

Comparative Studies between Chemical and Tribochemical Reactions of Some Metal Complexes Derived from *N*-(*O*-Hydroxyphenyl)-*N'*-phenylthiourea (L)

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Abstract

The reactions of *N*-(*O*-hydroxyphenyl)-*N'*-phenylthiourea (L) derived from with Cu⁺, Cu²⁺, Co²⁺ and Co³⁺ chloride and/or iodide afford new metal complexes. The isolated complexes were synthesized by two different techniques (chemical and tribochemical methods). Two complexes were synthesized by the direct chemical reactions of *N*-(*O*-hydroxyphenyl)-*N'*-phenylthiourea (L) with MCl₂·XH₂O (M = Co²⁺ and Cu²⁺; X = 6 in case of Co²⁺ and X = 2 in case of Cu²⁺) in absolute EtOH. The general formulae of the two complexes derived by the chemical method are [Cu(L)₂(EtOH)₂]Cl₂ and [Co(L)₂Cl₂]Cl. These complexes were used to synthesize another two complexes using tribochemical reaction by grinding the previous chloride complexes with excess KI in agate mortar in the solid state. The isolated complexes have the general formulae, [Cu(L)I·H₂O]·1/2H₂O and [Co(L)I₃(EtOH)]·3EtOH. The results indicate the substitution of the chloride by iodide ions during grinding and extraction of the complexes by solvents. The IR spectra of the complexes suggest that L acts in a bidentate manner towards the metal ions. Moreover, the results of electronic spectra and magnetic measurements for the chloride complexes suggest distorted-octahedral structure for Cu²⁺ and low-spin octahedral structures around the Co^{II} and Cu²⁺ ions, respectively. On the other hand the data suggest that the iodide complexes have square-planer and low-spin for the Cu⁺ and Co³⁺ ions, respectively. The results of mass spectra confirm the formulae proposed for the isolated complexes. The mechanisms of reduction of Cu^{II} and oxidation of Co^{II} for the metal complexes were elucidated.

Keywords

Tribochemical Reactions, Derivatives of Thiourea Complexes, Cu²⁺ and Co³⁺ Complexes

1. Introduction

Thiourea is the analogue compound to urea and has a considerably wide range of applications. The properties of urea and thiourea differ significantly because of the difference in electronegativity between sulfur and oxygen [1]. Thiourea derivatives are selective analytical reagents, especially for the determination of transition metal in complexes [2]. The biological activity of thiourea complexes has been successfully screened for various biological actions. On the other hand some thiourea derivatives have been used in commercial fungicides [3]-[6]. Substituted thioureas have recently gained much interest in the synthesis of wide variety of biologically active compounds [7] [8]. The complexing capacity of thiourea derivatives has been reported in several papers [9] [10]. The metal complexes of thiourea are neutral and their colors vary with the nature of the metal ions. These chelating agents have been remarkable ones for analytical chemistry [11]. Also, thiourea coordinates to metal ions as neutral ligands, monoanions and dianions [12] [13]. Our goal in this paper is to prepare novel metal complexes via chemical and tribochemical methods. The isolated complexes were characterized by chemical and spectral measurements. Finally a comparative study has been described and discussed.

2. Experimental

N-(*O*-hydroxyphenyl)-*N'*-phenylthiourea (**L**) was synthesized by refluxing equivalent amounts of 2-aminophenol (10.9 g) dissolved in EtOH and phenyl isothiocyanate (12 ml) on hot plate for 2 h. The white product (m.p.; 138°C; yield: 93%) was obtained by cooling and characterized by chemical and spectral methods. The ligand (**L**) is insoluble in most organic solvents but easily soluble in DMF and DMSO.

2.1. Preparation of Metal Complexes

Preparation of Cu²⁺ and Co²⁺ Complexes by Chemical Method

Two complexes derived from Cu²⁺ and Co²⁺ ions with the general formulae, [Cu(**L**)₂(EtOH)₂]Cl₂ and [Co(**L**)₂-Cl₂]Cl, were synthesized by the direct reaction of CuCl₂·2H₂O (1.7 g, 0.01 mol) and/or CoCl₂·6H₂O (2.8 g, 0.01 mol) dissolved in EtOH (50 ml) with *N*-(*O*-hydroxyphenyl)-*N'*-phenylthiourea (4.8 g, 0.01 mol) dissolved in absolute EtOH (25 ml). The reaction mixtures were refluxed on a water bath for ~3 h. The two complexes were filtered off, washed several times with absolute EtOH followed by dry diethyl ether and finally dried in a vacuum desiccator over anhydrous CaCl₂. The results of elemental analyses and some physical properties are shown in Table 1.

2.2. Physical Measurements

The contents of copper and cobalt were carried using complexometric titration and xylenol orange as an indicator [14]. Elemental analyses contents (C, H and N) were determined at the Microanalytical Unit, Center of King Fahad Institute at Jeddah, Saudi Arabia. Molar conductivities measurements were carried out using Tacussel model CD 75. The chloride contents were determined as AgCl [14]. The IR spectra in the 200 - 4000 cm⁻¹ range were recorded in KBr on a Mattson 5000 FTIR Spectrometer. The electronic spectra of the Cu⁺, Cu²⁺, Co²⁺ and Co³⁺ complexes were recorded in Nujol mull in the range (200 - 900 nm) using Unicam spectrometer model

Table 1. Physical and chemical analysis of **L** and its complexes.

Compound; Empirical formula	(F. Wt)	Color	M.p. (°C)	% Found (Calcd.)				A _m ⁺ (DMSO)	Yield (%)
				C	H	N	S		
L ; C ₁₃ H ₁₂ N ₂ OS	244.321	White	137 - 139	63.7 (63.9)	5.0 (5.0)	11.3 (11.5)	13 (13.1)	-	94
[Cu(L)EtOH] ₂ Cl ₂ ; C ₃₀ H ₃₆ CuN ₄ O ₂ Cl ₃	715.228	Yellowish-green	171	50.4 (50.4)	4.2 (5.1)	7.2 (7.8)	9.6 (9.9)	66.3	83
[Co(L) ₂ Cl ₂]Cl; C ₂₆ H ₂₄ CoN ₄ O ₂ Cl ₃	653.931	Brown	146	47.8 (47.8)	3.6 (3.7)	9.2 (8.6)	8.8 (9.8)	49	80
[Cu(L)I(H ₂ O)·1/2H ₂ O; C ₁₃ H ₁₅ CuN ₂ O _{2.5} I	461.795	Pale yellow	260	33.3 (33.8)	2.9 (3.3)	6.8 (6.1)	6.2 (6.9)	10.2	74
[Co(L)I ₃ EtOH]·3EtOH; C ₂₁ H ₃₆ CoN ₂ O ₅ I ₃	868.261	Yellowish-brown	154	28.1 (29.1)	4.3 (4.2)	3.4 (3.2)	3.6 (3.8)	6.7	71

UV2. ^1H -NMR spectra of the free ligand and some of its metal complexes (Cu^+ and Co^{3+}) were recorded on Jeol-90Q Fourier transform (200 MHz) in CDCl_3 and ^1H -NMR Spectrometer (400 MHz) in d_6 -DMSO at King Saud University at Riyadh, Saudi Arabia. Magnetic moments were determined using a Sherwood balance at room temperature (25°C) with $\text{Hg}[\text{Co}(\text{NSC})_4]$ as a calibrate. The diamagnetic corrections for the ligand and the metal atoms were computed using Pascal's constants [15].

3. Results and Discussion

The results of the isolated solid complexes are listed in Table 1. All the isolated metal complexes are colored, stable against light and insoluble in most common organic solvents but easily soluble in DMF and DMSO. The molar conductivities for the chloride complexes, $[\text{Cu}(\text{L})\text{EtOH}]_2\text{Cl}_2$ and $[\text{Co}(\text{L})_2\text{Cl}_2]\text{Cl}$, in DMSO at 25°C are 66.3 and $49.0 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ indicating 1:2 and 1:1 electrolyte, respectively. The electrolytic nature of these complexes [16], except the two iodide complexes of the general formulae, $[\text{Cu}(\text{L})\text{I}\cdot\text{H}_2\text{O}]\cdot 1/2\text{H}_2\text{O}$ and $[\text{Co}(\text{L})\text{I}_3\cdot\text{EtOH}]\cdot 3\text{EtOH}$ are non-conducting in DMSO. Also, the results show that the metal complexes have comparatively low melting points (146°C - 260°C) suggesting a weak bonding between the metal ions and L. The structure of the ligand (L) is shown in Figure 1.

The IR spectrum of L in KBr (Figure 2) shows several bands at 3530, 3220, 3156 and 2948 cm^{-1} assigned to $\nu(\text{OH}; \text{free})$, $\nu(\text{NH}; \text{free})$, $\nu(\text{NH}; \text{hydrogen-bonded})$ and $\nu(\text{OH}; \text{hydrogen-bonded})$ vibrations, respectively. The bands observed at 1594, 1267 and 765 cm^{-1} are assigned to $\nu(\text{C}=\text{C})$ vibration while the latter two bands are assigned to $\nu(\text{CS})$ vibrations, respectively. The observation of broad weak bands in the 1940 - 1700 and 2750 - 2500 cm^{-1} region suggests the presence of intra-molecular hydrogen bonding of the types $\text{O-H}\dots\text{N}$ and/or $\text{N-H}\dots\text{O}$ [17] [18]. The results suggest that the first type of the hydrogen bonding ($\text{O-H}\dots\text{N}$) is more likely occurred.

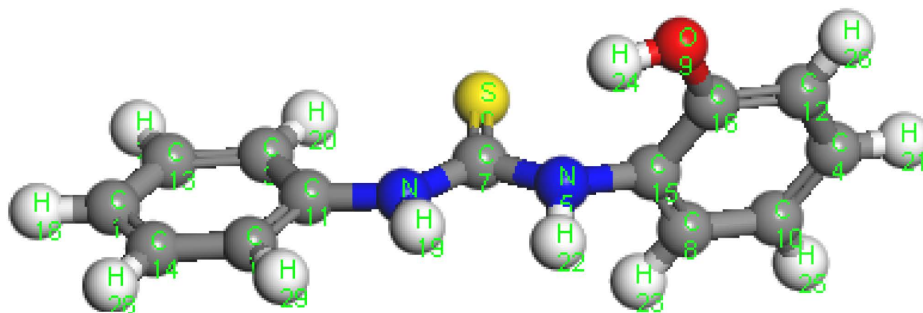


Figure 1. Structure of the ligand (L).

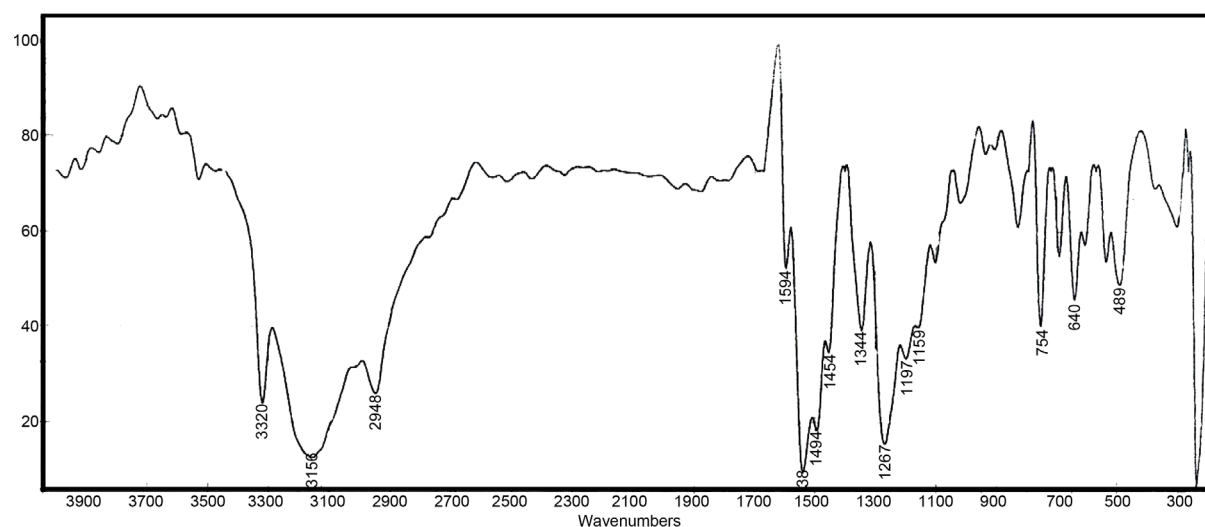


Figure 2. IR spectrum of L in KBr.

The ^1H -NMR spectrum of **L** in d_6 -DMSO (**Figure 3**) displays four signals with equal intensities at 9.98, 9.82, 9.12 and 8.1, relative to TMS. The first two signals are assigned to the OH (hydrogen-bonded) and OH (free) protons, respectively. The results are taken as strong evidence for the existence of hydrogen bonding and confirm the results from IR spectrum. The latter two signals are attributed to the protons of NH attached to (NH-CS) and (NH-Ph), respectively. The multiplet signals in the (7.57 - 6.79) ppm region are assigned to the protons of the two phenyl rings attached to the thiourea moiety.

A comparison of the IR spectra of **L** with Cu^{2+} and Co^{2+} complexes allows us to determine the mode of bonding. The IR spectra of the two complexes obtained by chemical method with the general formulae, $[\text{Cu}(\text{L})\text{EtOH}]_2\text{Cl}_2$ (**Figure 4**) and $[\text{Co}(\text{L})_2\text{Cl}_2]\text{Cl}$ (**Figure 5**), indicate that the **L** behaves in a bidentate manner and coordinates *via* the OH and NH groups forming five-member ring around the metal ions (**Figure 6** and **Figure 7**). The negative shifts of these two bands to lower wave numbers show the involvement of both the OH and NH groups in bonding. In comparing the IR data of **L** with the complexes we observed that the CS group remains more or less at the same position excluding the participation of this group in bonding.

The electronic spectra of the complexes of the Cu^{2+} and Co^{3+} with the general formulae, $[\text{Cu}(\text{L})\text{EtOH}]_2\text{Cl}_2$ (**Figure 8**) and $[\text{Co}(\text{L})_2\text{Cl}_2]\text{Cl}$ (**Figure 9**), were carried out in Nujol mull. The spectra of the first Cu^{2+} complex show a band at $14,368\text{ cm}^{-1}$ for the former Cu^{2+} complex which is attributed to $^2\text{E}_g \rightarrow ^2\text{T}_{2g}$ transition [19] in a distorted-octahedral geometry around the Cu^{2+} ion. The value of magnetic moment is 1.8 B.M. is taken as additional evidence for the existence of distorted-octahedral geometry around the Cu^{2+} ion. On the other hand, the diamagnetic nature of the Co^{2+} complex suggests the oxidation of Co^{2+} to Co^{3+} and the complex has a d^6 -configuration (low-spin). The electronic spectrum of $[\text{Co}(\text{L})_2\text{Cl}_2]\text{Cl}$ in Nujol mull shows three bands in the 15,700,

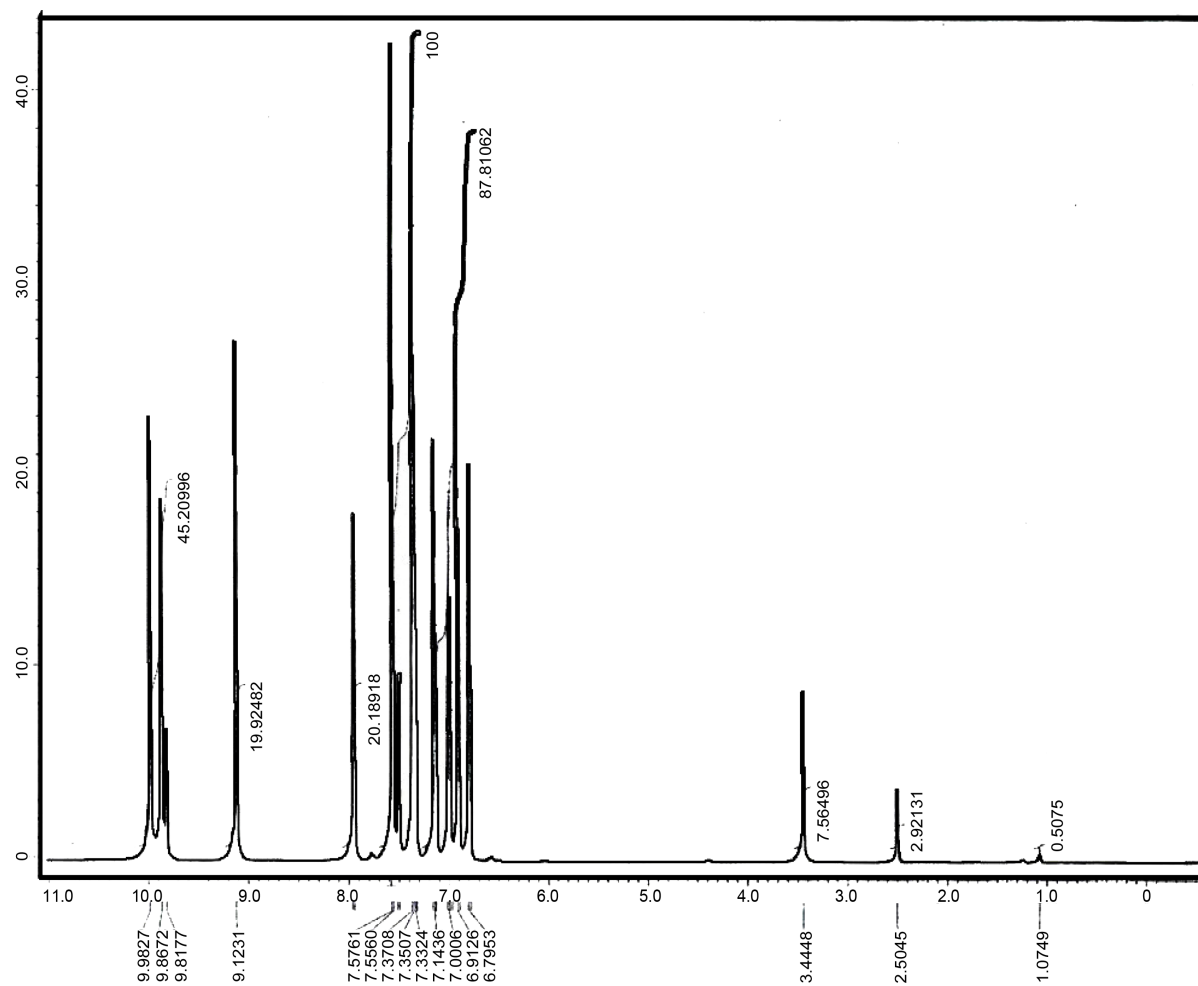


Figure 3. ^1H -NMR spectrum of **L** in d_6 -DMSO.

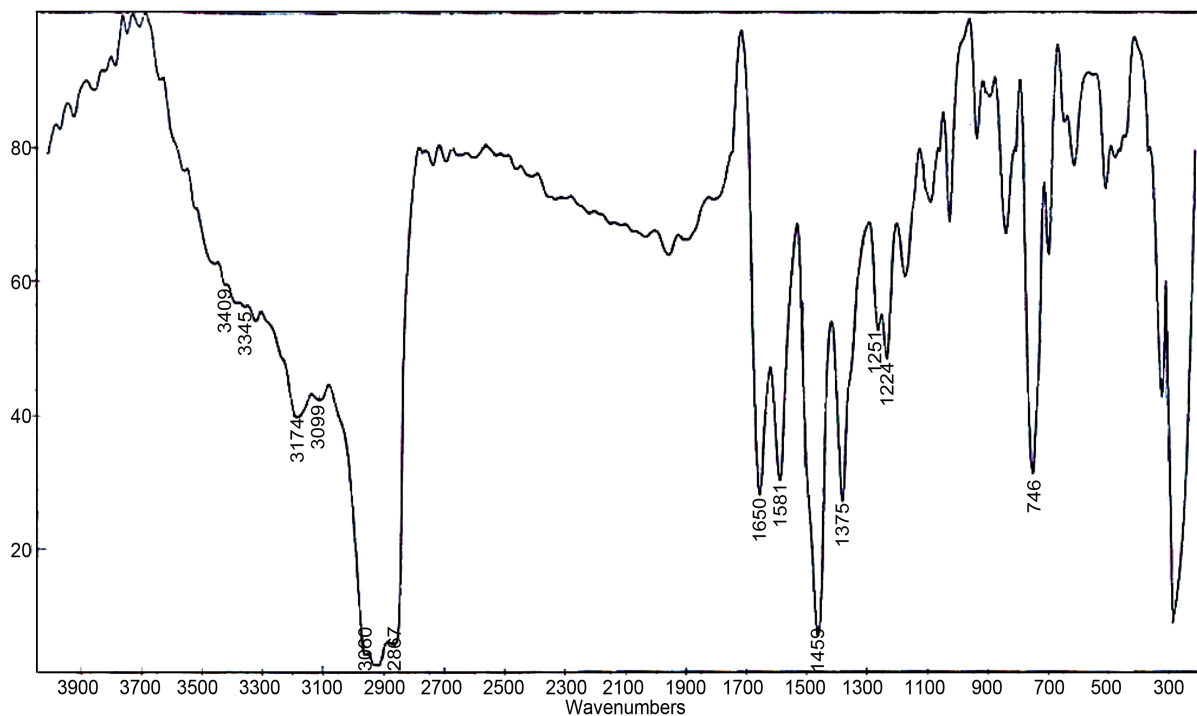


Figure 4. IR spectrum of $[\text{Cu}(\text{L})\text{EtOH}]_2\text{Cl}_2$ in nujol mull.

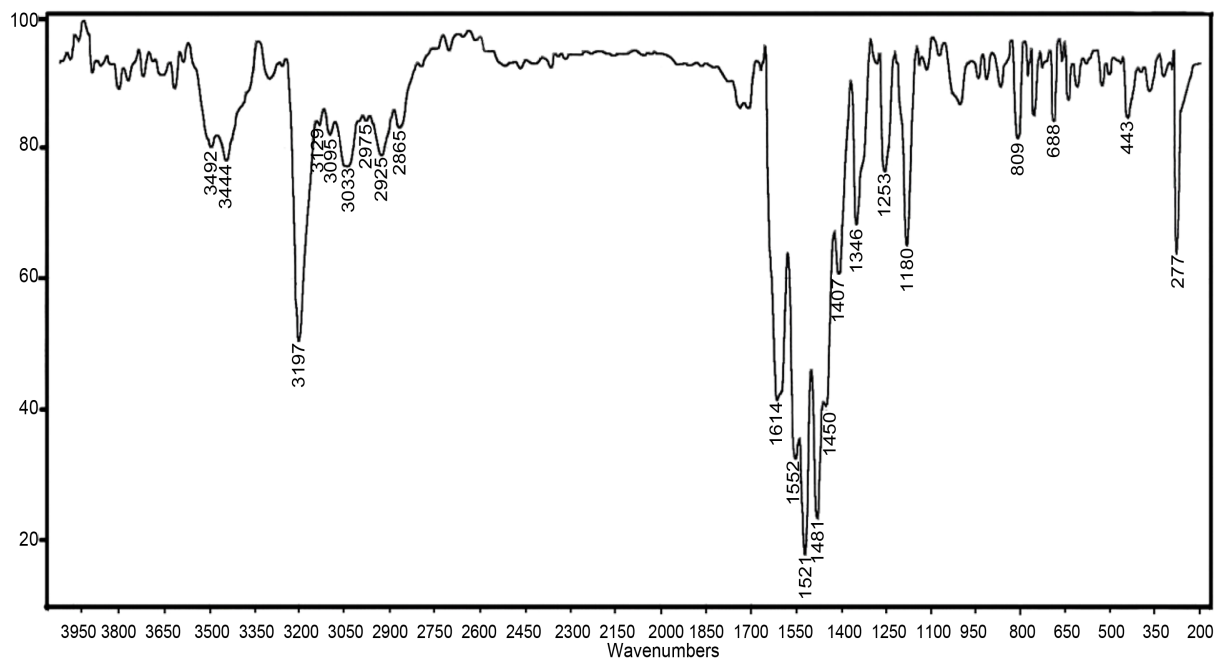


Figure 5. IR spectrum of $[\text{Co}(\text{L})_2\text{Cl}_2]\text{Cl}$ in nujol mull.

19,840 and 21,740 - 28,900 cm^{-1} regions attributed to the $^1\text{A}_{1g} \rightarrow ^3\text{T}_{2g}$, $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ and $^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$ transitions, respectively, in a low-spin Co^{3+} system. The observation of these three bands may also suggest that the complexes have *trans*-configuration [20] [21].

The Cu^+ and Co^{3+} complexes synthesized by tribochemical reaction are diamagnetic in nature. Also, the absent of any d-d transition bands in case of the Cu^+ complex synthesized is taken as evidence for the reduction of Cu^{2+} to Cu^+ . Figure 10 illustrates the structure of the iodide complex $[\text{Cu}(\text{L})\text{I} \cdot \text{H}_2\text{O}] \cdot 1/2\text{H}_2\text{O}$. The mechanism of

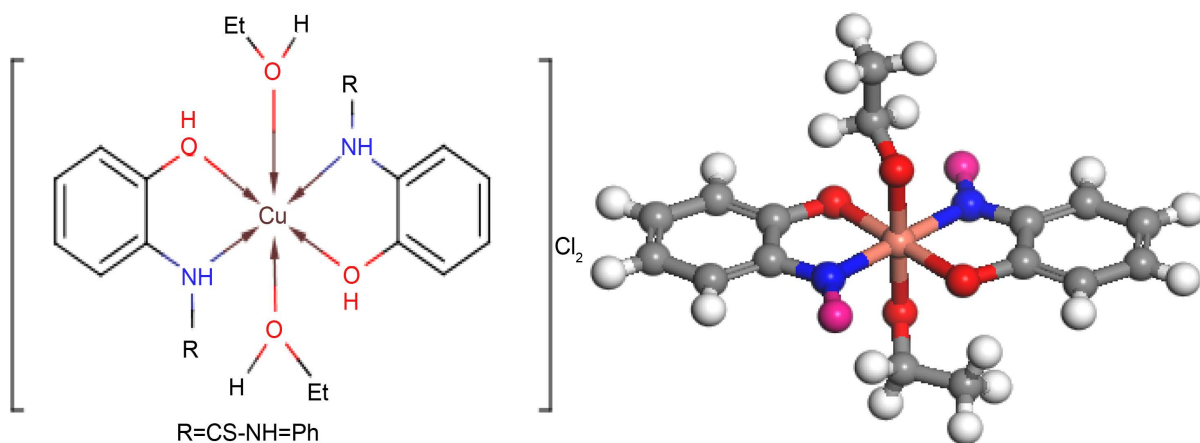


Figure 6. Structure of $[Cu(L)(EtOH)_2]Cl_2$.

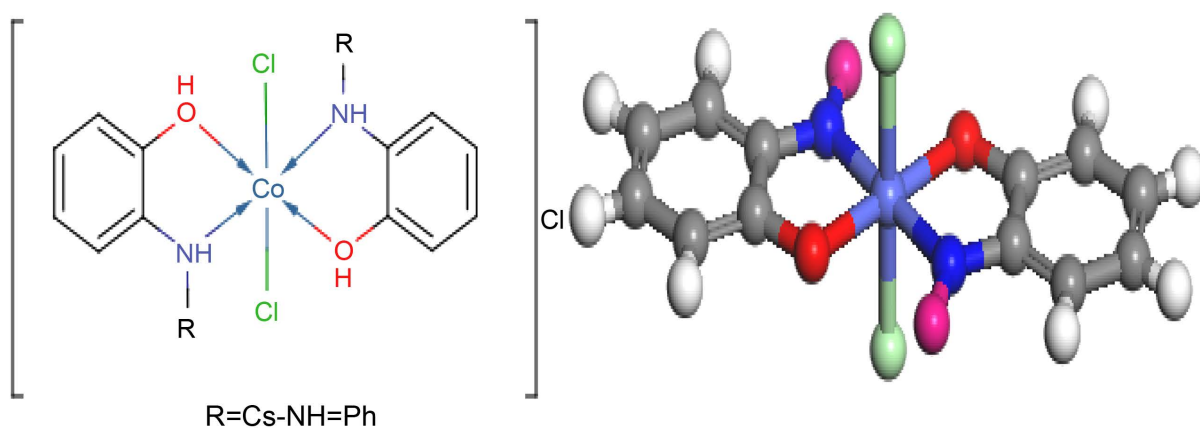


Figure 7. Structure of $[Co(L)_2Cl_2]Cl$.

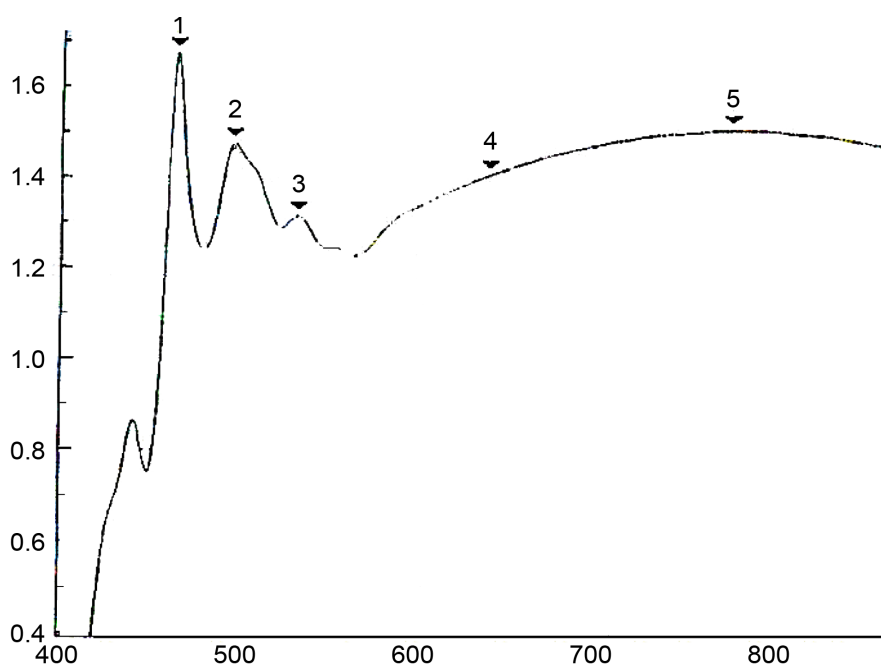


Figure 8. The electronic spectrum of $[Cu(L)(EtOH)_2]Cl_2$ in nujol mull.

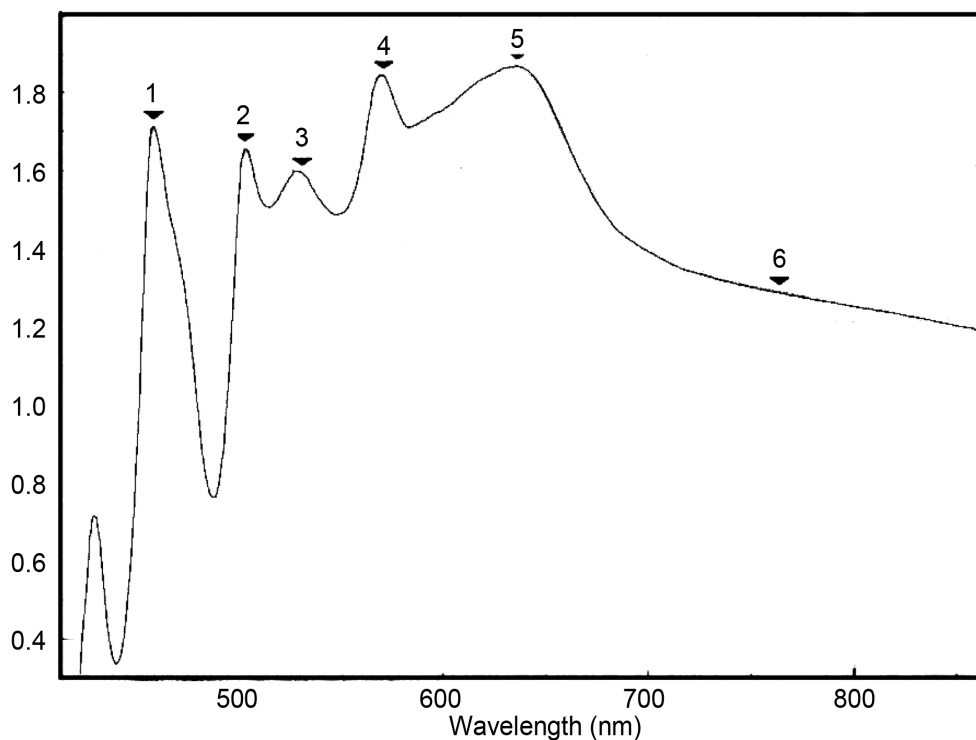


Figure 9. The electronic spectrum of $[\text{Co}(\text{L})_2\text{Cl}_2]\text{Cl}$ in nujol mull.

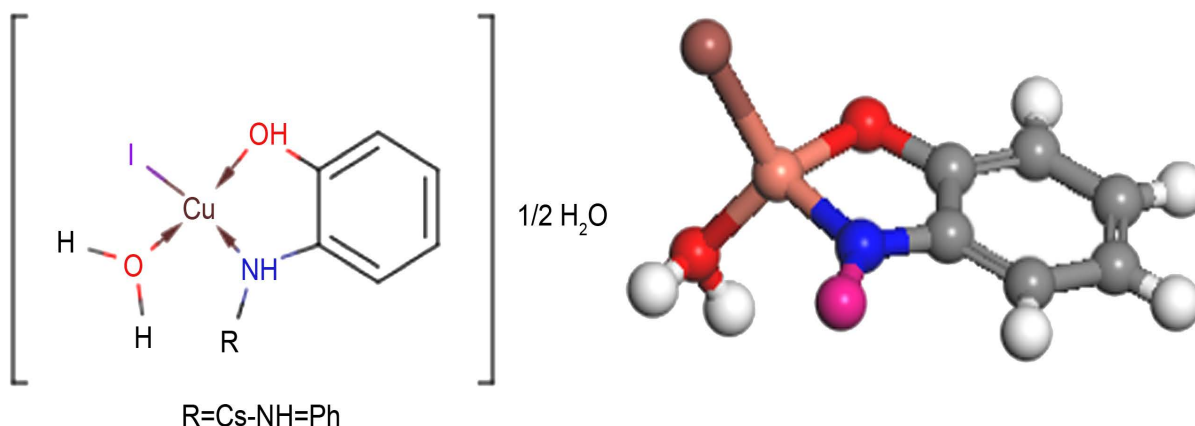


Figure 10. Structure of $[\text{Cu}(\text{L})\text{I}\cdot\text{H}_2\text{O}]\cdot\frac{1}{2}\text{H}_2\text{O}$.

reduction of Cu^{2+} to Cu^+ as well as the substitution of chloride by iodide ions during grinding and extraction by solvent is reported in our earlier work [22].

The IR spectrum of the Co^{3+} complex with the general formula, $[\text{Co}(\text{L})\text{I}_3(\text{EtOH})]\cdot 3\text{EtOH}$ (Figure 11), shows that the ligand behaves in a bidentate manner *via* the OH of the phenolic group and NH groups as discussed above. Also, the mechanism of oxidation of Co^{2+} to Co^{3+} as well as the substitution of chloride by iodide ions during grinding and extraction by solvent is reported earlier by Mostafa *et al.* [22]. The reduction process is observed in case of the reduction of Cu^{2+} to Cu^+ while the oxidation process in case of Co^{2+} to Co^{3+} complexes. Both types are diamagnetic in nature, which explains the nature of the isolated complexes.

The ^1H -NMR spectra of the Cu^+ and Co^{3+} complexes in d_6 -DMSO (Figure 12 and Figure 13) with the general formulae, $[\text{Cu}(\text{L})\text{I}\cdot\text{H}_2\text{O}]\cdot\frac{1}{2}\text{H}_2\text{O}$ and $[\text{Co}(\text{L})\text{I}_3(\text{EtOH})]\cdot 3\text{EtOH}$, are more less the same except that the former shows the signals of the OH proton due to the water molecule at 6.5 ppm. The latter complex exhibits signals at 13.7, 4.1 and 3.2 ppm assigned to the protons of OH, CH_2 and CH_3 of EtOH molecule, respectively.

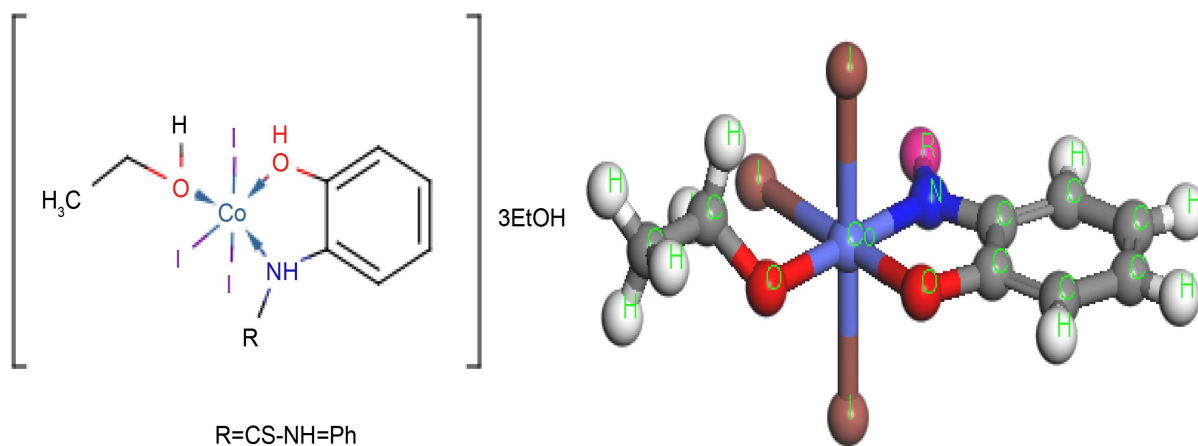


Figure 11. Structure of $[\text{Co}(\text{L})\text{I}_3(\text{EtOH})] \cdot 3\text{EtOH}$.

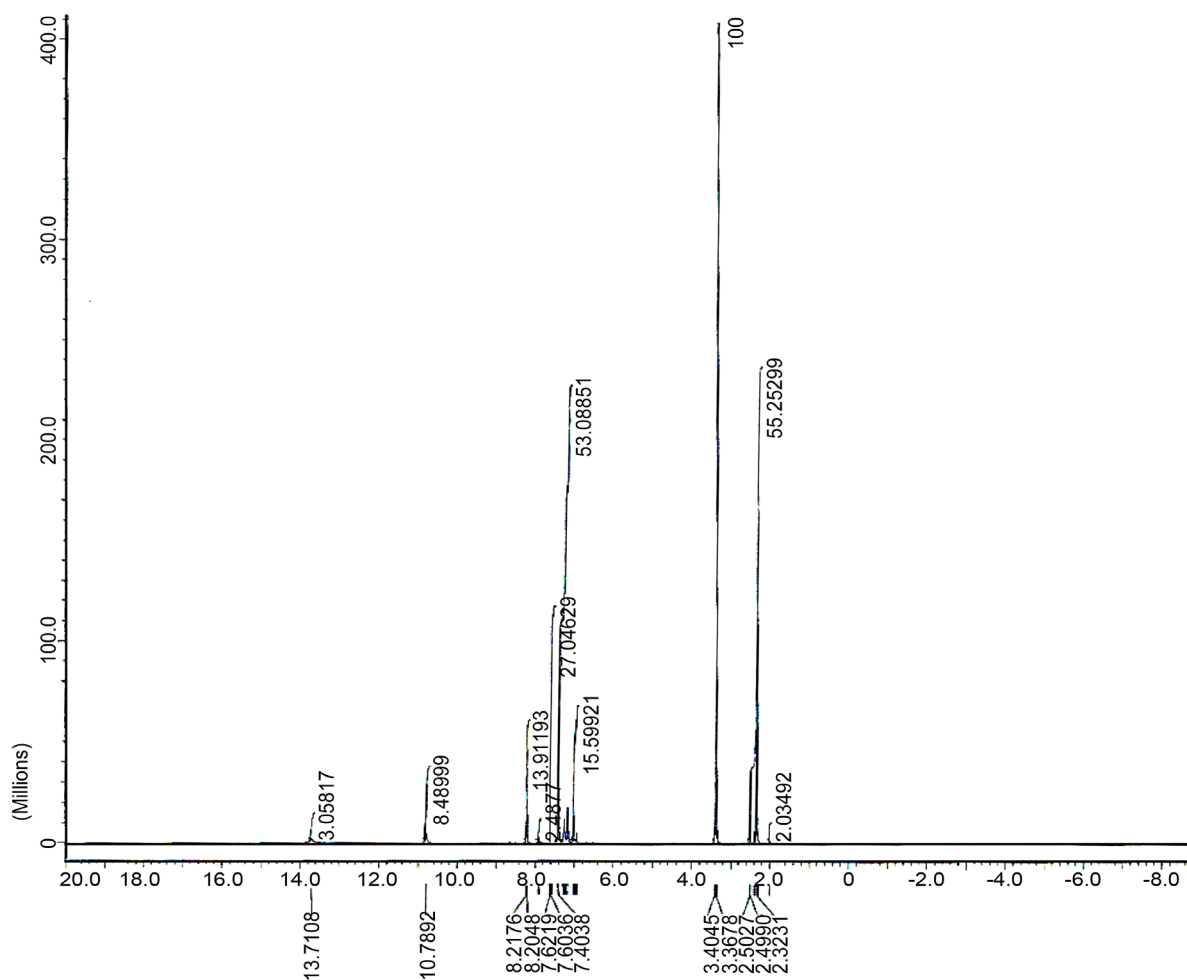


Figure 12. ^1H -NMR spectrum of $[\text{Co}(\text{L})\text{I}_3(\text{EtOH})] \cdot 3\text{EtOH}$ in d_6 -DMSO.

4. Conclusion

In continuation of our earlier work on tribochemical reactions and the role of metal ions as well as the ligand used in reduction of Cu^{2+} and oxidation of Co^{2+} , we extend our work to include *N*-(*O*-hydroxyphenyl)-*N'*-phenylthiourea (**L**) with Cu^+ , Cu^{2+} , Co^{2+} and Co^{3+} by chemical and tribochemical reactions. The ligand coordinates

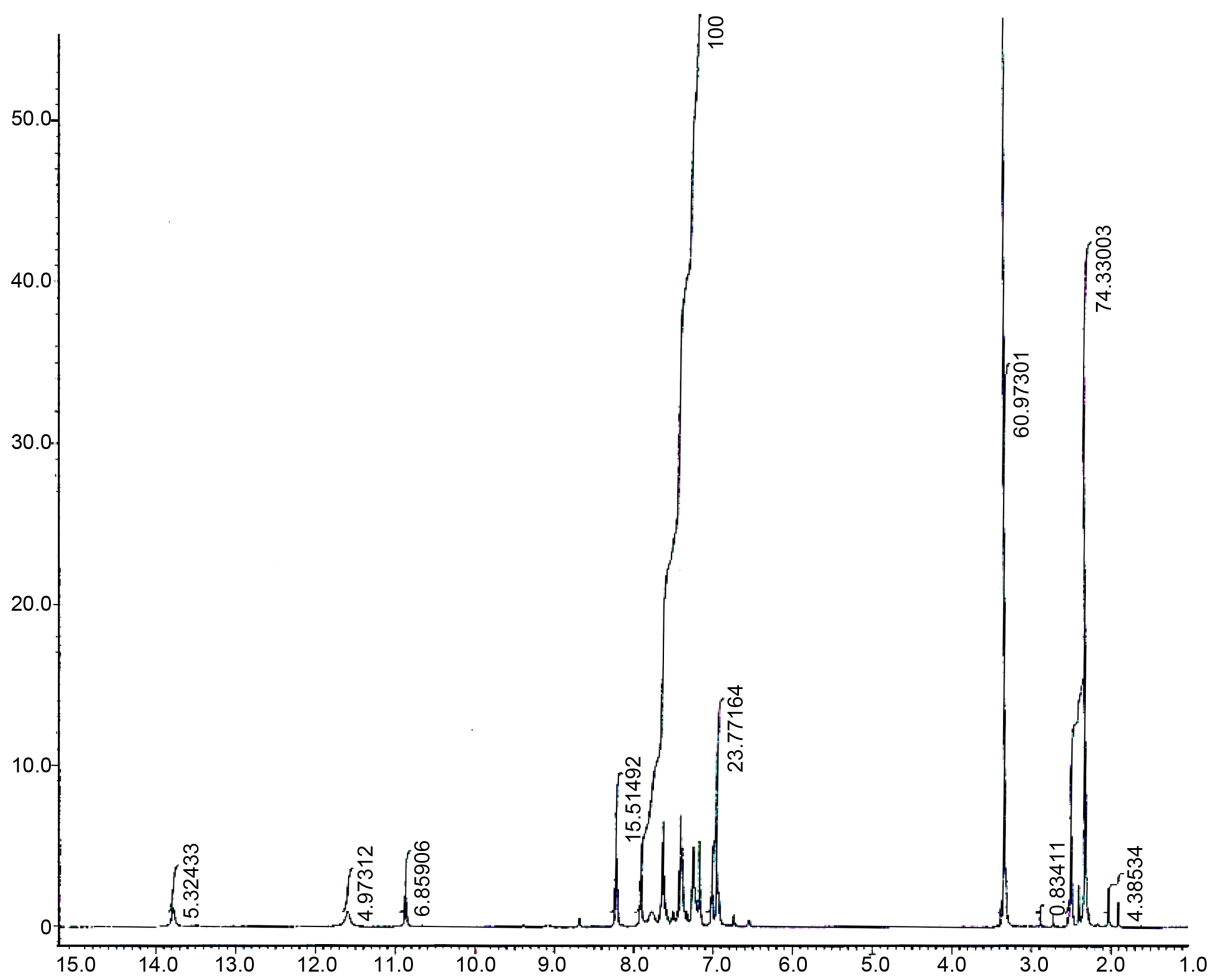


Figure 13. ^1H -NMR spectrum of $[\text{Co}(\text{L})\text{I}_3(\text{EtOH})]\cdot 3\text{EtOH}$ in $\text{d}_6\text{-DMSO}$.

in a bidentate manner towards the metal ions. The results indicate that the substitution of the chloride by iodide ions has occurred in Cu^{2+} and Co^{2+} complexes. Also, the reduction of Cu^{2+} to Cu^+ and the oxidation of Co^{2+} to Co^{3+} have occurred and been confirmed by chemical, spectral and magnetic measurements.

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