



Synthesis, Characterization of Mixed-Ligand Copper (II) Complexes Involving Diethylenetriamine, 2,6-Pyridinedicarboxylic Acid and Pyrazine in Dimethylsulfoxide

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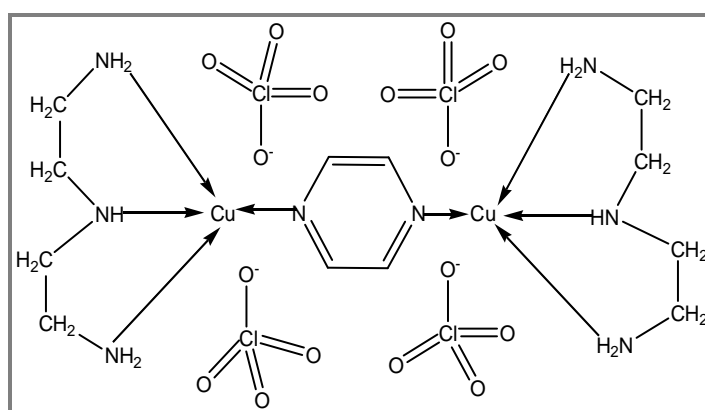
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ABSTRACT

The mixed ligand copper (II) complexes involving diethylenetriamine with 2,6-pyridinedicarboxylic acid and pyrazine were synthesized complexes $[Cu(dien)(pdc)(H_2O)]$ and $[Cu_2(dien)_2(pyrazine)](ClO_4)_4$ and characterized by elemental analyses (C,H,N), UV-Visible, FT-IR and TGA methods. The electrochemical behaviors of both the complexes were studied in dimethylsulfoxide (DMSO) containing 0.2M Sodium perchlorate ($NaClO_4$) as supporting electrolyte at a glassy carbon disc working electrode using cyclic voltammetry. It should be mentioned that the cyclic voltammograms of the mixed ligand complexes (1) and (2) in DMSO showed a quasireversible redox couple corresponding to Cu^{2+}/Cu^+ with formal potentials $E^0' = -204$ mV and $E^0' = 274.5$ mV vs Ag/AgCl, at the scan rate of 25 mV/s in the potential ranges +800 to -500 V and +800 to -750 V respectively. The UV-Visible spectra of the mixed ligand complexes were also studied in DMSO at room temperature.

Graphical Abstract



Structure of Complex (2) $[Cu_2(dien)_2(pyrazine)](ClO_4)_4$.

Keywords: Electrochemistry, UV-Visible spectra, IR Spectra, TGA, Copper, Diethylenetriamine, 2,6-pyridinedicarboxylic Acid, Pyrazine

INTRODUCTION

Copper, among other transition metals, is essential for many enzymes, particularly those catalyzing physiologically important reactions. It has strong ability to form complexes with proteins, peptides, amino acids as well as other organic substances in the living organisms [1]. It is a biologically relevant element and many enzymes that depend on copper for their activity have been identified. Copper(II) is a substitutionally labile metal ion, so multidentate ligands are believed to be better than bidentate ligands in keeping the copper (II) ion chelated in solution. Typically, upon association with dioxygen or hydrogen peroxide these copper complexes are thought to perform reactive intermediates [2]. Examples of copper-containing compounds include electron-transfer (ET) proteins (e.g., azurin, plastocyanin, laccase), oxygen-binding enzymes (e.g., ferroxidase, tyrosinase, ascorbate oxidase), and in oxygen transport proteins (hemocyanin) [3]. Copper (II)-organic frameworks possess enormous structural diversity due to its flexible coordination sphere around the copper (II) ion, in combination with steric and packing forces. It is one of the most important transition metal ions, not only because of its relevance as the active-site structure of metalloproteins, but also due to its magnetochemistry [4]. Several Cu(II) complexes, which possess biologically active ligands, demonstrate high nucleobase affinity and nuclease activity and are found to have the potential to serve as anticancer agents [5] and have shown a significant decrease in tumor volume, mitotic and proliferation indices in different types of human cancer cells [6].

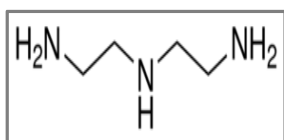
Transition metal compounds containing diethylenetriamine have been of interest for many years [7]. It is a tridentate nitrogen donor ligand with donor groups suitably placed for forming 2 five membered chelate rings. It serves as a tridentate ligand forming complexes in co-ordination chemistry [8]. Copper(II) complexes having diethylenetriamine found possible medical uses in treatment of many diseases including cancer. It has been known that the anti-cancer activity of some copper(II) complexes may be based on their ability to inhibit DNA synthesis [9]. The Diethylenetriamine is a common curing agent for Epoxy-resins in epoxy adhesives. It is used in oil industry for the extraction of acid gas [10]. It can also be used to sensitize nitromethane, making a liquid explosive compound, it was used as Hydryne when Mixed with unsymmetrical dimethylhydrazine, a propellant for liquid-fuel rockets [11].

Pyridinedicarboxylic acids (pdcs) have been widely used as organic ligands to the construction of metal organic coordination polymers (MOCPs) or metal organic frameworks (MOFs), which is of intense interests in recent years [12] for their potential application in molecular sieve, optoelectronics, magnetism, chemical sensors and so on [13]. Pyridine-2,6-dicarboxylic acid (pydcH₂) is such a ligands with variety of coordination fashions [14] through its one nitrogen atom and four carboxylate oxygen atoms, diverse substituent groups on the pyridine ring are possible to form hydrogen bonds, which is helpful for self assembly. The pydcH₂ is therefore an excellent candidate for constructing heterometallic complex [15]. However, the construction of designed and predictable heterometallic coordination frameworks with potential properties is still a formidable task because of the coordinative complexity of the heterometallic ions involved in the self-assembly process [16, 17].

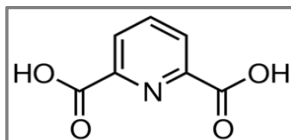
Pyrazines play an important role as intermediates for perfumes, pharmaceuticals and agricultural chemicals. Especially, amides and sulfonamides of pyrazines have been used on various topics as anti-tuberculosis, oral anti-diabetics, nutrition supplement, insecticides and fungicides [18]. The use of trace amounts of pyrazines as flavour and fragrance enhancers in the foodstuffs and tobacco industries is well documented. One approach that in principle offers the possibility of facilitating some control or fine tuning over physical properties such as volatility/high vapour pressure is stabilization via complexation with metal ions [19]. Pyrazine and substituted pyrazines have the ability to form linear bridges between metal ions to generate oligomeric species or polymeric arrays in the presence of metals atoms containing more than the oxidation state [20]. The electrochemical behaviour of pyrazine derivative is highly dependent on the pH [21].

Thus, keeping in mind the above mentioned importance and properties a successful attempt has been made for synthesizing two mixed-ligand copper(II) complexes, taking diethylenetriamine as a primary ligand while 2,6-pyridinedicarboxylic acid and pyrazine as secondary ligands. In this study we describe the synthesis, spectroscopic, elemental, thermal analysis and electrochemical studies of the complexes (1) $[\text{Cu}(\text{dien})(\text{pdc})(\text{H}_2\text{O})]$ and (2) $[\text{Cu}_2(\text{dien})_2(\text{pyz})](\text{ClO}_4)_4$.

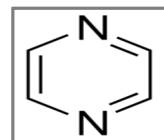
Structures of diethylenetriamine, 2,6-pyridinedicarboxylic acid and pyrazine ligands are given below:



Diethylenetriamine



2,6-pyridinedicarboxylic Acid



Pyrazine

MATERIALS AND METHODS

Copper Perchlorate hexahydrate $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, diethylenetriamine, 2,6-pyridinedicarboxylic acid (2,6-Pdc), pyrazine and Sodium Perchlorate were procured from Sigma Aldrich Chemicals Pvt. Ltd. Dimethylsulfoxide (DMSO) was procured from Merck Specialities Pvt. Ltd. The software driven BAS Electrochemical System, Model EPSILON (Bioanalytical System, Inc, USA) was employed for all the electrochemical studies. The working electrode was glassy carbon disc electrode (GCE), the auxiliary electrode was platinum wire and reference electrode was Ag/AgCl in saturated KCl ($E^{0'} = +199$ mV vs. NHE). Purging and blanketing of nitrogen (99.999% pure) were done for analytical solution placed in the electrochemical cell, of 15 mL capacity for 20 min. Great care was taken in the electrode pre-treatment. Mechanical polishing of the working electrode (GCE) was done over a velvet micro cloth with an alumina suspension. All the electrochemical experiments were performed at a constant temperature of $25 \pm 0.5^\circ\text{C}$. IR compensation and background subtraction have also been done. Electronic absorption spectra of the complexes have been recorded in DMSO at room temperature by Perkin-Elmer UV-Visible Spectrophotometer Model Lambda-35. Elemental (C, H, N) analyses were done on Elemental Analyzers (EUROVECTOR EA 3000). IR Spectra recorded on Agilent Cary 630 FTIR Spectrometer in the range of $4000\text{--}450\text{ cm}^{-1}$. Thermal stability (TG/DTG/DTA) of complexes was studied in the range of $35\text{--}900^\circ\text{C}$ by controlling the heating rates $10^\circ\text{C min}^{-1}$ in nitrogen atmosphere.

Synthesis of the mixed ligand complex (1): $[\text{Cu}(\text{dien})(\text{pdc})(\text{H}_2\text{O})]$: 5 mL methanolic solution of Copper Perchlorate hexahydrate $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, (1 mM, 370 mg) was added to a 5 mL methanolic solution of diethylenetriamine (1 mM, 103 mg) with constant stirring, light blue coloured solution obtained. Then a 5 mL methanolic solution of 2,6-pyridinedicarboxylic acid (1 mM, 167 mg) was added to the reaction mixture with constant stirring at 40°C for 1 h. The result was immediate precipitation of the desired dark blue product. Filtered the content, washed with ethanol several times and dried at room temperature inside a vacuum desiccator over P_2O_5 (yield: 440 mg, 68% based on Cu).

Synthesis of the mixed ligand complex (2): $[\text{Cu}_2(\text{dien})_2(\text{pyz})](\text{ClO}_4)_4$: 5 mL methanolic solution of Copper Perchlorate hexahydrate $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, (2 mM, 741 mg) was added to a 5 mL methanolic solution of diethylenetriamine (2 mM, 206 mg) with constant stirring, dark blue coloured solution obtained. Then a 5-mL methanolic solution of pyrazine (1 mM, 80 mg) was added to the reaction mixture with constant stirring at 40°C for 1 h. The desired shining violet precipitate product obtained [9]. Filtered the content, washed with diethyl ether several times and dried at room temperature inside a vacuum desiccator over P_2O_5 (yield: 364 mg, 56% based on Cu).

RESULTS AND DISCUSSION

Electrochemical behavior of mixed ligand complex [Cu(dien)(pdc)(H₂O)] in DMSO: Cyclic voltammetric (CV) behaviors of the complex were studied in DMSO containing 0.2M NaClO₄ as a supporting electrolyte at GCE in the scan rate 25 to 500 mVs⁻¹. The cyclic voltammetric data are given in table 1 and their voltammogram at 25 mVs⁻¹ are illustrated in figure 1. It should be noted that one redox couple appeared between the potential limit of 800 mV to -500mV. The observed formal potentials and anodic to cathodic peak potential difference are: E⁰=204mV and ΔE_p=204 mV in DMSO at the scan rate 25 mV/s, assigned to quasi reversible Cu^{2+/+} one electron transfer electrochemical reactions. The values of peak potential difference (ΔE_p) was greater than 60 mV also justified the quasi-reversible nature of redox couple. On increasing the scan rate the cathodic peak potential shifts more negatively showing difficult reduction and easier oxidation. A plot of cathodic peak current (I_{pc}) vs square root of scan rate (v^{1/2}) gave a straight line with positive intercept Figure 3 showing that the electron transfer is preceded by a chemical reaction (CE Mechanism) [28, 29].

Table 1. CV data for mixed ligand [Cu(dien)(pdc)(H₂O)] complex in DMSO containing 0.2 M NaClO₄

scan rate (mVs ⁻¹)	E _{pc} (mV)	E _{pa} (mV)	I _{pc} (μA)	I _{pa} (μA)	E ⁰ (mV)	ΔE _p (mV)	I _{pa} /I _{pc}
25	-306	-102	3.0	3.0	-204	204	1.0
50	-350	-70.3	4.4	4.5	-210.1	279.7	1.0
100	-375	-64.4	6.4	6.2	-219.7	310.6	1.0
200	-412	-62.0	8.5	7.8	-237	350	0.9
300	-420	-60.0	10.3	8.8	-240	360	0.8
400	-426	-60.0	12.5	9.0	-243	366	0.7
500	-445	-60.0	14.0	9.8	-252.5	385	0.7

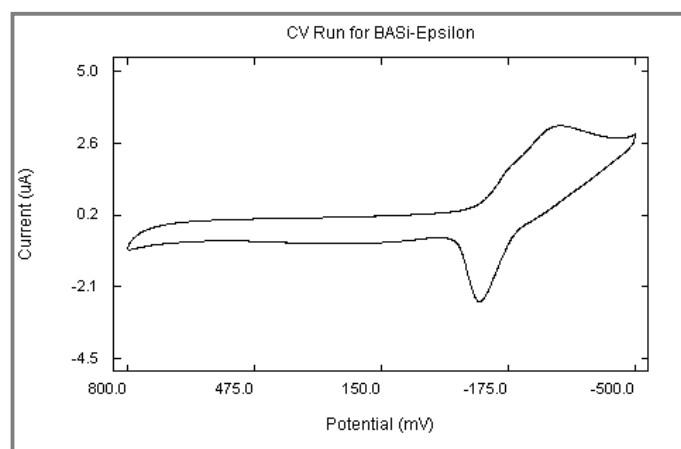


Figure 1. CV of mixed ligand complex (1) in DMSO containing 0.2M NaClO₄ at 25 mVs⁻¹.

Electrochemical behavior of mixed-ligand complex [Cu₂(dien)₂(pyz)](ClO₄)₄ in DMSO: Cyclic voltammetric (CV) behaviors of the mixed ligand complex were recorded in DMSO containing 0.2M NaClO₄ as a supporting electrolyte at GCE at the scan rate 25 to 500 mVs⁻¹. The cyclic voltammetric data are given in table 2 and the cyclic voltammograms at 25 mVs⁻¹ are shown in figure 2. It should be noted that in the case of mixed ligand Cu(II) complex, one redox couple appeared between the potential limit of 800 mV to -750mV. The observed formal potentials and anodic to cathodic peak potential difference are: E⁰ = 274.5 mV and ΔE_p = 102mV in DMSO at the scan rate 25 mV/s, assigned to quasi reversible Cu^{2+/+} one electron transfer electrochemical reactions. The values of peak potential difference (ΔE_p) was greater than 60 mV also justified the quasi-reversible nature of

redox couple. On increasing the scan rate the cathodic peak potential shifts more negatively shows difficult reduction. A plot of cathodic peak current (I_{pc}) vs square root of scan rate ($v^{1/2}$) gave a straight line with positive intercept figure 3, showing that the electron transfer is preceded by a chemical reaction (CE Mechanism) [28, 29].

Table 2. CV data for mixed ligand complex $[Cu_2(dien)_2(py_2z)](ClO_4)_4$ in DMSO containing 0.2M $NaClO_4$

scan rate (mVs^{-1})	E_{pc} (mV)	E_{pa} (mV)	I_{pc} (μA)	I_{pa} (μA)	E^0 (mV)	ΔE_p (mV)	I_{pa}/I_{pc}
25	-325	-224	15.26	-8.78	274.5	102	0.5
50	-333	-216	21.10	-11.75	274.5	117	0.5
100	-339	-211	30.51	-16.12	275	128	0.5
200	-354	-207	39.57	-19.07	280.5	147	0.4
300	-357	-203	48.54	-22.23	280	154	0.4
400	-362	-198	53.86	-25.52	280	164	0.4
500	-365	-194	59.13	-26.10	279.5	171	0.4

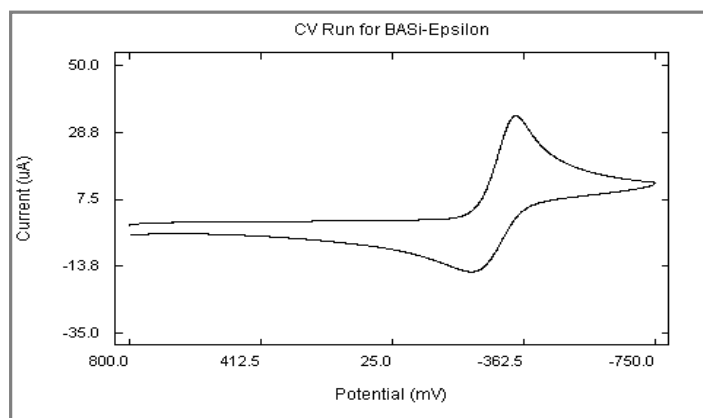


Figure 2. CV of mixed ligand complex (2) in DMSO containing 0.2M $NaClO_4$ at $25 mVs^{-1}$

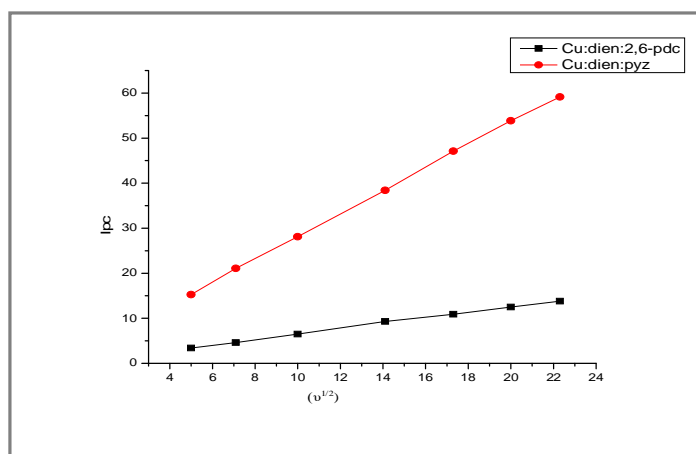


Figure 3. Plot of I_{pc} Vs $v^{1/2}$ for both mixed ligand complex (1) and (2).

Electronic absorption spectral studies of mixed ligand complexes in DMSO: The electronic absorption spectra of mixed ligand complexes (1) and (2) were studied in DMSO. The results are given in table 3. A broad band appeared at 622 nm and at 618 nm in DMSO for mixed ligand

complexes respectively which are attributed to d-d transitions. On the basis of electronic absorption spectral band it could be clear that a six coordinated copper complex species are predominantly present in complex (1) and a four coordinated copper complex species are predominantly present in complex (2) [30, 31].

Table 3. UV-Visible spectra of mixed ligand complexes (1) and (2) in DMSO

Solvent	System	Colour	λ_{\max} (nm)	ϵ (L mol ⁻¹ cm ⁻¹)
DMSO	[Cu(dien)(pdc)](H ₂ O) (1)	Light Blue	622	0.3
	[Cu ₂ (dien) ₂ (pyz)](ClO ₄) ₄ (2)	Light Blue	618	0.1

Elemental analyses: The mixed ligand complexes (1) and (2) were characterized by elemental analyses (C, H, N) were performed on a Euro Vector EA 3000 Elemental Analyser and the results are given in table 4. The elemental analyses were consistent with their chemical formulae.

Table 4. Elemental analysis

Complexes	C%		H%		N%	
	calculated	found	calculated	found	Calculated	Found
[Cu(dien)(pdc)](H ₂ O) (1)	34.33	36.17	4.5	5.4	13.17	15.34
[Cu ₂ (dien) ₂ (pyz)](ClO ₄) ₄ (2)	18.62	17.56	3.9	3.65	14.37	13.7

IR Spectra: FTIR of the complexes were recorded in the range of 4000-450cm⁻¹ using a KBr pellet. The FTIR spectra of the **complex (1) [Cu(dien)(pdc)(H₂O)]** (Figure 4) shows the peak at 3296 cm⁻¹ in the region of 3200-3600 cm⁻¹ can be attributed to the presence of hydroxyl ion. The carboxylate stretching vibration (ν_{COOH}) for free 2,6-pdc ligand was observed at 1717 cm⁻¹, but the band for ν_{COOH} disappeared when pdc is coordinated to Cu (II) ion. It exhibited an asymmetric $\nu_{\text{as}}(\text{COO}^-)$ and symmetric $\nu_{\text{s}}(\text{COO}^-)$ carboxylate stretching vibrations observed at 1581 and 1359 cm⁻¹. The difference between asymmetric and symmetric carboxylate stretching frequencies ($\Delta = \nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)$) is often used to correlate the carboxylate coordination mode [22, 23]. The difference of asymmetric to symmetric stretching frequency comes out to be is more than 200 cm⁻¹, confirms the monodentate coordination mode of the carboxylate group in the complex [24, 25]. It is to be noted that the complex show sharp and medium band at 668 cm⁻¹ attributed to pyridyl vibration and at 3020 cm⁻¹ assigned to aromatic $\nu_{\text{C-H}}$ [25]. The FT-IR spectra of complex showed sharp and medium band at 3344 cm⁻¹ which was assigned to $\nu_{\text{N-H}}$ of primary amine of diethylenetriamine and finally the $\nu(\text{Cu-N})$ bands appear in far IR region 620 cm⁻¹, which supports the coordination of diethylenetriamine through their N-donor atoms with the Copper in the complex [26].

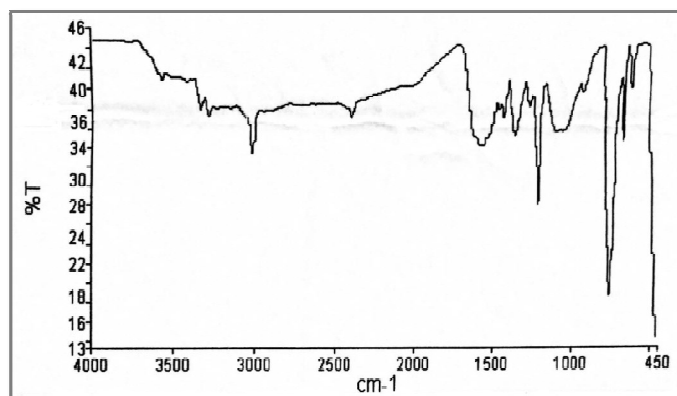


Figure 4. FTIR spectra of the complex (1)[Cu(dien)(pdc)(H₂O)].

The FT-IR spectra of **complex (2)** $[\text{Cu}_2(\text{dien})_2(\text{pyz})](\text{ClO}_4)_4$ (Figure 5) showed sharp and medium band at 3330cm^{-1} which was assigned to $\nu\text{N-Hof}$ primary amine of diethylenetriamine and the $\nu(\text{Cu-N})$ bands appear in far IR region 620cm^{-1} , which supports the coordination of diethylenetriamine through their N-donor atoms with the Copper in the complex [26]. It showed a sharp and medium band at 667cm^{-1} attributed to pyridyl vibration and at 3020cm^{-1} assigned to aromatic $\nu\text{C-H}$. The presence of perchlorate is confirmed by the sharp band at 1095cm^{-1} [25]. The bands at 1430cm^{-1} and 761cm^{-1} are due to presence of pyrazine in the mixed ligand complex [27].

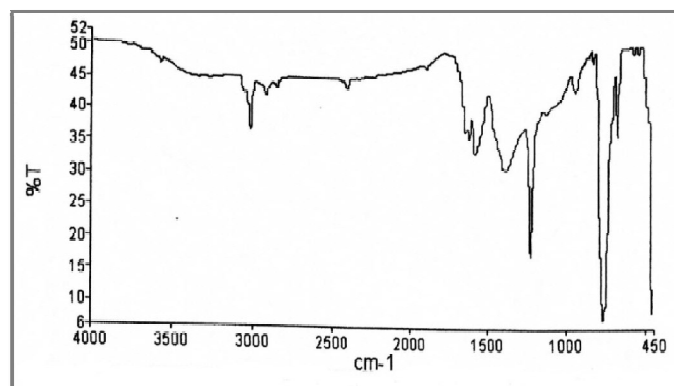


Figure 5. FTIR spectra of the complex (2) $[\text{Cu}_2(\text{dien})_2(\text{pyz})](\text{ClO}_4)_4$.

Thermal analysis of mixed ligand complexes (1) and (2): Thermal stability of complexes was studied in the range of $35\text{-}900^\circ\text{C}$ by controlling the heating rates $10^\circ\text{C}/\text{min}$. The simultaneous TG/DTG/DTA curves in nitrogen atmosphere of all the complexes are depicted in figures 6 and 7. The TGA curve of **Complex (1)** $[\text{Cu}(\text{dien})(\text{pdc})(\text{H}_2\text{O})]$ shows almost no weight loss upto 150°C showing the absence of uncoordinated solvent molecules. A weight loss of about 5% (19) observed in the temperature range $150\text{-}218^\circ\text{C}$ which is assumed for the removal of the one coordinated water. Further, a weight loss of 74.6% in the temperature range $218\text{-}274^\circ\text{C}$ suggest the decomposition of the complex framework. The final residual product at 494°C appears to be Cu metal in Nitrogen atmosphere, 20.99% residue (Calcd. 21.16%) In this complex the DTG curve displays one peak at 273°C and the DTA curve displayed one exothermic peak at 272°C . The TGA profile for **complex (2)** $[\text{Cu}_2(\text{dien})_2(\text{pyz})](\text{ClO}_4)_4$ is almost similar to that of **complex 1**. It only differs in term of stability where it does not show any weight loss up to 245°C , suggests the absence of water molecules. After which a weight loss of about 84.2% occurs between $245\text{-}270^\circ\text{C}$, which suggests the decomposition of the complex framework. The final residual product appears to be Cu metal in Nitrogen atmosphere at 899°C as shown by the 16.8% residue (Calcd. 15.48%). In this complex the DTG curve displays one peak at 268°C and the DTA curve displayed one exothermic peak at 268°C .

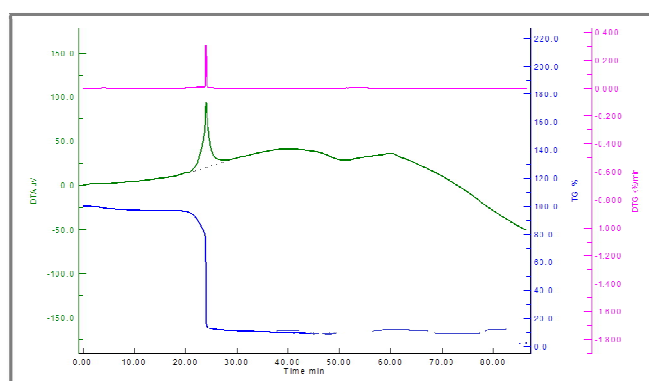


Figure 6. TGA Curve of Complex (1) $[\text{Cu}(\text{dien})(\text{pdc})(\text{H}_2\text{O})]$.

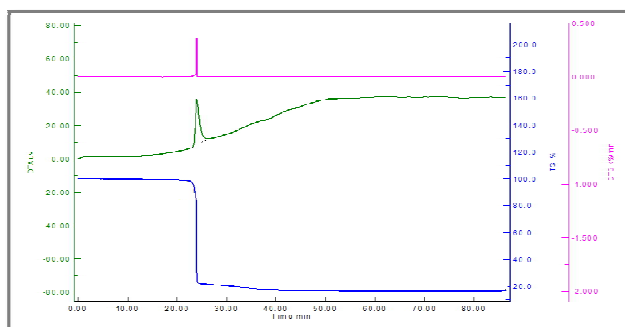


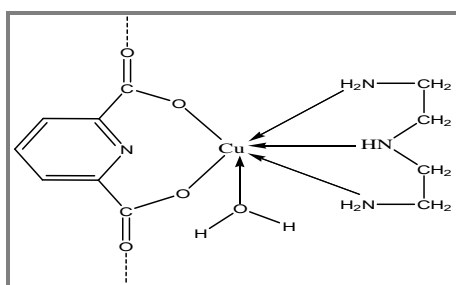
Figure 7. TGA Curve of Complex (2) $[\text{Cu}_2(\text{dien})_2(\text{pyz})](\text{ClO}_4)_4$.

APPLICATION

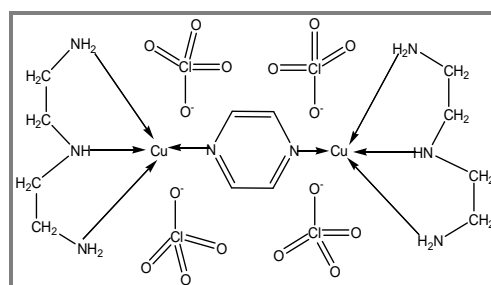
The vibrational study of complexes reveals the coordination mode and presence of ligands. Thermal stability showed the chemical decomposition of complexes. It corresponds with the presence of co-ordinate water and the expulsion of organic components.

CONCLUSION

The mixed ligand complexes (1) $[\text{Cu}(\text{dien})(\text{pdc})(\text{H}_2\text{O})]$ and (2) $[\text{Cu}_2(\text{dien})_2(\text{pyz})](\text{ClO}_4)_4$ were synthesized in methanolic medium and investigated by elemental, electrochemical, spectral and TGA studies and their electrochemical investigations shows that both the complexes undergo a quasi-reversible single-electron redox process ($\text{Cu}^{2+/+}$) with formal potentials $E^0 = -204$ mV and $E^0 = 274.5$ mV vs Ag/AgCl, at the scan rate of 25 mV/s in the potential ranges +800 to -500 V and +800 to -750 V respectively. On the basis of electronic absorption spectral band it could be clear that a six coordinated copper complex predominant species are present in the mixed ligand complexes. The elemental analyses were consistent with their chemical formulae. The vibrational study of complexes reveals the coordination mode and presence of ligands. Thermal stability (TG/DTG/DTA Curves) showed the chemical decomposition of complexes. It corresponds with the presence of co-ordinate water and the expulsion of organic components. The proposed molecular structures of the synthesized complex (1) and (2) are given below:



Structure of Complex(1) $[\text{Cu}(\text{dien})(\text{pdc})(\text{H}_2\text{O})]$



Structure of Complex (2) $[\text{Cu}_2(\text{dien})_2(\text{pyz})](\text{ClO}_4)_4$.

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