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Synthesis and characterization of Copper (II) complexes with new ligand obtained from 4-hydroxybenzoic acid hydrazide and 2-hydroxyacetophenone

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Abstract: Three new Cu(II) complexes of the type [Cu(phen-dione)(L)]$(NO_3)_2$ **(1)**, [Cu (opd) (L)]$(NO_3)_2$ **(2)** and [Cu(dpa)(L)]$(NO_3)_2$ **(3)** that phen-dione= 1,10-phenanthroline-5,6-dione, opd=ortho-phenylenediamine, dpa=2,2´dipyridilamine and L=2-hydroxyacetophenone4-hydroxybenzoicacidhydrazone have been synthesized and characterized using the IR, UV-Vis, ^{1}H-NMR spectroscopies and cyclic voltammetery method. The effective magnetic moment (μ_{eff}) of paramagnetic complex **(3)** was consistent with the spin only values for mononuclear d^9 copper (II) systems. The FT-IR results showed that the H_2L ligand adduct to metal center as a tridentate ligand by nitrogen and oxygen atoms. Electrochemical data for all complexes showed quasi-reversible reduction process for ligands and copper ions in DMF solution. Also ligand center transition, ligand field and charge transfer (LMCT) bands have been observed in the synthesized complexes.

Keywords: Copper(II) complex; Ligand; Voltammetery; Magnetic moment; Charge transfer.

Introduction

The chemical properties of hydrazone have been intensively investigated in several research areas because of their chelating capability and their pharmacological applications [1] and very good antifungal and antibacterial properties [2,3]. The Copper (II) complex of salicylaldehyde benzoylhydrazone was shown to be a potent inhibitor of DNA synthesis and cell growth [4,5,6]. In continuation of our previous studies with heterocyclic base adducts of copper (II) [7], we now report the syntheses, spectral characterization, cyclic voltammetric of three coordinate mixed ligand complexes of Copper (II) with 2-hydroxyacetophenone 4-hydroxybenzoic acid hydrazide (H_2L) and Heterocyclic bases. A bidentate base 1,10-phenanthroline (phen) was used as an auxiliary ligand [8]. Electrochemical behavior of complexes has been studied by cyclic voltammetry method. The reduction/oxidation potential depends on the structure and conformation of the central atom in the coordination compounds [9].

Results and discussion

The IR spectrum of the free H_2L has a band at 1607 cm^{-1} associated to the stretching frequency of the C=N bond [10]. On complexation this frequency observed to be shifted to 1584cm^{-1}. This observation suggests involvement of unsaturated nitrogen atoms of the C=N moieties groups in bonding with the central metal ions [11]. The band at 436 cm^{-1} was assigned to $\boldsymbol{\upsilon}$ (Cu-N) stretching bond [12]. The increase in $\boldsymbol{\upsilon}$ (N-N) in the spectra of these complexes from 1033 to 1091 cm^{-1} is due to the increase in double bond character via loss of electron density and donation to the metal and is a confirmation of the coordination of the ligand through

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the azomethine nitrogen atom . The appearance of a new medium peak at 1445-1510 cm^{-1} in the complex is due to asymmetric stretching vibration of the newly formed N=C bond as a result of enolisation of the principal H_2L [13]. The band at ~1240cm^{-1} attributed to ***υ***(C-O) that decrease from 1272cm^{-1} when complexes were formed. The second OH group in the aromatic ring remains uncomplexed indicated by a band at 2923-3063 cm^{-1} in the complexes.

The ^{1}H-NMR is a very powerful tool for characterization of paramagnetic complexes in solution. The ^{1}H-NMR spectra of [(Cu(L)(dpa] is shown in Figure **1**. The effective magnetic moment (μ_{eff}) of paramagnetic complex was measured 2.51BM per Cu(II) ion by ^{1}H-NMR (evans's method) for [(Cu(L)(dpa]**(3)**. The magnitude of μ_{eff} is consistent with the expected value of magnetic moment for Cu(II) complexes in literature and one unpaired electron in title complexes [14-15].

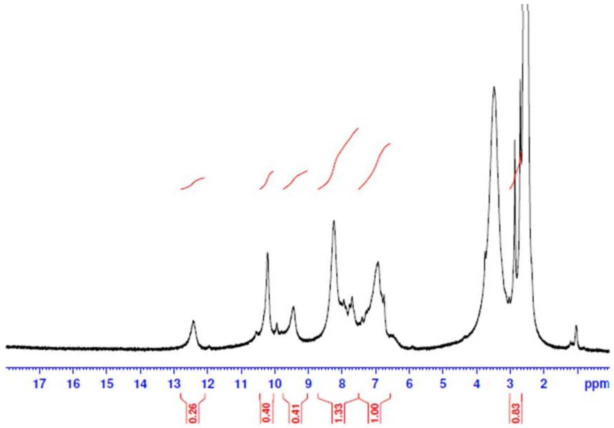


Figure 1: ^{1}H NMR spectrum of [(Cu(L)(dpa] **(3)** in DMSO-d_6.

Electronic spectra:

The electronic spectra of the complexes were taken in a DMF solution and exhibits several absorption bands in the UV and visible region. The 2-hydroxyacetophenone 4-hydroxy benzoicacid hydrazide (H_2L) has a band at 235nm attributed to π→π* and two bands at 315nm 359nm as to n→π* transitions [16]. As shown in Table **1**, these bands have slight shift during complexation. Other bonds at visible region may be assigned to an O→ Cu charge transfer 'LMCT' and d-d transitions [16-17]. The cyclic voltammogram of the complex was similar with those of other typical compounds containing bipyridine, phenanthroline and terpyridine ligands [18]. The ligand H_2L exhibits one irreversible reduction step approximately at −2 V Figure **2**. The electrochemical behavior of complexes was carried out in the range from +1.0 to -2.5 V. One irreversible reduction wave in the negative potential at approximately −2 V, assigned to reduction of H_2L in title compounds**.** Cyclic voltammograms between +1 and -0.5 v showed quasi-reversible reduction attributed to the Cu(II)/Cu(I) process in **(1)**, **(2)** and **(3)** [19-20]. The cyclic voltammograms of compounds **(1)**, **(2)** and **(3)** shown in Figures **3-5**, respectively.

Table 1: Hydroarylation reaction of phenylacetylene **1** with mesitylene **2d** in the presence of BF_3 catalyst under different reaction conditions.

Compound	d→d	LMCT	n→π*	π→π*
H_2L	-	-	315	235
	-	-	359	
[Cu (phen-dione) (L)]$(NO_3)_2$ **(1)**	679	382	304	212
[Cu (opd) (L)]$(NO_3)_2$ **(2)**	658	386	309	232
[Cu (dpa)(L)]$(NO_3)_2$ **(3)**	643	316	312	215

Electrochemical Studies:

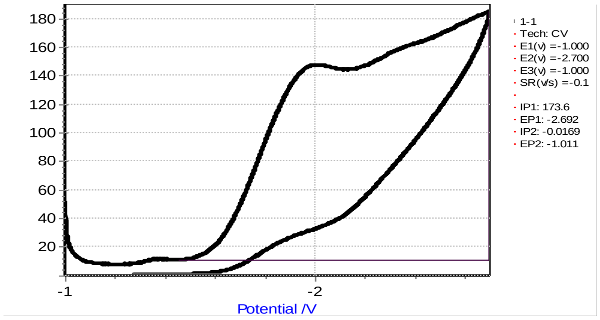


Figure 2: Cyclic voltammogram of H_2L in DMF, 0.1 M TBAH as a supporting electrolyte.

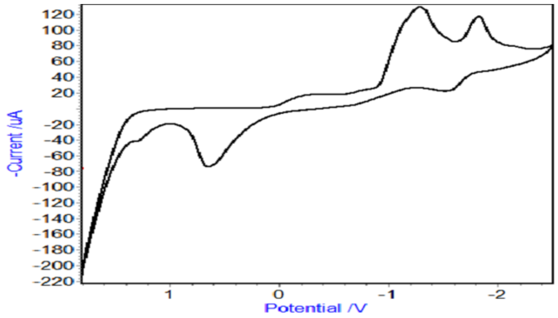


Figure 3: Cyclic voltammogram of compound **(3)** in DMF, 0.1 M TBAH as a supporting electrolyte.

Conclusion

Structures of three new synthesized Copper (II) complexes have been characterized. The IR spectra suggest involvement of unsaturated nitrogen atoms of the C=N moieties groups in bonding with the central metal ions. The increase in ***υ***(N-N) in the spectra of these complexes from 1033 to 1091 cm^{-1} was due to the increase in double bond character via loss of electron density and donation to the metal and is a confirmation of the coordination of the ligand through the azomethine nitrogen atom. The magnitude of μ_{eff} obtained from ^{1}HNMR was consistent with the expected value of magnetic moment for Cu(II) complexes in literature. One irreversible reduction wave in the negative potential assigned to reduction of H_2L in the synthesized compounds.

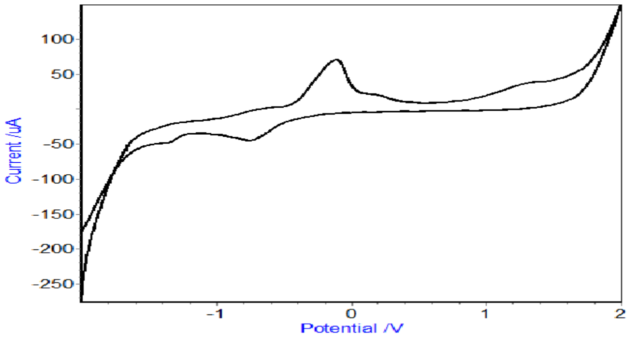


Figure 4: Cyclic voltammogram of compound **(1)** in DMF, 0.1 M TBAH as a supporting electrolyte.

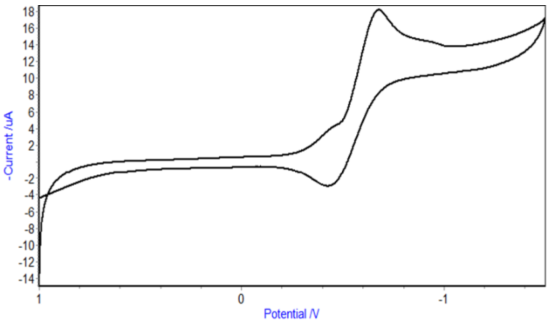


Figure 5: Cyclic voltammogram of compound **(2)** in DMF, 0.1 M TBAH as a supporting electrolyte.

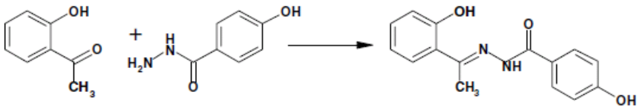
Experimental

Materials:

All chemicals and solvents obtained from Merck and Aldrich and used without further purification. All the solvents were dried using standard methods before use. Infrared spectra (4000–250 cm^{-1}) of solid samples were taken as 1% dispersion in KBr pellets using a Shimadzu-470 spectrometer. Electronic absorption spectra in DMF solution were taken at room temperature on a Cary Bio 300 spectrometer. Cyclic voltammograms were recorded using a SAMA500. Three electrodes were utilized in this system: a glassy carbon working electrode, a platinum wire auxiliary electrode, and an Ag wire reference electrode. The glassy carbon working electrode was manually cleaned with 1-μm diamond polish prior to each scan. The supporting electrolyte, 0.1 M tetrabutylammonium hexafluorophosphate (TBAH), was recrystallized twice from ethanol-water (1/1) and vacuum-dried at 110°C overnight. A sweep rate of 100–500 mVs^{-1} was used for all the scans. Ferrocene was used as an internal standard to compensate for the junction potential variability among experiments. Melting point is uncorrected and was obtained from an electrothermal type 9100 melting point apparatus. Elemental analysis was performed using a Heraeus CHN-O rapid analyzer.

Synthesis of H_2L:

To a methanolic solution (20 ml) of 4-Hydroxybenzoic acid hydrazide (1 mmole) were added 2-hydroxyacetophenone (1 mmole) and a few drops of glacial acid (Scheme **1**). This mixture was refluxed for 6 h. The solid (desired product) was collected by suction filtration and recrystallized from absolute methanol and characterized by analytical and different spectral methods.



Scheme 1: Synthesis reaction of 2-hydroxyacetophenone 4-hydroxy benzoicacid hydrazide (H_2L)

Synthesis of complexes:

For preparation of complexes to mixture solution of 1 mmol L(2-hydroxyacetophenone 4-hydroxybenzoic acid hydrazine) and 1 mmol B (phendione, opd and dpa for compounds **1**, **2**, **3** respectivaly) in 50 ml methanol solution was added a filtered solution of 1mmol $Cu(NO_3)_2$ in ethanol. The mixture was heated under reflux in 55–60°C for 12 h. The formed blue products were filtered and washed with ethanol then dissolved in DMF solution and were left to evaporate slowly at room temperature. After 10 days blue crystals were isolated (yield69% m.p>300).

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