counter ions accept two H-bonds from one NH group by 2.0 Å length.

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