

Chemical and Electrochemical synthesis for some Metal Complexes of 6-Phenyl-2-thioxo-1,2-dihydropyridine-3-carbonitrile Derivatives

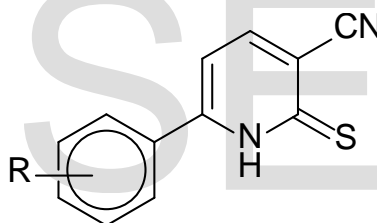
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Abstract— A new metal Chelates of 6-Phenyl-2-thioxo-1,2-dihydropyridine-3-carbonitrile (HL¹) and its derivatives, 6(4-Methylphenyl)-2-thioxo-1,2-dihydropyridine-3-carbonitrile (HL²), 6(4-Chlorophenyl)-2-thioxo-1,2-dihydropyridine-3-carbonitrile (HL³) were prepared and yields complexes of the compositions [M(L)₂.(H₂O)₂] and [M(L)₂.(acetone)(H₂O)], where M = Cu(II), Co(II), Ni(II) and L is the ligand. Chemical analysis, infrared as well as thermal analysis are presented to confirm the formulation of the complexes. The spectral data show that the ligands are coordinated to the metal via the thioenol sulfur atom and the nitrogen atom of cyano groups.

Index Terms— 6-Phenyl-2-thioxo-1,2-dihydropyridine-3-carbonitrile (HL¹), 6(4-Methylphenyl)-2-thioxo-1,2-dihydropyridine-3-carbonitrile (HL²), 6(4-Chlorophenyl)-2-thioxo-1,2-dihydropyridine-3-carbonitrile (HL³), complexes, ligand.

1 INTRODUCTION

Pyridine-2-(1H)-thiones, Mercaptopurine and 2(2H)-Pyridinethione Glycosides have been prepared¹⁻¹³. Most of these compounds have clinical importance and biological activity. We report and complete the chemical synthesis of some M(II) complexes of a new series of pyridinethione ligands as shown in Fig. 1.



Ligand	R
HL ¹ :	H
HL ² :	CH ₃
HL ³ :	Cl

Fig. 1. The Structures of Pyridinethione Derivatives

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2 EXPERIMENTAL

2.1 Chemicals and Materials

All the chemicals (Aldrich) were subjected to purification before use. The solvents used were reagent grade. DMF (BDH) (Analar), absolute ethanol and methanol (Fluka) were used as supplied.

2.2 Preparation of the Organic Compound

All the organic compounds were previously prepared¹⁻¹³. The structure of the ligand was determined by elemental analysis, IR ¹H and ¹³C-NMR spectroscopies.

2.3 Chemical Preparation of the Complexes

Preparation of the Complexes

The complex $[\text{Cu}(\text{L}^1)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ was prepared by the following procedures. An aqueous solution of hot ethanol of the ligand, 6-Phenyl-2-thioxo-1,2-dihydropyridine-3-carbonitrile (HL^1) (2.12 g, 0.02 mol) dissolved in absolute ethanol solution of (60 mL) was added to Copper(II) acetate anhydrous (1.82g, 0.01 mol) and stirred for about 2 hrs. The complex $[\text{M}(\text{L}^2)_2(\text{acetone})_2]$ was prepared by the following procedures. An aqueous solution of acetone solution of the ligand, 6(4-Methylphenyl)-2-thioxo-1,2-dihydropyridine-3-carbonitrile (HL^2), (2.26 g, 0.01 mol) dissolved in absolute ethanol solution of (60 mL) was added to Copper(II) acetate anhydrous (1.82g, 0.01 mol) and stirred for about 2 hrs. The complex $[\text{Cu}(\text{L}^3)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ was prepared by the following procedures. An aqueous solution of hot ethanol of the ligand, 6(4-Chlorophenyl)-2-thioxo-1,2-dihydropyridine-3-carbonitrile (HL^3), (2.45 g, 0.01 mol) dissolved in absolute ethanol solution of (60 mL) was added to Copper(II) acetate anhydrous (1.82g, 0.01 mol) and stirred for about 2 hrs., leave the reaction mixtures which produced a colored compound overnight. All the precipitates were filtered, washed with ethanol and dried¹⁴. The Cobalt and Nickel complexes were prepared in the same way.

3 ELECTROCHEMICAL SYNTHESIS OF THE COMPLEXES

3.1 Materials

Copper and nickel were used as sheets (2 x 2 cm); cobalt was used in the form of rods (Alfa). Acetone (reagent grade) was dried over anhydrous MgSO_4 . The ligands were prepared following the literature procedures⁶.

3.2 Electrochemical Procedure

The electrochemical technique was essentially the same as reported previously⁹⁻¹¹. A cell unit consisted of a 100 mL beaker containing anhydrous acetone solution of the thione derivative with a platinum cathode and a sacrificial anode (Co, Ni or Cu) immersed in the liquid phase. A

3.3 Electrochemical Synthesis of $\text{Cu}(\text{L}^3)_2 \cdot (\text{acetone})_2$

Electrolysis of copper into 60 mL of anhydrous acetone solution of the organic ligand HL^3 (0.49 g, 2 mmol), 2.5 mg Et_4NClO_4 dissolved in two drops of water and 40 mA current led to dissolution of 34 mg of Cu during 30 min. ($E_f = 0.5 \text{ mol.F}^{-1}$). Since, most of the products are insoluble in the reaction mixture, the collection procedure involved filtration, after which the solid was washed with diethyl ether. The resulting powder (0.51 g, 100 %) was collected and analyzed as $[\text{Cu}(\text{L}^3)_2 \cdot (\text{acetone})_2]$.

4 SPECTRAL, ANALYTICAL AND PHYSICAL MEASUREMENTS

4.1 IR, Raman and 1H-NMR spectra

Infrared spectra for the samples were recorded by Perkin Elmer FTIR 1605 using KBr pellets. The 1H NMR spectra were recorded on a Varian Mercury VX-300 NMR spectrometer. 1H-NMR spectra were run at 300 MHz and ¹³C-NMR spectra were run at 75.46 MHz in deuterated dimethylsulphoxide (DMSO-d_6). Chemical shifts are quoted in δ and were related to that of the solvents.

4.2 Electronic spectra

The electronic spectra of solutions were measured in UV/Vis range (190-1100) nm using UV Spectrometer at Nahda University.

4.3 Magnetic Molar conductance measurements

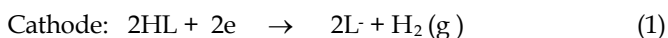
Magnetic measurements were carried out on a Sherwood Scientific magnetic balance using Gouy method. Molar conductivities of freshly prepared $1.0 \times 10^{-3} \text{ mol L}^{-1}$ DMSO solutions were measured using Jenway 4010 conductivity meter.

4.4 Microanalytical, Magnetic and Molar measurements

Carbon and hydrogen contents were determined using a Perkin-Elmer CHN 2400 analyser. Magnetic measurements were carried out on a Sherwood Scientific magnetic balance using Gouy method. Molar conductivities of freshly prepared $1.0 \times 10^{-3} \text{ mol/dm}^3$ solutions of the complexes in DMSO were measured using Jenway 4010 conductivity meter.

5 RESULT AND DISCUSSION

The preparative results show that the direct electrochemical oxidation of the metals in the presence of a ligand solution is a one-step process and represents a convenient and simple route to a variety of main group and transition metal complexes. Measurements of the electrochemical efficiency, E_t , defined as moles of metal dissolved per Faraday of electricity, for the M/L system (where M = Co, Ni, Cu and L = ligand used) gave $E_t = 0.5 \pm 0.05 \text{ mol F}^{-1}$. The values listed in Table I show that the reaction of the pyridinethione ligands with copper, cobalt and nickel anodes is compatible with the following equations¹⁴⁻¹⁹.



The pyridinethione derivatives may be represented by the two tautomeric forms *i.e.*, the thione form (I) and thiol form (II), in Fig. 2.

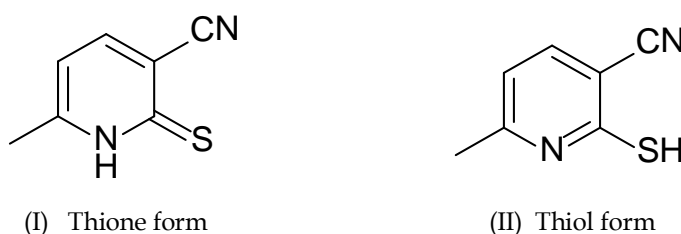


Fig. 2. Tautomeric Forms of Pyridinethione Derivatives.

5.1 Elemental analysis of pyridinethions

The isolated complexes of the pyridinethione derivatives were characterized by elemental analyses, IR, TG and DTG measurements. The results of the elemental analyses are in good agreement with the calculated values and the data are summarised in Table II. The complexes are stable in air and do not melt easily, are insoluble in H_2O , CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, CHCl_3 and soluble in acetone, dimethyl formide (DMF) and dimethyl sulfoxide (DMSO).

6-Phenyl-2-thioxo-1,2-dihydropyridine-3-carbonitrile: Orange crystals, (78%), crystallized from dioxane, m.p. 248°C , IR (v cm^{-1}): 3163 (NH), 3058 (aromatic-CH) and 2225 (CN); MS(z/m) = 212 (M^+ , 100% which corresponds to the molecular weight), 211 (M^+-H , 78%); 179 (M^+-SH , 18.2%); $^1\text{HNMR}$ (DMSO- D_6) (δppm): 7.228-7.722(m, 5H, Ar H's), 8.183-9.021 (m, 2H, pyridine Hs) and 14.23 (s, br, 1H, SH); MS (z/m) = 212; Anal. for $\text{C}_{12}\text{H}_8\text{N}_2\text{S}$ (212) Calcd./Found (%): C(67.90/67.91), H(3.80/3.82), N(13.20/13.23), and S (15.11/15.13).

6(4-Methylphenyl)-2-thioxo-1,2-dihydropyridine-3-carbonitrile: Red crystals, (67%), crystallized from ethanol, m.p. 180°C , IR (v cm^{-1}): 3178 (NH), 3065 (aromatic-CH) and 2226 (CN); MS (m/z) = 226 (M^+ , 100% which corresponds to the molecular weight), 225 (M^+-H , 69%); 193 (M^+-SH , 17.1%); $^1\text{HNMR}$ (DMSO- D_6) (δppm): 2.123 (s, 3H, CH_3), 7.205-7.728 (m, 4H, Ar H's), 8.273-9.032 (m, 2H, pyridine Hs) and 14.14 (s, br., 1H, SH); Anal. for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{S}$ (226) Calcd./Found (%): C(69.00/69.03), H(4.45/4.43), N(12.38/12.40), and S (14.17/14.20%).

6(4-Chlorophenyl)-2-thioxo-1,2-dihydropyridine-3-carbonitrile: Orange crystals (70%), crystallized from ethanol, m.p. 170°C , IR (v cm^{-1}): 3172 (NH), 3069 (aromatic-CH) and 2221 (CN); MS (m/z) = 246 (M^+ , 100% which corresponds to the molecular weight), 245 (M^+-H , 84%); 213 (M^+-SH , 12.5%); $^1\text{HNMR}$ (DMSO- D_6) (δppm): 7.209-7.721(m, 4H, ArH's), 8.271-9.028 (m, 2H, pyridine H's) and 14.17 (s, br., 1H, SH); Anal. for $\text{C}_{12}\text{H}_7\text{ClN}_2\text{S}$ (246) Calcd./Found (%): C(58.42/58.45), H(2.86/2.89), N(11.35/11.37), Cl(14.37/14.40) and S(13.00/13.03).

5.1 Infrared Spectra

A comparison of the infrared spectra of the pyridinethiones and their metal complexes show the following:

- The band at 3314.5 and 3200 cm^{-1} due to $\nu(\text{NH})$ in the ligand spectrum is absent in the spectra of the complexes indicating thioenolization.
- The band at 872.1 cm^{-1} , assigned to $\nu(\text{C}=\text{S})$, is absent in the spectra of the complexes indicating the rearrangement of $\text{C}=\text{S}$ *via* thioenolization¹².
- The 1578.6 and 1557.8 cm^{-1} bands [(thioamide III), $\nu(\text{CN}) + \nu(\text{CS})$] are absent in the complexes.

d. The shift to lower frequency of the cyano group by 10-15 cm⁻¹ may suggest the participation of the nitrogen atom in complexation. All of these observations may suggest the participation of the thiol sulphur and the nitrogen of the cyano group in bonding as well as the release of a proton¹⁴ on coordination of the pyridinethione ligands with the metal ions in a molar ratio M:L = 1:2¹⁴. Most of the complexes exhibit ν(OH) and σ(H₂O) bands in the 3400-3450 and 680-690 cm⁻¹ regions which are indicative of coordinated water in these complexes¹⁴⁻²⁰. The non-ligand bands appearing at 440-450 and 410-420 cm⁻¹ in the complex spectra are tentatively assigned to ν(Cu - S)¹⁵⁻¹⁸ and ν(Cu ← N)¹⁵, respectively.

5.2 Electronic Spectra

The electronic spectrum of [Cu(L¹)₂(H₂O)₂].H₂O has bands characteristic for an octahedral geometry¹⁵⁻²³. The spectrum shows two bands at 17,850 and 19,230 cm⁻¹ assigned to the ⁴T_{1g} → ⁴A_{2g} (ν₂) and ⁴T_{1g} → ⁴T_{1g} (P) (ν₃) transitions, respectively, in an octahedral structure. These bands were used to calculate the third spin-allowed band, ⁴T_{1g} → ⁴T_{1g}¹⁷⁻²³. The value of ν₁ was found to be 9,520 cm⁻¹. The shoulder at 25,000 cm⁻¹ is due to a charge transfer transition, probably, HL⁶ → Cu(II)¹⁶. The crystal field splitting energies, Δ_o in kilojoules per mole for Cu(II) metal complexes can be calculated from the following relation: ⁽¹⁶⁾

$$\Delta_o \text{ (kJ/mol)} = hc N / \lambda$$

where h = 6.626 × 10⁻³⁴ (J.s), c = 3.00 × 10⁸ (m/s), λ = wavelength (m) and N = 6.023 × 10²³ (ions/mol). The calculated values of the crystal field splitting energies, Δ_o, were tabulated in table.¹⁶. The values of the crystal field splitting energies, Δ_o indicates that the size of the central metal ion affect on the degree of splitting of the d orbitals¹⁶.

The electronic spectrum of [Ni(L²)₂(H₂O)₂].4H₂O shows a broad band centered at 18,020 cm⁻¹ attributed to the ³A_{2g} → ³T_{1g} (F) transition (ν₂). The other shoulder band, (ν₃), was observed at 22,988 cm⁻¹ related to the ³A_{2g} → ³T_{1g} (P) transition. The experimental values were used to calculate ³A_{2g} → ³T_{2g} by the d⁸ equations reported for octahedral structures¹⁷⁻¹⁹ and it was found to be 10,073 cm⁻¹. The parameters B, β, 10Dq and the ν₂/ν₁ values were calculated to be 778 cm⁻¹, 0.75, 673, 8 cm⁻¹ and 1.78, respectively. These data confirm the suggested octahedral structure for Ni(L⁵)₂(H₂O)₂.4H₂O.

The electronic spectrum of [Co(L²)₂(H₂O)₂].H₂O has bands characteristic for an octahedral geometry¹⁷⁻¹⁹. The spectrum shows two bands at 17,850 and 19,230 cm⁻¹ assigned to the ⁴T_{1g} → ⁴A_{2g} (ν₂) and ⁴T_{1g} → ⁴T_{1g} (P) (ν₃) transitions, respectively, in an octahedral structure. These bands were used to calculate the third spin-allowed band, ⁴T_{1g} → ⁴T_{1g}^{12,17-20}. The value of ν₁ was found to be 9,520 cm⁻¹. The shoulder at 25,000 cm⁻¹ is due to a charge transfer transition, probably, HL⁶ → Co(II)¹⁶. The other ligand field parameters, B, β, 10Dq and the ν₂/ν₁ values were calculated to be 906 cm⁻¹, 0.88, 9,065 cm⁻¹ and 1.87, respectively, and are in good agreement with those reported for octahedral Co(II) complexes.

The electronic spectrum of [Cu(L³)₂(H₂O)₂].4H₂O shows weak shoulders at 18,370 and 13,300 cm⁻¹. The observed bands are due to ²B_{1g} → ²E_g and ²B_{1g} → ²A_{1g} transitions, on the basis of which a distorted octahedral geometry is suggested¹⁷⁻¹⁹. The broadening of the bands may be due to the Jahn-Teller effect¹⁸⁻²⁰. However, the 23,364 cm⁻¹ band is due to a d-π* transition²⁰.

Complex	Δ _o , (cm ⁻¹)	Δ _o (KJ/mol)	ν ₁	ν ₂	ν ₃	ν ₂ /ν ₁	B (cm ⁻¹)	β
			(calculated)					
[CoL ¹ (H ₂ O) ₂].2H ₂ O	11,950	130.08	10,900	23,500	29,850	2.16	1040	1.10
[Co L ² (H ₂ O) ₂].H ₂ O	11,740	127.79	14,300	23,800	32,600	1.66	900	0.86
[Co L ³ (H ₂ O) ₂].H ₂ O	11,700	127.34		25,000	30,000			
[Co L ⁴ (H ₂ O) ₂]	11,695	127.30	-	-	30,300	-	-	-
[Co L ⁵ (H ₂ O) ₂]	11,720	127.64	10,700	22,900	30,500	2.15	1100	1.10
[Co L ⁶].H ₂ O	11,680	127.19	-	-	29,850			
[Cu L ¹ (ac)(H ₂ O) ₂].H ₂ O	00,000	127.94	14,300	23,800	32,600	1.66	900	0.86
[Cu L ² (ac)(H ₂ O) ₂].H ₂ O	00,000	125.58	14,300	23,800	32,600	1.66	900	0.86

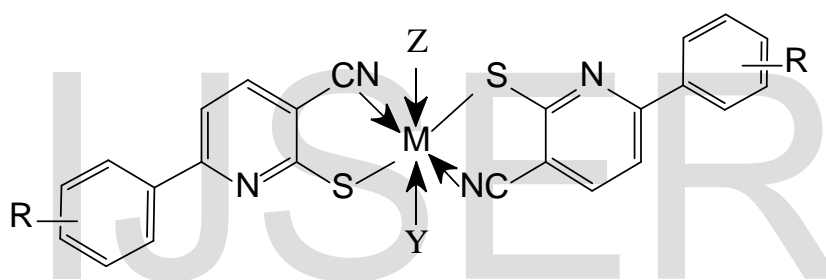
Table I. The crystal field splitting energies, Δ_o and some electronic ligand field parameters for Co(II) and Cu(II) complexes of Pyridinethione Derivatives.

5.3 Thermal Studies

The thermal behavior of the Cu(II) complexes of some of the pyridinethione derivatives were studied by thermogravimetric (TG) and differential thermal analysis (DTA). The TG thermaograms of $[Cu(L^3)_2 \cdot (H_2O)_2]$ show a weight loss at 190 °C of 6.0% (calc. 5.4%) corresponding to loss of water from the coordination sphere of the complex. The anhydrous Cu(II) thione complex begins to decompose at 190 °C, a process continuing up to 800 °C through a series of exothermic peaks at 231, 370, 501 and 698 °C, corresponding to decomposition of the organic ligand (calc. 78.8%; found 79.2%)¹⁶⁻²². Thermoanalytical methods, such as thermogravimetry, are excellent tools to follow the thermal decomposition of the complexes. The weight percent present at each interval temperature (*i.e.*, every 20 °C) in the TG run was determined and used to calculate the activation energies, ΔE , in each of the weight loss regions. It may be obtained from the following equation²²⁻²⁵

$$dw/dt = Aw^n e^{-\Delta E/RT}$$

Where A is a constant, E is the activation energy, n is the order of transition, R is the universal gas constant and T is the absolute temperature. According to the above equation, plots of $\ln(dw/dT)$ against $1/T$ for the Cu-complexes of pyridinethione derivatives result in straight lines. The activation energy may be estimated from the slope. The difference in the energy of activation may be due to various factors²⁵, mainly to differences in the electron withdrawing or electron donating groups in the molecules of the pyridinethione derivatives. In general, the effect of substituents on the hetero ring system and also on the phenyl group will lead to a decrease of cohesive forces and, consequently, will lead to a decrease of the activation energy.



M = Co(II), Cu(II) or Ni(II) , R = H, CH₃, Cl

Compound	M	Y	Z
$[M(L^1)_2(H_2O)_2]$	Cu	H ₂ O	H ₂ O
$[M(L^1)_2(H_2O)_2] \cdot 4H_2O$	Co	H ₂ O	H ₂ O
$[M(L^1)_2(\text{acetone})_2]$	Ni	CH ₃ COCH ₃	CH ₃ COCH ₃
$[M(L^2)_2(H_2O)_2]$	Cu	H ₂ O	H ₂ O
$[M(L^2)_2(H_2O)_2] \cdot 4H_2O$	Ni	H ₂ O	H ₂ O
$[M(L^3)_2(\text{acetone})_2]$	Cu	CH ₃ COCH ₃	CH ₃ COCH ₃
$[M(L^3)_2(H_2O)_2] \cdot H_2O$	Co	H ₂ O	H ₂ O
$[M(L^3)_2(\text{acetone})_2]$	Ni	CH ₃ COCH ₃	CH ₃ COCH ₃

Fig. 3. Suggested Structures for some of the isolated Complexes.

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