



Original Article

Synthesis and Structural Characterization of Zn(II) and Co(III) Complexes of Picolinoyl(4-ethylthiosemicarbazide)

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Abstract: Reaction of $ZnCl_2$ and two equivalents of picolinoyl(4-ethylthiosemicarbazide), **HL**, in MeOH in the presence of a supporting base like Et_3N results in the neutral complex $[Zn(L)_2]$ (**1**). A similar reaction of $CoCl_2$, however, brings about a cobalt(III) cationic complex, which could be separated as its chloride salt $[Co(L)_2]Cl$ (**2**). The spectroscopic studies and X-ray structure analyses indicate that in **1** and **2**, the metal ions are octahedrally coordinated by two ($N_{pyridine}$, S , N') chelates belonging to two singly deprotonated tridentate ligands $\{L^-\}$.

Keywords: Acyl thiosemicarbazides, Zn(II) complexes, Co(III) complexes.

1. Introduction

Acyl thiosemicarbazides (Figure 1a) possessing several donor atoms with various basicities, namely hard O , borderline N , and soft S donors, could form stable complexes with a wide range of transition metal ions [1]. However, due to challenges in controlling the convertible coordination fashions as well as the labile deprotonation(s) of the organic compounds [2, 3], there has been a limited number of reports relating to the structural chemistry of acyl thiosemicarbazides in

comparison to thiosemicarbazones, the most well-known derivative of thiosemicarbazides. To increase the selectivity in metal-ligand coordination, a potential donor atom X is generally introduced in the acyl moiety [2, 4-6]. The resulting acyl thiosemicarbazides are expected to bond with metal ions through (X , N' , S) chelates (Figure 1b). Such bonding feature (Figure 1c) is observed in several homoleptic and heteroleptic complexes of picolinoyl thiosemicarbazides [3, 6-8]. In continuation to explore the coordination chemistry of such thiosemicarbazide derivatives, herein the synthesis and structural characterization of homoleptic Zn(II) and Co(III) complexes with picolinoyl (4-ethylthiosemicarbazide) are presented.

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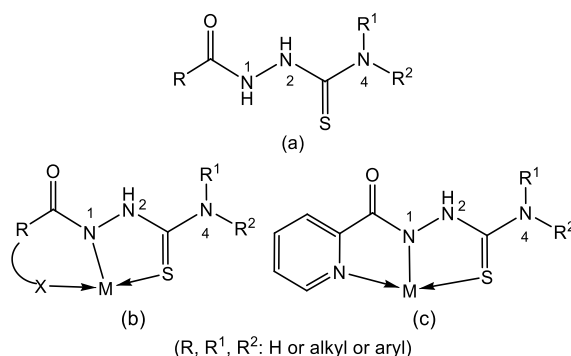


Figure 1. (a) General structure of acyl thiosemicarbazides; (b) Tridentate coordination modes of modified acyl thiosemicarbazides, and (c) picolinoyl thiosemicarbazides.

2. Materials and Methods

2.1. Materials

All chemicals used in this study were reagent-grade and used without further purification. Solvents were distilled before use.

2.2. Physical Measurements

IR spectra were measured from KBr pellets on an IRAffinity-1S spectrometer between 400 and 4000 cm^{-1} at the Department of Inorganic Chemistry, Faculty of Chemistry, VNU University of Science.

^1H NMR spectra in DMSO-d_6 were recorded on an AscendTM-500MHz spectrometer at the Faculty of Chemistry, VNU University of Science.

ESI mass spectrum was measured with an UPLC-MS/MS, XevoTQD mass spectrometer at the University of Science and Technology of Hanoi. All MS results are given in the form: m/z , assignment.

2.3. Synthetic Procedures

Synthesis and characterization of picolinoyl 4-ethylthiosemicarbazide (**HL**) have been recently reported [8].

Synthesis of $[\text{Zn}(\text{L})_2]$ (**1**): ZnCl_2 (13.6 mg, 0.1 mmol) was dissolved in 1 mL of MeOH. The ligand **HL** (44.8 mg, 0.2 mmol) was added, and the reaction mixture was stirred at 40°C for 30 min. A pale-yellow precipitate was

deposited immediately after adding Et_3N (0.03 mL, 0.2 mmol). After stirring for a further 1 hour at 40 °C, the product was filtered off, washed with a small amount of MeOH, and dried in a vacuum. The yield achieved was approximately 75%.

Synthesis of $[\text{Co}(\text{L})_2]\text{Cl}$ (**2**): **HL** (44.8 mg, 0.2 mmol) was added to a solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (13.0 mg, 0.1 mmol) in 1.0 mL of MeOH. During stirring at room temperature for 15 min, the colour of the solution changed gradually to dark purple. After adding Et_3N (0.03 mL, 0.2 mmol), the reaction mixtures were stirred at 40 °C for 1 hour. Slow evaporation of the solvent at room temperature resulted in the deposition of dark purple crystals, which were suitable for X-ray analysis. The product was filtered off, washed with cold MeOH, and dried in a vacuum. The yield achieved was approximately 62%.

2.4. Crystallography

The intensities for the X-ray determinations of the complex $2[\text{Co}(\text{L})_2]\text{Cl} \cdot 0.5\text{H}_2\text{O}$ were collected on a Bruker D8 QUEST instrument at 170 K with Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) using a TRIUMPH monochromator. Standard procedures were applied for data reduction and absorption correction [9]. Structure solution and refinement were performed with the SHELXT and SHELXL 2014/7 programs included in the OLEX2-1.5 program package [10].

Table 1. Crystal data and structure refinement for the hydrated complex $2[\text{Co}(\text{L})_2]\text{Cl} \cdot 0.5\text{H}_2\text{O}$

Formula	$\text{C}_{36}\text{H}_{45}\text{O}_{4.5}\text{N}_{16}\text{S}_4\text{Cl}_2\text{Co}_2$
Mw	1090.88
Crystal system	Monoclinic
$a/\text{\AA}$	12.016(3)
$b/\text{\AA}$	12.327(3)
$c/\text{\AA}$	17.945(4)
$\alpha/^\circ$	90
$\beta/^\circ$	99.794(5)
$\gamma/^\circ$	90
$V/\text{\AA}^3$	2619.2(1)
Space group	$\text{P}2_1$
Z	2
$D_{\text{calc}}/\text{g}\cdot\text{cm}^{-3}$	1.383
μ/mm^{-1}	0.947
No. reflect.	24170
No. indep.	12916
R_{int}	0.0407
No. param.	620
R_1/wR_2	0.0581/0.1423
GOF	1.035
CCDC	2290435

More information on collections and structural calculations are provided in Table 1. CCDC 2290435 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

3. Results and Discussion

Two equivalents of picolinoyl (4-methylthiosemicarbazide) **HL** readily react with one equivalent of ZnCl_2 or CoCl_2 in MeOH. The addition of a supporting base like Et_3N could facilitate the deprotonation of the ligand,

therefore, accelerating the complexation. Product **1** was directly deposited from the reaction with ZnCl_2 . While in the reaction with CoCl_2 , the metal complex **2** was separated as a crystalline solid by slow solvent evaporation from the reaction mixture.

In comparison with the IR spectrum of the uncoordinated ligand **HL**, the spectra of the complexes show the absence of some broad absorptions above 3100 cm^{-1} corresponding to NH groups (Figure 2). Moreover, there are bathochromic shifts of the C=O and C=S vibrations (Table 2). Thus, the IR spectral studies indicate partial deprotonation of NH groups via HL's keto-enol and/or thione-thiol tautomerism during the complexation.

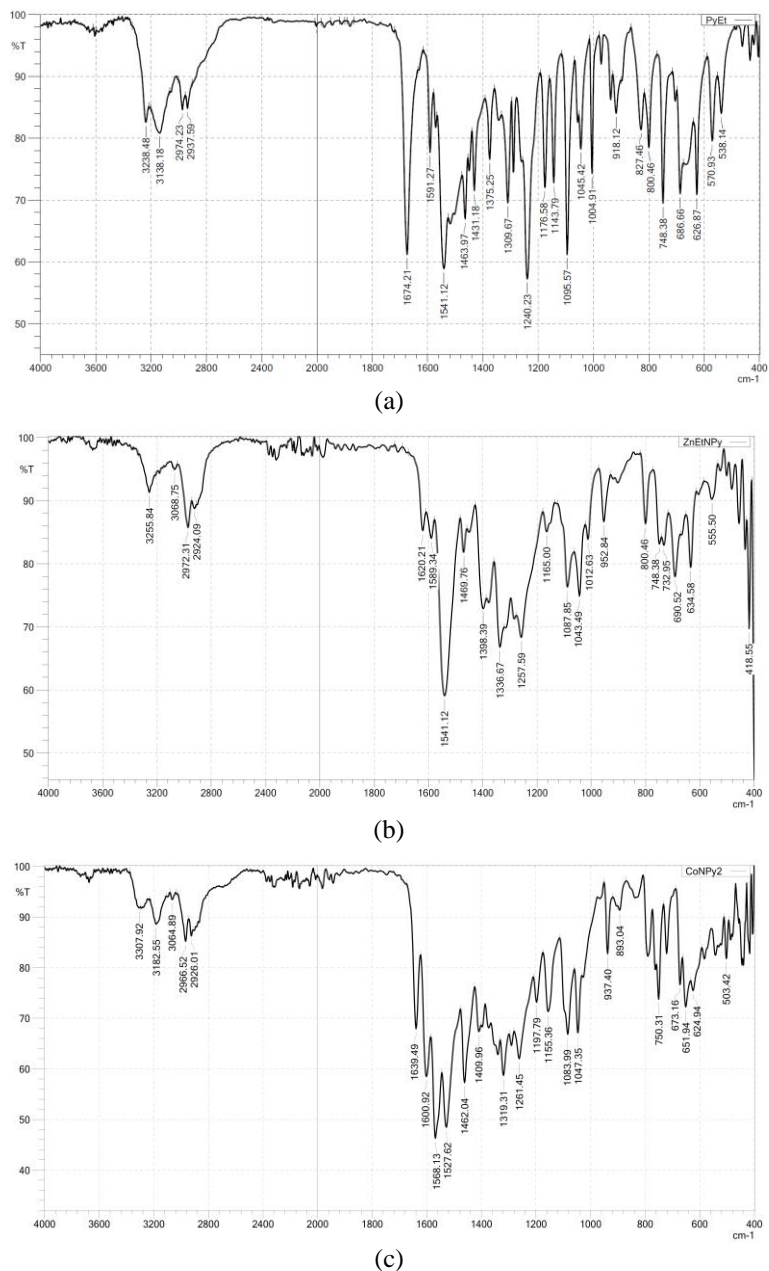


Figure 2. IR spectrum of (a) HL, (b) 1 and (c) 2.

Table 2. IR spectral data of HL, 1 and 2

	IR bands (cm ⁻¹)		
	ν_{NH}	$\nu_{\text{C=O}}$	$\nu_{\text{C=S}}$
HL	3239, 3138 (br, m)	1674 (s)	918 (m)
1	3256 (br, w)	1620 (w)	909 (w)
2	3308, 3182 (br, w)	1639 (m)	893 (w)

Structural features of the metal complexes are also investigated by ^1H NMR spectroscopy. The ^1H NMR spectrum of **1** in DMSO-d_6 (Figure 3b) exclusively displays signals

ascribed to pyridyl ring and ethyl group protons. Chemical shifts of such protons fall within the same ranges found in the spectrum of **HL** (Figure 3a).

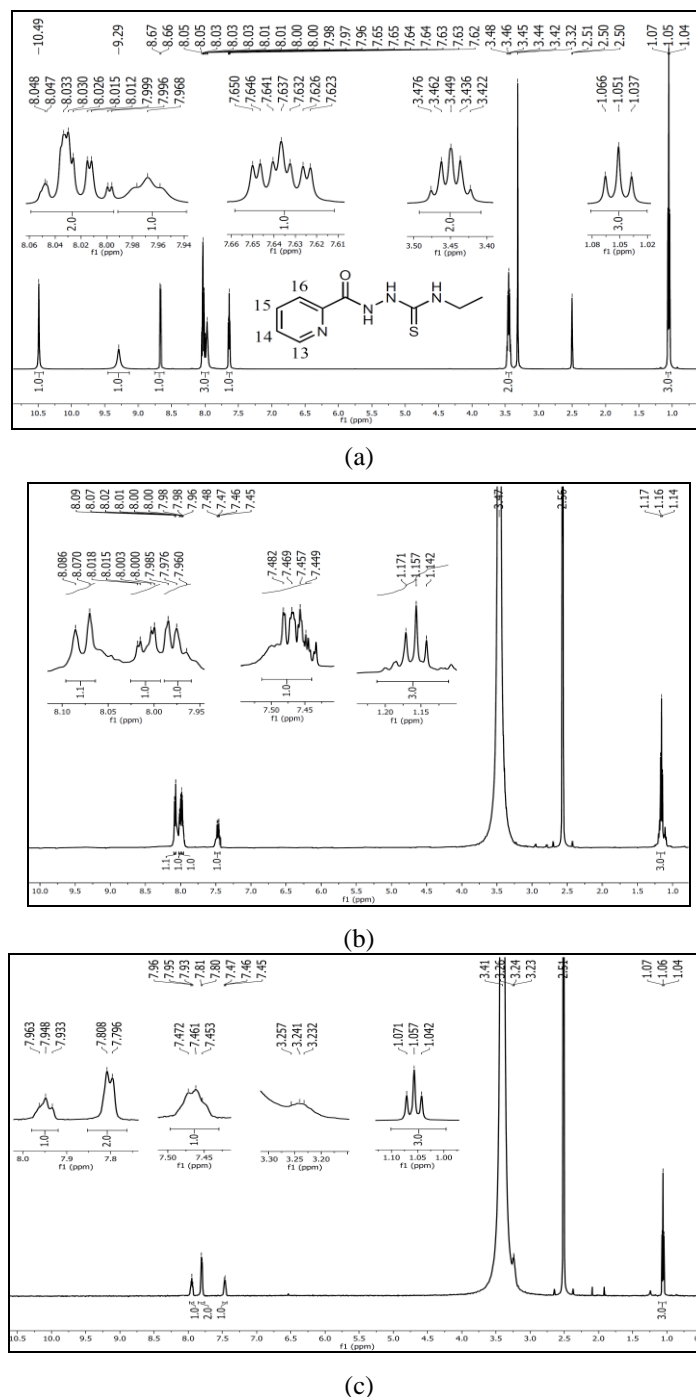


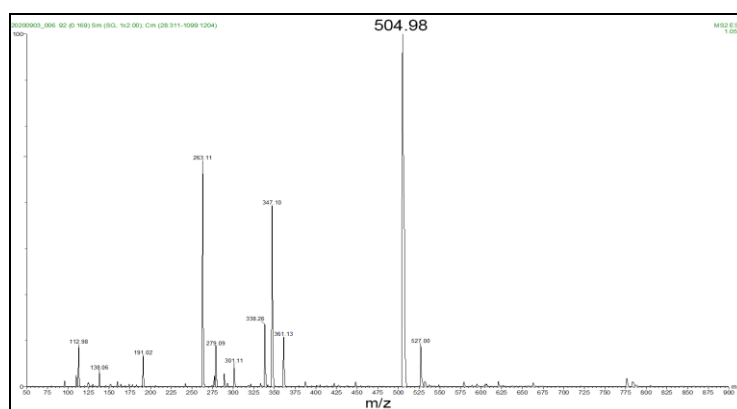
Figure 3. ^1H NMR spectra of (a) **HL**, (b) **1**, and (c) **2** in DMSO-d_6 .

Table 3. ^1H NMR spectral data of **HL**, **1** and **2**

	HL	1	2
N^2H	10.49 (s, 1H)	-	-
N^1H	9.29 (s, br, 1H)	-	-
N^4H	7.97 (t, br, $J = 5.0$ Hz, 1H)	-	-
C^{13}H	8.67 (d, $J = 4.5$ Hz, 1H)	8.08 (d, $J = 8.0$ Hz, 1H)	7.96–7.93 (m, 1H),
C^{16}H	8.05 (d, $J = 7.5$ Hz, 1H)	8.01 (dd, $J = 8.0$ Hz, 1.5 Hz, 1H)	7.81 (br, s, 1H)
C^{15}H	8.01 (dt, $J = 1.5$ Hz, 8.0 Hz, 1H)	7.97 (d, $J = 8.0$ Hz, 1H)	7.80 (br, s, 1H)
C^{14}H	7.64 (ddd, $J = 2.0$ Hz, 5.0 Hz, 7.0 Hz, 1H, Py)	7.50–7.40 (m, 1H)	7.46 (br, 1H)
CH_2	3.45 (dq, $J = 7.0$, 7.0 Hz, 2H)	hidden	3.24 (br)
CH_3	1.05 (t, $J = 7.5$ Hz, 3H)	1.16 (t, $J = 7.5$ Hz, 3H)	1.06 (t, $J = 7.5$ Hz, 3H)

The resonances of aromatic protons are observed in the region of 7.0 - 8.5 ppm. The triplet signal at 1.16 ppm is accompanied by protons of the methyl group, while the signals of the methylene group are unexpectedly hidden by those of the DMSO- d_6 solvent. A similar situation is detected in the ^1H NMR spectrum of **2** (Figure 3c). However, methylene protons' resonance partially overlaps with solvent signals. The assignment of remaining signals in the spectrum of **2** resembles the results obtained in the case of **1** (Table 3). It is remarkable that the well-resolved ^1H NMR spectrum of **2**

reveals its diamagnetism, and, thus, indicates the formal oxidation state "+3" of the cobalt ion in **2**. Perhaps, cobalt(II) ions in the starting material were oxidized by atmospheric dioxygen during the complexation. The existence of cobalt(III) ion in **2** is indirectly confirmed by mass spectrometry. Indeed, the ESI $^+$ spectrum of **2** exhibits the base peak with $m/z = 504.98$ (Figure 4) assigned to the cation $[\text{Co}(\text{L})_2]^+$ (calcd. 505.06) consisting of one cobalt(III) ion and two singly deprotonated ligands $\{\text{L}^-\}$.

Figure 4. ESI $^+$ mass spectrum of **2**.

The structural features deduced from spectroscopic studies are verified by X-ray crystallography. Single crystals of **1** were

obtained by recrystallizing the compound in hot DMSO. The quality of the crystals, however, was not appropriate for a detailed discussion

about the bond lengths and angles. But the molecular structure of **1** could be revealed, obviously. It is shown in Figure 5 that **1** is a mononuclear octahedral Zn(II) complex, in which the zinc(II) ion is coordinated with two singly deprotonated ligands $\{L^-\}$ through ($N_{\text{pyridine}}, N^1, S$) donor sets.

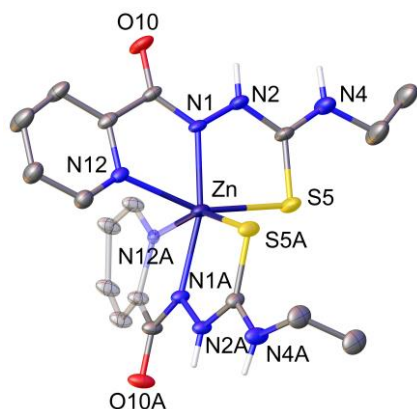


Figure 5. Molecular structure of the complex $[Zn(L)_2]$ (**1**). Hydrogen atoms bonded to carbons are omitted for clarity.

The metal complex **2** crystallizes in the monoclinic non-centromeric space group $P2_1$ with two crystallographically independent molecules in the asymmetric unit. Selected

bond lengths are introduced in Table 4. As expected from spectroscopic studies, the X-ray structure analysis indicates that **2** is a cationic Co(III) complex. The structure of the complex cation in **2** closely resembles the structure of **1**. Particularly, the cobalt(III) ions are octahedrally bonded to two tridentate ligands $\{L^-\}$ via ($N_{\text{pyridine}}, N^1, S$) chelates (Figure 6). The charge compensation is done by the counteranion Cl^- . The $Co^{III}-N$ and $Co^{III}-S$ bonds (Table 4) are shorter than the similar bonds detected in several homoleptic complexes of divalent metal ions with picolinoyl (4-phenylthiosemicarbazide) [6].

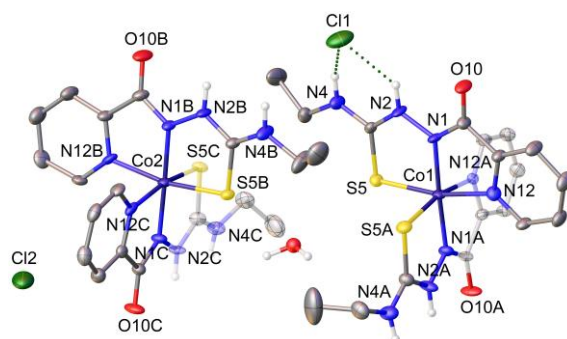


Figure 6. Molecular structure of the asymmetric unit of $[Co(L)_2]Cl$ (**2**). Hydrogen atoms bonded to carbons are omitted for clarity—the dotted lines present hydrogen bonds.

Table 4. Selected bond lengths (Å) in $2[Co(L)_2]Cl \cdot 0.5H_2O$

Co1–S5	2.246(8)	Co2–S5B	2.248(2)
Co1–N1	1.872(5)	Co2–N1B	1.877(5)
Co1–N12	1.983(5)	Co2–N12B	1.986(5)
Co1–S5A	2.240(2)	Co2–S5C	2.248(8)
Co1–N1A	1.888(5)	Co2–N1C	1.864(5)
Co1–N12A	2.006(5)	Co2–N12C	1.981(6)
C10–O10	1.242(7)	C10B–O10B	1.243(8)
N1–C10	1.312(8)	N1B–C10B	1.326(8)
N1–N2	1.410(7)	N1B–N2B	1.372(7)
N2–C3	1.330(8)	N2B–C3B	1.325(8)

C3–N4	1.333(8)	C3B–N4B	1.301(8)
C3–S5	1.716(6)	C3B–S5B	1.728(6)
C10A–O10A	1.238(7)	C10C–O10C	1.258(8)
N1A–C10A	1.306(8)	N1C–C10C	1.319(8)
N1A–N2A	1.374(7)	N1C–N2C	1.392(7)
N2A–C3A	1.341(8)	N2C–C3C	1.318(8)
C3A–N4A	1.308(9)	C3C–N4C	1.337(8)
C3A–S5A	1.726(7)	C3C–S5C	1.721(7)

The partial double bond character of C–O, C–N, C–S, and N–N bond distances (Table 4) indicates the typical π -electron delocalization within the acylthiosemicarbazide skeletons [2-3, 8, 11]. In comparison with the structure of the uncoordinated ligand **HL** [3], the elongation of the C–O bond and the contraction of the C–N¹ bond could account for the bathochromic shift of the C=O absorption band in the IR spectra of the complexes despite the exclusion of O atoms from the coordination spheres of the metal ions.

4. Conclusion

Two new Zn(II) and Co(III) homoleptic complexes derived from picolinoyl (4-ethylthiosemicarbazide), **HL**, have been synthesized and characterized by spectroscopic methods as well as single crystal X-ray diffraction. The studies demonstrate mononuclear octahedral complexes, in which the metal ions are coordinated with two singly deprotonated tridentate ligands {L⁻} through (*N*_{pyridine}, *N*¹, *S*) chelates.

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