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Synthesis, Spectral Characterization and Electrolytic Nature of Cu(II) Complexes of Azo-Carboxylate Ligands

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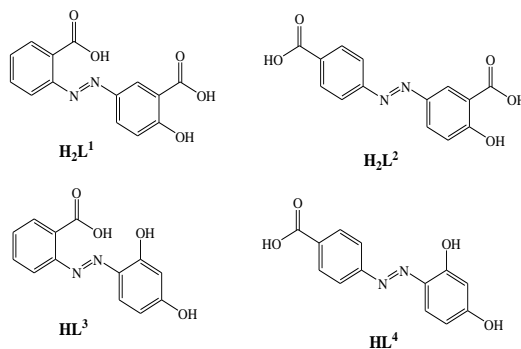
ABSTRACT

Six new Cu(II) complexes of azo-carboxylate ligands were synthesized using 1:1 and 1:2 metal-ligand stoichiometric ratio. The complexes were characterized by UV-visible and IR spectroscopy in combination with elemental analysis. The electrolytic nature of the complexes was determined by conductivity study. IR spectroscopy study indicated that the carboxylate ligands act as bidentate mode of coordination through the carboxylic oxygen atoms. UV-visible spectral study suggested four coordinate square planar geometry of the complexes in the solution state.

1. Introduction

Cu(II) complexes have received much attention in coordination chemistry due to their structures, spectral, redox properties [1, 2] and copper containing metalloproteins [3, 4]. Cu(II) complexes play a significant role in biological systems as pharmacological and physiological agents [5-7]. Large number of Cu(II) complexes have been screened for both *in vivo* and *in vitro* anticancer properties and found to be potential anticancer agents [8, 9]. It was reported that Cu(II) complexes have shown antifungal, antibacterial and herbicidal properties [10-12]. In addition to this, Cu(II) complexes of macrocyclic ligands are of great importance in enhancing various industrial applications [13]. Cu(II) chemistry of macrocyclic ligands is important both for chemical and biochemical applications [14, 15]. Cu(II) complexes are regarded as a potential alternative agent and possess effective cytotoxic property in a variety of cancer cell lines [16, 17]. It has also been reported that many Cu(II) complexes efficiently cleave DNA by oxidative, hydrolytic, photolytic or electrolytic mechanisms [18]. In particular, DNA cleavage by Cu(II) complexes containing poly-pyridyl ligands and their derivatives have been reported [16]. In addition to this, azo-copper compounds are important class of chemical compounds receiving attention in scientific research. They are highly coloured and have been used as dyes and pigments for a quite long time [19]. Furthermore, they have been studied widely because of their excellent thermal and optical properties such as optical recording medium [20], toner [21], ink-jet printing [22, 23] and oil-soluble lightfast dyes. Recently, azo-metal chelates have also attracted increasing attention due to their interesting electronic and geometrical features in connection with their applications for molecular memory storage, nonlinear optical elements and printing systems [19, 20]. Furthermore, Cu(II) complexes of azo-carboxylates have been studied in the recent years owing to their antibacterial activity, fungal growth retardation activity, catalytic activity, enzymatic activity etc. [24, 25]. It was found that dimeric Cu(II) complexes of carboxylate ligands are known to form different kind of structures even with same kind of ligands [26]. The most common geometry exhibited by the Cu(II) complexes include four coordinate square planar, five coordinate square pyramidal or trigonal bipyramidal and six coordinate distorted octahedral geometry [27, 28]. Moreover, synthesis, structures and biological properties of a large number of Cu(II) complexes of Schiff base ligands have been reported during past years [29, 30]. However, the

chemistry of Cu(II) complexes of azo-carboxylates have not been explored and studied in details. Therefore, in our present investigation, we have synthesized six Cu(II) complexes of azo-carboxylate ligands using different metal-ligand stoichiometric ratio. These complexes were characterised by elemental analysis, UV-visible and IR spectroscopy. The electrolytic nature of the complexes was also determined by their conductivity studies. The ligand skeletons used in the present work have been shown in Scheme 1.

Scheme 1 Ligands skeleton ($H_2L^1 - HL^4$)

2. Experimental Methods

2.1 Materials and Method

Copper chloride dihydrate [$CuCl_2 \cdot 2H_2O$], *o*-amino benzoic acid, *p*-amino benzoic acid, salicylic acid, resorcinol were used without further purification. AR grade solvents were used in all the reactions and dried using standard procedures. Electronic spectra of complexes and the ligands were recorded in UV-1800 Shimadzu spectrometer. IR spectra in the range of $4000-400\text{ cm}^{-1}$ were obtained on Shimadzu spectrophotometer using KBr discs.

2.2 Synthesis of (*E*)-5-((4-Carboxyphenyl)Diazenyl)-2-Hydroxybenzoic Acid (H_2L^1)

The synthetic procedure of the ligand has been mentioned in our earlier report [31] where *o*-amino benzoic acid (5 g, 36.46 mmol) diazotized with ice cold aq. $NaNO_2$ solution (2.5 g, 20 mL). The diazonium salt was then

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coupled with cold alkaline solution of salicylic acid (5 g, 30 mL). The red dye obtained was kept in refrigerator and allowed to stay at room temperature for 3 hours. It was then acidified with dil. CH_3COOH and the precipitate obtained was filtered, washed several times with water and then dried in air. The crude product was washed with hexane and dried in vacuum and recrystallized from methanol. Yield: 65%; m.p.: 204–206 °C. *Anal. Calc.* for $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_5$: C, 58.74; H, 3.49; N, 9.79. Found: C, 58.90; H, 3.54; N, 9.71%. UV-Vis (DMF) λ_{max} (nm): 240, 397. IR (cm^{-1}): 1722 $\nu_{\text{asy}}(\text{OCO})$, 1683 $\nu_{\text{sym}}(\text{OCO})$, 1475, 1380, 1270, 1245.

2.3 Synthesis of (E)-5-((2-Carboxyphenyl)Diazenyl)-2-Hydroxybenzoic Acid (H_2L^2)

The ligand (H_2L^2) was prepared by following the same procedure as described for ligand (H_2L^1) using *p*-amino benzoic acid instead of *o*-amino benzoic acid. Yield: 70%; m.p.: 235–237 °C. *Anal. Calc.* for $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_5$: C, 58.74; H, 3.49; N, 9.79. Found: C, 58.26; H, 3.38; N, 9.57%. UV-Vis (DMF) λ_{max} (nm): 246, 395. IR(cm^{-1}): 1680 $\nu_{\text{asy}}(\text{OCO})$, 1609 $\nu_{\text{sym}}(\text{OCO})$, 1410, 1378, 1348.

2.4 Synthesis of (E)-2-((3,4-Dihydroxyphenyl)Diazenyl)Benzoic Acid (HL^3)

The method of preparation of ligand (HL^3) has been discussed in our earlier report [32] in which diazo-coupling reaction between *o*-amino benzoic acid and resorcinol was carried out in cold alkaline medium and the ligand was purified using standard process. Yield: 75%; m.p.: 242–245 °C. *Anal. Calc.* for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_4$: C, 60.46; H, 3.90; N, 10.85. Found: C, 60.77; H, 3.83; N, 10.96%. UV-Vis (DMF) λ_{max} (nm): 265, 412. IR (KBr, cm^{-1}): 1681 $\nu_{\text{asy}}(\text{COO})$, 1599 $\nu_{\text{sym}}(\text{OCO})$, 1486, 1362, 1282.

2.5 Synthesis of (E)-4-((3,4-Dihydroxyphenyl)Diazenyl)Benzoic Acid (HL^4)

Ligand (HL^4) was prepared by following the same procedure as described for ligand (HL^3) using *p*-amino benzoic acid as precursor. Yield: 70%; m.p.: 248–251 °C. *Anal. Calc.* for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_4$: C, 60.46; H, 3.90; N, 10.85. Found: C, 60.71; H, 3.91; N, 10.72%. UV-Vis (DMF) λ_{max} (nm): 265, 408. IR (KBr, cm^{-1}): 1686 $\nu_{\text{asy}}(\text{COO})$, 1603 $\nu_{\text{sym}}(\text{OCO})$, 1456, 1354, 1287.

2.6 Synthesis of $[\text{Cu}_2(\text{II})(\text{Cl})_2(\text{H}_2\text{O})_2(\text{L}^1)]$ (1)

To 40 mL methanolic solution of H_2L^1 (0.5 g, 1.75 mmol), triethylamine (0.35 g, 3.34 mmol) was added dropwise with continuous stirring. To this stirred solution, methanolic solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.59 g, 3.46 mmol) was added. A brown colour solution developed immediately. The reaction mixture was refluxed for 3 hours and filtered. The residue was washed with water, methanol and diethyl ether and dried in air. Yield: 45%; m.p.: 340–342 °C. *Anal. Calc.* for $\text{C}_{14}\text{H}_{12}\text{Cl}_2\text{Cu}_2\text{N}_2\text{O}_7$: C, 32.45; H, 2.33; N, 5.41. Found: C, 33.86; H, 2.36; N, 5.49%. UV-Vis (DMF) λ_{max} (nm): 262, 397, 404, 461. IR (cm^{-1}): 1598 $\nu_{\text{asy}}(\text{OCO})$, 1466 $\nu_{\text{sym}}(\text{OCO})$, 1430, 1304, 1255, 1176, 829, 661.

2.7 Synthesis of $[\text{Cu}_2(\text{II})(\text{Cl})_2(\text{H}_2\text{O})_2(\text{L}^2)]$ (2)

The synthetic procedure of this complex is the same as described in case of complex 1. Yield: 40%; m.p.: 300–304 °C. *Anal. Calc.* for $\text{C}_{14}\text{H}_{12}\text{Cl}_2\text{Cu}_2\text{N}_2\text{O}_7$: C, 32.45; H, 2.33; N, 5.41. Found: C, 33.78; H, 2.35; N, 5.47%. UV-Vis (DMF) λ_{max} (nm): 264, 399, 458. IR (cm^{-1}): 1593 $\nu_{\text{asy}}(\text{OCO})$, 1466 $\nu_{\text{sym}}(\text{OCO})$, 1447, 1347, 662.

2.8 Synthesis of $[\text{Cu}(\text{II})\text{Cl}(\text{H}_2\text{O})(\text{L}^3)]$ (3)

To 40 mL methanolic solution of (E)-2-((3,4-dihydroxyphenyl)diazenyl)benzoic acid (HL^3) (0.5 g, 1.93 mmol), triethylamine (0.19 g, 1.93 mmol) was added dropwise with continuous stirring. To this reaction mixture, methanolic solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.33 g, 1.93 mmol) was added dropwise. A brown colour solution developed immediately. The reaction mixture was refluxed for 3 hours and filtered. The residue was washed with water, methanol and diethyl ether and dried in air. Yield: 42%; m.p.: 320–322 °C. *Anal. Calc.* for $\text{C}_{13}\text{H}_{11}\text{ClCuN}_2\text{O}_5$: C, 41.72; H, 2.96; N, 7.49. Found: C, 41.96; H, 2.99; N, 7.40%. UV-Vis (DMF) λ_{max} (nm): 253, 364, 410, 460. IR (cm^{-1}): 1593 $\nu_{\text{asy}}(\text{OCO})$, 1410 $\nu_{\text{sym}}(\text{OCO})$, 1454, 1345, 661.

2.9 Synthesis of $[\text{Cu}(\text{II})(\text{L}^3)_2]$ (4)

0.39 g, 3.87 mmol triethylamine was added dropwise to 40 mL methanolic solution of (E)-2-((3,4-dihydroxyphenyl)diazenyl)benzoic acid (HL^3) (1 g, 3.86 mmol) with constant stirring. To this solution, methanolic solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.33g, 1.93 mmol) was added with stirring. A brown colour developed immediately and the reaction mixture was refluxed for 3 hours and filtered. The residue was washed with water, methanol and diethyl ether and dried in air. Yield: 38%; m.p.: 358–361 °C.

Anal. Calc. for $\text{C}_{26}\text{H}_{28}\text{CuN}_4\text{O}_8$: C, 54.03; H, 3.14; N, 9.69. Found: C, 54.29; H, 3.18; N, 9.80%. UV-Vis (DMF) λ_{max} (nm): 252, 387, 457. IR (cm^{-1}): 1598 $\nu_{\text{asy}}(\text{OCO})$, 1474 $\nu_{\text{sym}}(\text{OCO})$, 1452, 1354, 622.

2.10 Synthesis of $[\text{Cu}(\text{II})\text{Cl}(\text{H}_2\text{O})(\text{L}^4)]$ (5)

Complex (5) was prepared following same procedure as described for complex (3). Yield: 43%; m.p.: 315–318 °C. *Anal. Calc.* for $\text{C}_{13}\text{H}_{11}\text{ClCuN}_2\text{O}_5$: C, 41.72; H, 2.96; N, 7.49. Found: C, 41.96; H, 2.92; N, 7.40%. UV-Vis (DMF) λ_{max} (nm): 252, 396, 459. IR (cm^{-1}): 1586 $\nu_{\text{asy}}(\text{OCO})$, 1459 $\nu_{\text{sym}}(\text{OCO})$, 1456, 1356, 645.

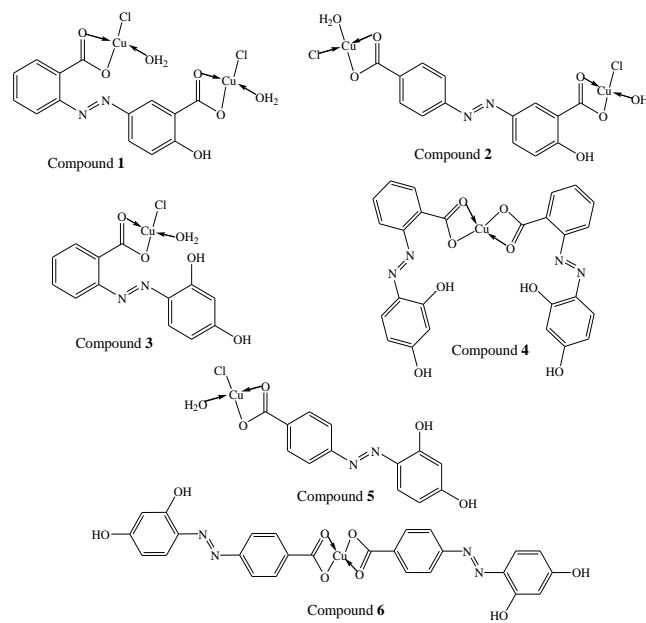
2.11 Synthesis of $[\text{Cu}(\text{II})(\text{L}^4)_2]$ (6)

Complex (6) was prepared following same procedure as that of complex (4) using 1:2 metal-ligand ratio. Yield: 37%; m.p.: 327–330 °C. *Anal. Calc.* for $\text{C}_{26}\text{H}_{28}\text{CuN}_4\text{O}_8$: C, 54.03; H, 3.14; N, 9.69. Found: C, 54.37; H, 3.11; N, 9.89%. UV-Vis (DMF) λ_{max} (nm): 253, 396, 462. IR (cm^{-1}): 1576 $\nu_{\text{asy}}(\text{OCO})$, 1467 $\nu_{\text{sym}}(\text{OCO})$, 1457, 1348, 647.

3. Results and Discussion

3.1 Synthesis

Ligands (H_2L^1) and (H_2L^2) were prepared by diazo-coupling of *o*-amino/*p*-amino benzoic acid with salicylic acid under alkaline cold condition while (HL^3) and (HL^4) were prepared by diazo-coupling of *o*-amino/*p*-amino benzoic acid with resorcinol. Six new Cu(II) complexes were synthesized by stirring and then refluxing the methanolic solution of the ligands with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ following 1:1 and 1:2 metal-ligand stoichiometric ratio. The proposed square planar geometry of Cu(II) complexes 1–6 have been shown in Scheme 2.



Scheme 2 Proposed structure of the complexes (1–6)

3.2 Spectroscopic Characterization

3.2.1 UV-Visible Spectroscopy

Electronic absorption spectra of the Cu(II) complexes were recorded in 10^{-4} molL⁻¹ DMF solutions in the range of 200–800 nm at room temperature and their results were presented in experimental section. The spectra of the azo-carboxylate ligands and some of their Cu(II) complexes were presented in Fig. 1.

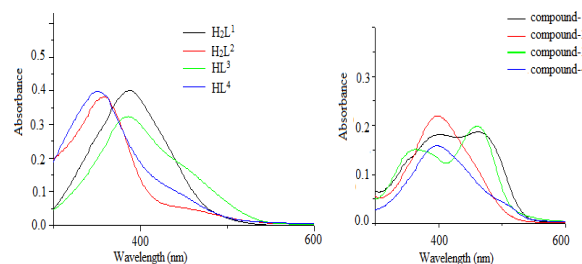


Fig. 1 UV-visible spectra of the ligands and complexes

The electronic spectra of the free ligands in DMF showed strong absorption bands in the UV-region (240–412 nm) that could be attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions in the azo and benzene ring respectively. In the complexes, the band arises at 252–461 nm, this slight increase in the wavelength from ligand to metal indicated the coordination of the ligand to metal. Electronic spectra of the Cu(II) complexes showed a broad band at around 410–461 nm. This broad band assigned to be the ${}^1B_{1g} \rightarrow {}^2E_g$ transition of four coordinate, square planar geometry [33]. The complexes also exhibited a broad UV absorption band at 364–399 nm which may be assigned to ligand to metal charge transfer.

3.2.2 Infrared Spectroscopy

The IR spectra of the azo-carboxylate ligands and their corresponding Cu(II) complexes, **1–6** were recorded using KBr disc. The IR data of the ligands and the complexes were shown in the experimental section while IR spectrum of complex **1** has been shown in Fig. 2. The IR absorption bands observed at 1604–1631 cm^{-1} in the metal complexes indicating participation of carboxylic oxygen in complex formation [34, 35]. Moreover, the coordination of the ligand to the metal centre through the carboxyl group can also be confirmed from the difference observed for $\nu_{\text{asy}}(\text{OCO})$ and $\nu_{\text{sym}}(\text{OCO})$ values. The difference in $\nu_{\text{asy}}(\text{OCO})$ and $\nu_{\text{sym}}(\text{OCO})$ i.e., $\Delta\nu$ observed in IR spectra of complexes are useful to predict whether the ligands coordinate to the metal in mono or bidentate fashion. For the free ligands, the IR bands for $\nu_{\text{asy}}(\text{OCO})$ and $\nu_{\text{sym}}(\text{OCO})$ were detected in the range 1680–1722 cm^{-1} and 1599–1683 cm^{-1} . After complexation, $\nu_{\text{asy}}(\text{OCO})$ and $\nu_{\text{sym}}(\text{OCO})$ were shifted at 1576–1598 cm^{-1} and 1410–1474 cm^{-1} respectively due to the coordination of the ligand to the metal. The $\Delta\nu$ values for all the complexes were found to be in the range of 109–132 cm^{-1} indicating that the carboxylic oxygen atoms coordinate to the metal atom in bidentate mode [36].

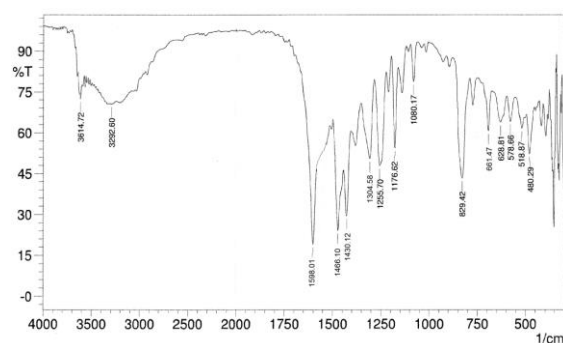


Fig. 2 IR spectrum of the complex **1**

3.3 Molar Conductance

The molar conductance of the synthesized Cu(II) complexes were measured in 10^{-3} molar DMF solution at room temperature (28 °C) and the molar conductance values of all the complexes are given in Table 1. The conductivity values of the complexes (**1–6**) are in the range of (7.5–13.5 $\Omega^{-1}\text{cm}^{-1}$). These values are too low to account for any dissociation of the complexes in DMF and thus, the observed values may be considered as a good evidence for the existence of a non-electrolytic nature of the complexes [37].

Table 1 Molar conductance data

| S.No. | Compounds | Observed Molar conductance ($\Omega^{-1}\text{cm}^{-1}$) | Nature of electrolyte |
|-------|--|--|-----------------------|
| 1 | $[\text{Cu}_2(\text{II})(\text{Cl})_2(\text{H}_2\text{O})_2(\text{L}^1)]$ (1) | 8.9 | Non electrolyte |
| 2 | $[\text{Cu}_2(\text{II})(\text{Cl})_2(\text{H}_2\text{O})_2(\text{L}^2)]$ (2) | 13.5 | Non electrolyte |
| 3 | $[\text{Cu}(\text{II})\text{Cl}(\text{H}_2\text{O})(\text{L}^3)]$ (3) | 8.0 | Non electrolyte |
| 4 | $[\text{Cu}(\text{II})(\text{L}^3)_2]$ (4) | 9.0 | Non electrolyte |
| 5 | $[\text{Cu}(\text{II})\text{Cl}(\text{H}_2\text{O})(\text{L}^4)]$ (5) | 7.8 | Non electrolyte |
| 6 | $[\text{Cu}(\text{II})(\text{L}^4)_2]$ (6) | 7.5 | Non electrolyte |

4. Conclusion

Azo- carboxylic acid ligands containing mono and dicarboxylic groups were synthesized and characterized with the help of UV-visible, IR spectroscopy studies in combination with elemental analysis. Cu(II) complexes of azo-carboxylic acid ligands were synthesized by taking different stoichiometric ratio of metal salts and ligands. The IR spectral data of the complexes indicated that the ligands coordinate to the metal atom in bidentate fashion. The electronic spectral studies of all the complexes showed UV absorption peak at 400–461 nm suggesting that the

complexes adopt 4-coordinate square planar geometry. The conductivity values of all the complexes indicated that the complexes are non-electrolyte in nature.

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