

**Spectroscopic studies of some Cu^I and Cu^{II} complexes derived by tribochemical reactions of some thiosemicarbazide derivatives containing Girard's P with KI**

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Received: 7th July, 2008 ; Accepted: 12th July, 2008**ABSTRACT**

The novel starting Cu^{II} complex with the general formula, [CuL₁Cl₂.H₂O]Cl. ½EtOH (L₁=N- {[(phenylaminomethyl) thioxomethyl] hydrazinocarbonyl methyl } pyridinium chloride (PTHPC), was synthesized by conventional chemical method. The tribochemical reaction of this Cu^{II} complex, [CuL₁Cl₂.H₂O]Cl. ½EtOH, with KI affords a novel Cu^I complex with the general formula, [Cu(L₁')I].7H₂O. The ligand (L₁') has the same formula as L₁, except that the ionizable chloride ion in L₁ is substituted by iodide ion in case of L₁' during the tribochemical reaction. Also, the Cu^{II} complex is reduced to Cu^I during the tribochemical reaction. The IR spectra of the Cu^{II} and Cu^I complexes suggest that both the ligands (L₁, L₂') coordinate in a tridentate manner via the carbonyl oxygen (C=O), NH² and thioketo (C=S) groups. The spectral and magnetic results suggest a distorted-octahedral geometry for the Cu^{II} complex prepared by conventional chemical method while a square-planar structure for the Cu^I complex synthesized by the tribochemical reaction. The mechanism of the reduction of Cu^{II} complex to Cu^I as well as the change of the color during the tribochemical reaction is discussed.

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KEYWORDS

Tribochemical reactions;
Novel Cu^I;
Cu^{II} complexes;
Girard's P complexes;
derivatives of
thiosemicarbazide complexes.

1. INTRODUCTION

In continuation of our earlier work on tribochemical reactions^[1-5], we report herein the synthesis of [Cu(L₁)Cl₂.H₂O]Cl. ½EtOH (L₁= {[(phenyl-amino methyl) thioxomethyl] hydrazinocarbonyl methyl } pyridinium chloride; PTHPC), by conventional chemical method in absolute EtOH.

The isolated Cu^{II} complex was used as a starting material to prepare the novel Cu^I complex by tribochemical reaction using KI. In fact few studies are reported on the ligands under investigation containing thiourea and/or thiosemicarbazide moieties and their

ability to form complexes with transition metal complexes either by conventional and/or tribochemical methods. The work in this paper was extended from studying Cu^{III}[3-4], Ru^{III}[5], to some Cu^{II} and Cu^I complexes with KI as a mulling agent using tribochemical reaction. Our goal in our earlier studies is to prepare Cu^{II} complex derived from this PTHPC^[6] as well as to characterize the stereochemistry of this complex in addition to some other transition metal complexes. Also, this study was undertaken in order to investigate the effect of KI on the composition of the isolated Cu^{II} complex as well as the stereochemistry of the isolated solid Cu^I complex derived from the ligand prepared from the reac-

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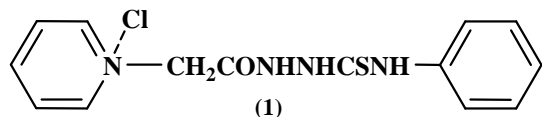
tion of phenyl isothiocyanate with Girard's P^{VI}. Hence, we extended our work to study tribochemical reaction for Cu^{II} complex containing thiosemicarbazide moiety with KI. Finally, the mechanism of reaction mixture and the type of bonding is discussed in details.

2. EXPERIMENTAL

All the chemicals used in this investigation were purchased from Aldrich and used as supplied.

2.1. Preparation of the ligand (PTHPC)

N-{(phenylamino) thioxomethyl} hydrazinocarboxyl methyl} pyridinium chloride (PTHPC, L₁=C₁₄H₁₅N₄OSCl) was prepared by refluxing a solution of Girard's P (18.9 g; 0.1 M) in absolute EtOH (100 ml) and phenyl isothiocyanate (12 ml; 0.1 M) in absolute EtOH (100 ml) for 4 h. The melting point of the ligand (PTHPC) is 194°C. The purity of the ligand (structure 1) was checked by elemental analysis and thin layer chromatography. Partial IR (cm⁻¹) (KBr) for PTHPC^[7]: ν(NH¹) 3286, ν(NH²) 3210, ν(NH⁴) 3021, ν(C=O) 1730, ν(C=S) 1290, 746, ν(N-N) 1020; ¹H-NMR 400 MHz, d₆-DMSO): δ 11.13 (NH¹), δ 10.09 (NH⁴), δ 9.88 (NH²), δ 5.75 CH₂ (N.CH₂), δ 7.17-9.17 (Py+Ph).



2.2. Preparation of Cu^{II}-G.P complex

[CuL₁Cl₂.H₂O]Cl. ½EtOH

Solutions of L₁ (3.2 g, 0.01 M) in absolute EtOH (50 ml) and CuCl₂.2H₂O (1.7 g, 0.01 M) in absolute EtOH (50 ml) in absolute EtOH (50 ml) were mixed and boiled under reflux on a water bath for 1h. The deep green crystals were filtered off, washed successively with EtOH and Et₂O, dried in an oven at 80°C for 1h and finally stored in a vacuum desiccator over silica gel (m.p., 154°C). Yield: 96%; partial IR (cm⁻¹) (Nujol): ν(Cu-O) 507, ν(Cu-S) 460, ν(Cu-Cl) 289, ν(Cu-N) 256, ν(Cu-Cl) 212, ν(C=O) 1662, ν(NH²) 3189, ν(C=S) 723, UV-Vis. (cm⁻¹) (Nujol): ²E_g → ²T_{2g} 14368.

2.3. Tribochemical reaction with KI

[Cu(C₁₄H₁₅N₄OS)]I.7H₂O

This complex was prepared by grinding 0.005 M (2.49 g) of the original complex, [CuL₁Cl₂.H₂O]Cl. ½EtOH, which was prepared by conventional chemical method, with KI (8 g) in agate mortar until the mixture became homogenous and deep red in color. A mixture of MeOH and EtOH (85/15 V/V) was added to the reactants and then the reaction mixture was stirred on a magnetic stirrer for 24h at room temperature (25 °C). The yellowish-brown product was filtered off hot, washed with EtOH (200 ml) and diethylether (100 ml), successively and finally the product was left to dry in a vacuum desiccator over silica gel (m.p., 170°C). Yield: 65%; partial IR (cm⁻¹) (Nujol): ν(Cu-O) 451, ν(Cu-N) 306, ν(Cu-S) 287, ν(C=O) 1658, ν(NH²) 3175, ν(C=S) 720, ¹H-NMR (400 MHz, d₆-DMSO): δ 10.84 (NH¹), δ 9.97 (NH⁴), δ 9.78 (NH²), δ 7.01-8.99 (Py+Ph).

2.4. Physical measurements

IR spectra were recorded in Nujol mull and/or KBr discs with a Mattson 5000 FTIR spectrometer. ¹H-NMR spectra of the Cu^I complex and the ligand (PTHPC) in d₆-DMSO were carried out on a Jeol NMR Spectrometer (400 MHz), eclips 400 (Japan), at Chemistry Department, Faculty of Science and Research Center at King Saud, Riyadh, KSA. The electronic spectra of the solid complexes in Nujol and/or DMSO were recorded on Unicam UV/vis spectrometer UV2. Magnetic measurements were carried out using Sherwood balance at room temperature and Hg[Co(SCN)₄] as calibrant. Molar conductance measurements were obtained with an YSI model 35 conductivity bridge using 10⁻³ M solution in DMSO at 25°C.

3. RESULTS AND DISCUSSION

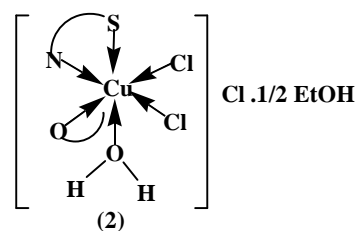
The Cu^{II} complex is quite stable in air and no changes of the complex was observed on leaving it for a long time on air and/or desiccator (3 months), while the Cu^I complex is less stable in air and its color changes from yellowish-brown to pale yellow on leaving the complex in air for three months. This suggests that the Cu^I is less stable than Cu^{II} complex towards air. The

Cu^I and Cu^{II} complexes are insoluble in most common non-polar organic solvents but easily soluble in H₂O, DMF and DMSO (polar solvents). This suggests the electrolytic nature of these complexes. The solubility of the Cu^I complex in polar solvents is mainly due to the disproportionation process, in addition to the electrolytic nature of this complex. The process of disproportionation is confirmed from the solubility of the complex as well as the observation of a pale blue color in solution during the solubility test suggesting the presence of Cu^{II} ion according to the following equilibrium:



The values of molar conductance for the Cu^I and Cu^{II} complexes in DMSO are 38.1 and 29.7 Ω⁻¹.cm².mol⁻¹ range, respectively, suggesting a 1:1 electrolyte^[8]. The infrared spectrum of the free ligand (PTHPC) was reported and discussed earlier by us^[6-7]. The ¹H-NMR spectrum of PTHPC in d₆-DMSO shows three singlet signals at 11.13, 10.09 and 9.88 ppm, downfield with respect to TMS, assignable to the protons of NH(1), NH(4) and NH(2) vibrations^[7], respectively. The singlet signal at 5.75 ppm is attributed to the protons of -CH₂(N-CH₂). The multiple signals in the 7.17-9.17 ppm region are attributed to the protons of the pyridyl and phenyl groups. The latter signals are commensurate with ten protons and are assigned to the protons of the pyridyl and phenyl groups. The value of molar conductance for the ligand (PTHPC) alone in DMF (32.1 Ω⁻¹.cm².mol⁻¹) suggests the electrolytic nature of the ligand together with the presence of one chloride ion outside the bracket^[8] as shown in structure 1. The results of the IR and ¹H-NMR spectra for PTHPC suggest that the ligand exists mainly in the keto form as well as the obscure of any type of hydrogen bonding (inter- or intra-) either in the solid state or in solution. The value of the magnetic moment for the deep green Cu^{II} complex, [Cu(C₁₄H₁₅N₄OS)Cl₂.H₂O]Cl.1/2EtOH, was found to be 1.89 B.M. which is very close to the spin-only value for one unpaired electron. Also, this value suggests the existence of a monomeric structure around the Cu^{II} ion and the absence of any copper-copper interaction^[9]. Moreover, it suggests that the orbital contribution is almost quenched by the crystal field^[10]. The value of molar conductance in DMF (38.1 Ω⁻¹.cm².mol⁻¹) suggests the presence of 1:1 electrolyte^[8]. This value is very close to

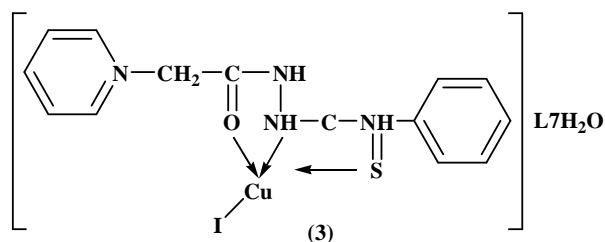
that observed in case of the free ligand (32.1 Ω⁻¹.cm².mol⁻¹) indicating the presence of one chloride ion outside the coordination sphere^[8]. The electronic spectrum of the Cu^{II} complex in Nujol mull shows a broad band centered at 14368 cm⁻¹ (696 nm) attributable to ²E_g → ²T_{2g} transition in a distorted-octahedral geometry around the Cu^{II} ion^[11]. The IR spectrum of the Cu^{II} complex in Nujol mull shows that the ligand (PTHPC) coordinates in a tridentate manner via the carbonyl oxygen(C=O), NH² and the thioketo(C=S) groups. These bands are observed in the spectrum of the Cu^{II} complex at 1662, 3189 and 723 cm⁻¹, respectively. The negative shifts of these bands to lower wavenumbers, on comparison to these observed in case of the free ligand, suggest the involvement of these groups in bonding. On the other hand, the bands observed at 507, 460, 289, 256 and 212 cm⁻¹ are assigned to ν(Cu-O), ν(Cu-S), ν(Cu-N) and ν(Cu-Cl) vibrations^[11-12], respectively, and are taken as additional evidences for the involvement of the abovementioned groups in bonding. Moreover, the observation of two bands assigned for the Cu-Cl vibration suggests that the two chloride ions are existed in a cis-position^[11]. All these foundations are taken as strong evidences for structure (2).



On the other hand, the IR spectrum of the Cu^I complex, [Cu(C₁₄H₁₅N₄OS)]I.7H₂O, in KBr which was prepared by tribochemical reaction, suggests that the ligand (PTHPC) coordinates in a tridentate manner toward the Cu(I) ion via the carbonyl oxygen(C=O), thioketo(C=S) and NH² groups. This is confirmed from the negative shifts of the above three IR bands to lower wavenumbers indicating the participation of these groups in bonding. Also, the bands observed at 451, 306, 287 cm⁻¹ assignable to ν(Cu-O), ν(Cu-N) and ν(Cu-S) vibrations^[11-13], respectively, are taken as additional evidences for the participation of these groups in bonding. The ¹H-NMR spectrum of the Cu(I) complex in d₆-DMSO shows three singlet signals with equal intensity

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(1:1:1) at 10.84, 9.97 and 9.78 ppm, downfield with respect to TMS, assigned to the protons of NH¹, NH⁴ and NH² groups, respectively. The multiple signals in the 7.01-8.99 ppm region are assigned to the protons of the pyridyl and phenyl groups. The signal at 5.58 ppm is assigned to the protons of CH₂(-CH₂CO-) group. The value of the molar conductance of the diamagnetic Cu^I complex in DMF (29.7Ω⁻¹.cm².mol⁻¹) indicates a 1:1 electrolyte^[8]. The diamagnetic nature of this complex suggests a square-planar geometry around the Cu^I ion^[14]. Also, the absence of any d-d band transitions in the electronic spectrum of the Cu^I complex is taken as additional evidence for the diamagnetic nature and the existence of d¹⁰ configuration. All these foundations suggest the reduction of Cu^{II} to Cu^I during the tribochemical reaction of the Cu^{II} complex with KI. The reduction process is also accompanied by substitution of chloride by iodide ions completely. The mechanisms of reduction and substitution processes are reported and discussed earlier by us^[3]. All these foundations suggest structure 3 for the Cu^I complex.



CONCLUSION

In conclusion, we report herein the tribochemical reaction results for the preparation of a novel complex containing thiosemicarbazide moiety and derived from Girard's reagent P. The data obtained confirm our earlier results³ and suggest that the alkali halides, i.e., KI reacts with the Cu(II) complex with the general formula, [CuL₁]Cl₂.H₂O]Cl.½EtOH, which was prepared by conventional method, affording a novel Cu^I complex with the general formula, [Cu(C₁₄H₁₅N₄OS)]I.7H₂O. Also, the results suggest that the tribochemical reaction is accompanied by substitution of chloride by iodide ions followed by the reduction process. This phenomenon is still investigated by us to throw more light on the tribochemical reactions including complex compounds. Also, we can prepare several metal com-

plexes in the solid state with economic way using tribochemical reactions. Moreover, this method throws more light on the danger of using alkali halides as mulling agents during the preparation of IR discs. Hence, we advice the researcher to use Nujol mull as a mulling agent for IR measurements instead of KBr to get a real spectra and preventing the tribochemical reactions between KBr and the chemical compounds. Finally, the importance of the ligands under investigation (L₁, L') and the isolated solid complexes (Cu^{II} and/or Cu^I) finds many applications in medicinal and analytical chemistry which is still under investigation.

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