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CHEMICAL AND ELECTROCHEMICAL PREPARATION FOR Co(II) COMPLEXES OF SOME NOVEL PYRIDINE-2-(1H)-THIONE RING FUSED CYCLOALKANE DERIVATIVES

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Anodic oxidation of cobalt and copper metals in an anhydrous acetone solution of pyridine-2-(1H)-thione-3-cyano-4-(2-bromophenyl)-5,6-ring fused cycloheptane (HL¹) and its derivatives, (HL²), (HL³), (HL⁴), (HL⁵), (HL⁶), (HL⁷), (HL⁸), and (HL⁹) yields complexes of composition [M(L)₂·(H₂O)₂]_n·H₂O and [M(L)₂·(acetone)₂], where M = Co(II) or Cu(II) and L is the ligand. Also, reaction of an aqueous ethanolic solution of Co(Ac)₂·2H₂O with the previous ligands was prepared. Elemental analysis, and infrared and electronic spectral data are presented to confirm the formulation of the amorphous complexes. The spectral data indicate that the ligands are coordinated to the metal via the thioenol sulfur atom and the nitrogen atom of cyano groups. The ligands react in the enol form through the anodic dissolution of the ligands or during the reaction with metal salts. The ligand field parameters and crystal field splitting energies, Δ_o, for different cobalt metal complexes were calculated.

Keywords Cobalt; crystal field parameter; electrochemical; infrared spectra; pyridine-thione

INTRODUCTION

In recent years, there has been an upsurge in interest in the coordination chemistry of heterocyclic thiones containing pyridyl groups.¹ Such ligands are of interest due to the various possibilities for reaction with metal ions,² and some pyridinethione complexes have been synthesized.³ Pyridine-2-(1H)-thiones, mercaptopurine, and 2(2H)-pyridinethione glycoside derivatives have been prepared by Elgemeie et al.^{4–8} Most of these compounds have clinical importance and biological activity. The present article deals with the synthesis of Co(II) complexes of a new series of pyridine-2-(1H)-thione ligands as shown in Figure 1. Most of these ligands act as bidentate chelating agents coordinating in the thioenol form during chemical or electrochemical synthesis. The effect of *o*-, *m*-, and *p*-substituents on the ligand field parameters and crystal field splitting energies, Δ_o, will be discussed.

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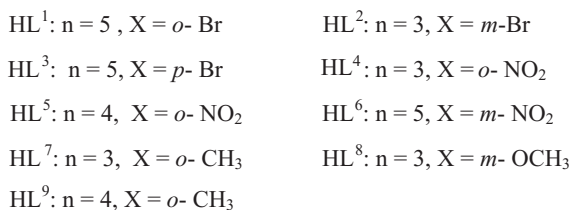
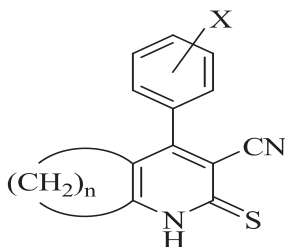
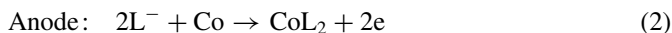
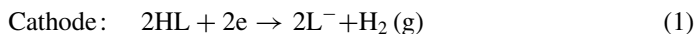


Figure 1 The structures of pyridinethione derivatives.

RESULTS 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 transition metal complexes.³ Measurements of the electrochemical efficiency, E_f , defined as moles of metal dissolved per Faraday of electricity, for the Co/L system (where L = ligand), gave $E_f = 0.5 \pm 0.05 \text{ mol F}^{-1}$. The values listed in Table I show that the reaction of the pyridinethione ligands with cobalt anode is compatible with the following equations³:



The pyridinethione derivatives may be represented by the two tautomeric forms.⁹ i.e., the thione form (I) and thiol form (II), as shown in Figure 2.

The isolated complexes of the pyridinethione derivatives were characterized by elemental analyses, IR, and electronic measurements. The results of the elemental analyses

Table I Electrochemical conditions for the synthesis of some pyridinethione complexes

Ligand	Amount of ligand mmol (g)	Metal used	Time of electrolysis at 40 mA, (min)	Metal consumed (mg)	Yield (g)	E_f
HL¹	0.11 (0.38)	Co	30	30	0.43	0.52
HL²	0.10 (0.33)	Co	30	29	0.39	0.51
HL³	0.1 (0.36)	Co	30	30	0.42	0.52
HL⁴	0.1 (0.32)	Co	35	40	0.38	0.53
HL⁵	0.1 (0.34)	Co	30	32	0.37	0.53
HL⁶	0.1 (0.32)	Co	30	35	0.35	0.51
HL⁷	0.1 (0.27)	Co	30	30	0.36	0.52

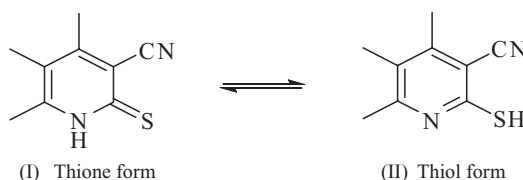


Figure 2 Tautomeric forms of pyridinethione derivatives. (I) Thione form; (II) thiol form.

are in good agreement with the calculated values, and the data are summarized in Tables II and III. The complexes are stable in air and do not melt easily.

IR Spectra

The infrared spectra of the metal complexes and the respective free pyridinethiones ligands are closely related. All complexes exhibit the expected bands for the thione derivatives, in particular the well-known four “thioamide bands” are observed.^{10,11} In the case of compound $[\text{Co}(\text{L}^7)_2(\text{H}_2\text{O})_2] \cdot 5\text{H}_2\text{O}$, for example, they are assigned as follows: 1560, 1220, 980, and 735 cm^{-1} , as the NH stretching vibration observed in the region $3010\text{--}2850\text{ cm}^{-1}$ overlapped with aliphatic CH stretching. The shift to lower frequency of the cyano group by $10\text{--}15\text{ cm}^{-1}$ may suggest the participation of the nitrogen atom in complexation. All of these observations may suggest the participation of the thiol sulfur² and the nitrogen of the cyano group in bonding, as well as the release of a proton on coordination of the pyridinethione ligands with the metal ions in a molar ratio $\text{M}:\text{L} = 1:2$, as shown in Figure 3. Most of the complexes exhibit $\nu(\text{OH})$ and $\sigma(\text{H}_2\text{O})$ bands in the $3400\text{--}3450$ and $685\text{--}700\text{ cm}^{-1}$ region, which is indicative of coordinated water in these complexes.³

The Crystal Field Splitting Energies and Electronic Spectra

The crystal field splitting energies, Δ_o , and some electronic ligand field parameters for Co(II) complexes of pyridinethione derivatives are listed in Table IV. The electronic spectrum of $[\text{Co}(\text{L}^1)_2 \cdot (\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, for example, has bands characteristic for an octahedral geometry.¹² The spectrum shows two main bands at $23,500$ and $29,850\text{ cm}^{-1}$, which are assigned to the ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g} (\nu_2)$ and ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g} (\text{P}) (\nu_3)$ transitions, respectively, in an octahedral structure. These bands were used to calculate the third spin-allowed band,

Table II Analytical results for the electrochemical preparation of pyridinethione complexes

Compound	Empirical formula	Formula weight	Color	Magnetic	% Found (Calc.)	
					C	H
$[\text{Co}(\text{L}^1)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	$\text{C}_{34}\text{H}_{36}\text{Br}_2\text{CoN}_4\text{O}_4\text{S}_2$	849.78	Violet	2.1 BM	48.0 (48.1)	4.5 (4.2)
$[\text{Co}(\text{L}^2)_2(\text{ac})_2]$	$\text{C}_{34}\text{H}_{32}\text{Br}_2\text{CoN}_8\text{O}_2\text{S}_2$	835.65	Brown	1.88 BM	52.4 (51.7)	4.2 (3.8)
$[\text{Co}(\text{L}^3)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	$\text{C}_{34}\text{H}_{36}\text{Br}_2\text{CoN}_4\text{O}_4\text{S}_2$	849.77	Faint brown	2.2 BM	47.5 (48.0)	4.0 (4.3)
$[\text{Co}(\text{L}^4)_2(\text{H}_2\text{O})_2]$	$\text{C}_{30}\text{H}_{24}\text{CoN}_6\text{O}_4\text{S}_2$	743.73	Brown	—	48.3 (48.5)	3.1 (3.3)
$[\text{Co}(\text{L}^5)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	$\text{C}_{32}\text{H}_{32}\text{CoN}_6\text{O}_8\text{S}_2$	807.79	Dark brown	—	47.2 (47.6)	3.6 (4.0)
$[\text{Co}(\text{L}^6)_2(\text{ac})_2] \cdot 2\text{H}_2\text{O}$	$\text{C}_{40}\text{H}_{44}\text{CoN}_6\text{O}_8\text{S}_2$	859.81	Faint brown	—	56.2 (55.9)	5.3 (5.1)

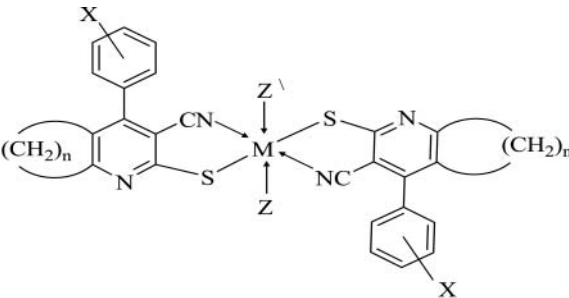
ac = acetone.

Table III Analytical results for the complexes of pyridinethione derivatives

Compound	Empirical formula	Formula weight	Color	Magnetic	% Found (Calc.)	
					C	H
[Co(HL ⁴)(OAc) ₂ (H ₂ O) ₂].5H ₂ O	C ₁₉ H ₃₁ CoN ₃ O ₁₃ S	600.39	Brown	4.32 BM	37.35 (38.0)	4.5 (3.8)
[Co(HL ⁵)(OAc) ₂ (H ₂ O) ₂]	C ₁₈ H ₁₉ CoN ₂ O ₁₂ S	546.15	Brown	—	54.0 (54.4)	4.7 (4.6)
[Co(L ⁷)(H ₂ O) OAc]	C ₁₈ H ₁₉ CoN ₂ O ₃ S	644.00	Brown	—	54.96 (55.00)	4.0 (4.3)
[Co(HL ⁸)(OAc) ₂].H ₂ O	C ₂₀ H ₂₂ CoN ₂ O ₆ S	477.41	Dark brown	1.94 BM	49.8 (50.3)	4.47 (4.6)
[Co(L ⁹) ₂ (H ₂ O) ₂].4H ₂ O	C ₃₄ H ₄₂ CoN ₄ S ₂ O ₆	726.84	Faint brown	—	56.2 (56.4)	5.7 (5.1)

⁴T₁g → ⁴T₁g¹³. The value of ν₁ was found to be 10,900 cm⁻¹. The other ligand field parameters, B, β, and the ν₂/ν₁ values were calculated to be 1040 cm⁻¹, 1.1, and 2.16, respectively, and are in good agreement with those reported for octahedral Co(II) complexes. The crystal field splitting energies, Δ_o, in kJ/mol for Co(II) metal complexes can be calculated from the following relation:^{14,15}

Δ_o (kJ/mol) = hcN/λ



Compound	n	M	Z	Z'	X
[M(L ¹) ₂ (H ₂ O) ₂].2H ₂ O	5	Co	H ₂ O	H ₂ O	<i>o</i> -Br
[M(L ²) ₂ (acetone) ₂]	3	Co	CH ₃ COCH ₃	CH ₃ COCH ₃	<i>m</i> -Br
[M(L ³) ₂ (H ₂ O) ₂].2H ₂ O	5	Co	H ₂ O	H ₂ O	<i>p</i> -Br
[M(L ⁴) ₂ (H ₂ O) ₂]	3	Co	H ₂ O	H ₂ O	<i>o</i> -NO ₂
[M(L ⁵) ₂ (H ₂ O) ₂].2H ₂ O	4	Co	H ₂ O	H ₂ O	<i>o</i> -NO ₂
[M(L ⁶) ₂ (acetone) ₂].2H ₂ O	5	Co	CH ₃ COCH ₃	CH ₃ COCH ₃	<i>m</i> -NO ₂
[M(L ⁷) ₂ (H ₂ O) ₂].5H ₂ O	3	Co	H ₂ O	H ₂ O	<i>o</i> -CH ₃
[M(L ⁹) ₂ (H ₂ O) ₂].2H ₂ O	4	Co	H ₂ O	H ₂ O	<i>o</i> -CH ₃

Figure 3 Suggested structures for all the isolated complexes in the enol-form.

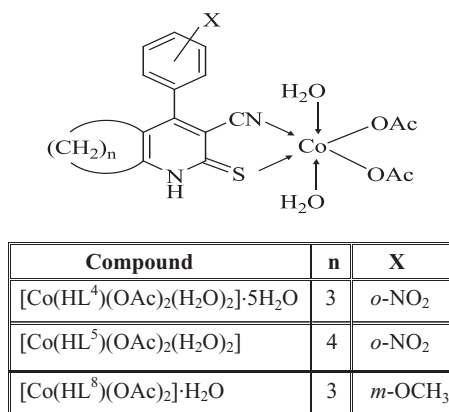
Table IV The crystal field splitting energies, Δ_o , and some electronic ligand field parameters for Co(II) complexes of pyridinethione derivatives

Complex	Δ_o , (cm^{-1})	Δ_o , (KJ/mol)	ν_1 , calculated	ν_2	ν_3	ν_2/ν_1	B (cm^{-1})	β
$[\text{Co}(\text{L}^1)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	11,950	130.08	10,900	23,500	29,850	2.16	1040	1.10
$[\text{Co}(\text{L}^2)_2(\text{acetone})_2]$	11,740	127.79	14,300	23,800	32,600	1.66	900	0.86
$[\text{Co}(\text{L}^3)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	11,700	127.34	15,020	25,000	30,000	1.67	810	0.85
$[\text{Co}(\text{HL}^4)(\text{OAc})_2(\text{H}_2\text{O})_2] \cdot 5\text{H}_2\text{O}$	11,695	127.30	14,245	23,700	30,300	1.66	800	0.85
$[\text{Co}(\text{HL}^5)(\text{OAc})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$	11,720	127.64	10,700	22,900	30,500	2.15	1100	1.10
$[\text{Co}(\text{L}^6)] \cdot \text{H}_2\text{O}$	11,700	127.75	10,800	23,300	29,850	2.16	1070	1.07
$[\text{Co}(\text{L}^7)_2(\text{H}_2\text{O})_2] \cdot 5\text{H}_2\text{O}$	11,680	127.19	14,230	23,200	29,850	1.63	1075	0.95
$[\text{Co}(\text{L}^8)] \cdot \text{H}_2\text{O}$	11,720	127.64	10,690	23,550	29,850	2.2	1130	1.1

where $h = 6.626 \times 10^{-34}$ (J.s), $c = 3.00 \times 10^8$ (m/s), λ = wavelength (m), and $N = 6.023 \times 10^{23}$ (ions/mol). The calculated values of the crystal field splitting energies, Δ_o , were tabulated in Table IV. These values indicate that the degree of splitting of the d orbitals affected by the type of the substituent, $\text{Cl} > \text{Br} > \text{I}$, following the spectrochemical series.^{14,15} Also, the values of the crystal field splitting energies, Δ_o , indicate that the differences in the electron-withdrawing or electron-donating groups in the molecules of the pyridinethione derivatives affect the degree of splitting of the d orbital.¹⁵

CONCLUSION

Upon comparing the solid complexes of pyridinethione derivatives obtained by either the chemical or electrochemical method, we found that there is a similarity in the structure between the isolated complexes for some ligands. The ligand HL^9 reacts in the enol form either by a chemical reaction with Co(II) acetate or by anodic oxidation of cobalt metal in non-aqueous solution. While the ligand HL^4 , as an example, reacts in the keto-form by a chemical reaction with Co(II) acetate as shown in Figure 4. The difference in the crystal field splitting energies, Δ_o , and some electronic ligand fields may be due to various

**Figure 4** Suggested structures for the keto-form complexes.

factors—mainly due to the differences in the electron-withdrawing or electron-donating groups in pyridinethione derivatives.

EXPERIMENTAL

The Organic Compounds

All the organic compounds, pyridine-2-(1H)-thione-3-cyano-4-(2-bromophenyl)-5,6-ring fused cycloheptane (**HL**¹), pyridine-2-(1H)-thione-3-cyano-4-(3-bromophenyl)-5,6-cyclopropane (**HL**²), pyridine-2-(1H)-thione-3-cyano-4-(4-bromophenyl)-5,6-cycloheptane (**HL**³), pyridine-2-(1H)-thione-3-cyano-4-(2-nitrophenyl)-5,6-cyclopentane (**HL**⁴), pyridine-2-(1H)-thione-3-cyano-4-(2-nitrophenyl)-5,6-cyclohexane (**HL**⁵), pyridine-2-(1H)-thione-3-cyano-4-(3-nitrophenyl)-5,6-cycloheptane (**HL**⁶), pyridine-2-(1H)-thione-3-cyano-4-(2-methylphenyl)-5,6-cyclopentane (**HL**⁷), pyridine-2-(1H)-thione-3-cyano-4-(3-methoxyphenyl)-5,6-cyclopentane (**HL**⁸), and pyridine-2-(1H)-thione-3-cyano-4-(2-methylphenyl)-5,6-cyclohexane (**HL**⁹) were prepared as described in the literature.^{4–8} The structures of the ligands were determined by elemental analysis, IR, ¹H and ¹³C NMR spectroscopies.

Materials

Cobalt was used in the form of rods (Alfa). Acetone (reagent grade) was dried over anhydrous MgSO₄. Cobalt acetate dihydrate was obtained from BDH company.

General Electrochemical Procedure

The electrochemical technique was essentially the same as reported previously.³ A cell unit consisting of a 100 mL beaker containing anhydrous acetone solution of the thione derivative with a platinum cathode and a sacrificial cobalt anode immersed in the liquid phase was used. A typical procedure for preparation of cobalt metal complex is described, and the electrochemical conditions are summarized in Table I.

Electrochemical Synthesis of [Co(L¹)₂·(H₂O)₂].2 H₂O

Electrolysis of cobalt metal into 60 mL of anhydrous acetone solution of **HL**¹ ligand as an example (0.36 g, 1 mmol), 1.5 mg Et₄NClO₄ dissolved in two drops of water, and 20 V current led to dissolution of 30 mg of Co over the course of 30 min ($E_f = 0.5 \text{ mol} \cdot \text{F}^{-1}$). 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 [Co(L¹)₂·(H₂O)₂].2 H₂O.

Chemical Synthesis of [Co(L⁹)₂·(H₂O)₂].4 H₂O

A hot ethanolic solution of the yellow colored ligand, **HL**⁹ (1 mmol, 0.31 g), was mixed with an aqueous ethanol solution of 0.5 mmol, 1.1 g of Co(OAc)₂·2H₂O. The reaction mixture was refluxed on a water bath for 1 h and then concentrated to one-third of its volume. The brown precipitate was filtered, washed several times with ethanol, and then dried. The elemental analysis of the cobalt complex, [Co(L⁹)₂(H₂O)₂].4H₂O, was found to be %C =

56.2 (56.4), %H = 5.7 (5.1). The solid cobalt complexes $[\text{CoHL}^4(\text{OAc})_2 \cdot (\text{H}_2\text{O})_2] \cdot 5\text{H}_2\text{O}$, $[\text{CoHL}^5(\text{OAc})_2 \cdot (\text{H}_2\text{O})_2]$, $[\text{CoL}^7(\text{OAc})_2 \cdot \text{H}_2\text{O}]_2 \cdot 5\text{H}_2\text{O}$, and $[\text{CoHL}^8(\text{OAc})_2] \cdot \text{H}_2\text{O}$ were prepared in a similar manner. Unfortunately, the resulting Co(II) complexes have an amorphous structure, so they can not be collected for X-ray crystals.

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