

Cyclic voltammetric behavior of binary and mixed ligand copper complexes with picolinic acid, nicotinic acid and diethyldithiocarbamate in acetone medium

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The solution chemistry of picolinic acid (PA), nicotinic acid (NA), diethyldithiocarbamate (Et_2dtc) ligands and their complexes has been studied by cyclic voltammetry on platinum working electrode and it was observed that the cyclic voltammetric behavior of ligands, binary complexes and mixed ligand complexes are distinctly different. The binary complexes of copper(II) with PA and NA in 1:1 (Cu:PA/NA) molar ratio and their mixed ligand complexes with diethyldithiocarbamate (Et_2dtc) in 1:1:1, Cu: Et_2dtc :PA/NA molar ratio in acetone medium was investigated by cyclic voltammetry and UV-Visible spectroscopy. The PA and NA ligand showed irreversible redox couple with ΔE_p values >120 mV. It was observed that mixed ligand complexes exhibits irreversible redox couple in positive potential region due to $\text{Cu}^{2+/3+}$ and $\text{Cu}^{3+/2+}$ change. The electronic absorption spectra of binary complexes showed only one peak in visible region while mixed ligand complexes exhibited two peaks, one in UV region while other visible region.

Keywords: Copper complexes, picolinic acid, nicotinic acid, diethyldithiocarbamate, electrochemistry.

Introduction

Picolinic (PA) and nicotinic (NA) acids are pyridine monocarboxylic acids, in which carboxylate group is attached on pyridine ring at two and three position respectively. During the binary complexes formation with copper perchlorate in acetone medium, the possibility of attachments of ligand to metal by nitrogen and carboxylate group both or any one. Diethyldithiocarbamate is sulfur donor ligand. Two sulfur groups can be involve in complex formation with copper. Cyclic voltammetry is a unique technique by which we can identify whether complex is formed in solution or not. If cyclic voltammetric behavior of ligand is differing from complex then one can say that some complex species is formed in solution.

Picolinic acid is a prime natural chelator in human body. This ligand is able to chelate with different types of metal ions and can exhibit various coordination behaviour as a multidentate ligand. In our body picolinic acid acts as most efficient chelator for metal cations such as chromium, zinc, manganese, copper, iron and molybdenum. The chemistry and properties of the picolinic acid can be understood by study the structures of its metal complexes¹⁻⁵.

Dithiocarbamate ligands have stabilizing ability towards

Cu^{2+} and their Cu(II) complexes undergo reversible oxidation ($\text{Cu}^{2+/3+}$) and reduction processes ($\text{Cu}^{2+}/+$) to their monocation and monoanion, respectively⁶. Magee *et al.*⁷ reported about the analytical chemistry of metal dithiocarbamate complexes in his review. Srivastava *et al.*⁸ studied the electrochemical and spectral properties of copper(II) mixed ligand complexes such as Cu^{II} -diethyldithiocarbamate-2-methylimidazole in different molar ratios (1:1:2, 1:1:100, 1:2:2 and 1:2:100) in acetone medium containing 0.2 M sodium perchlorate as a supporting electrolyte by using cyclic voltammetry (CV). The oxidation of sodium diethyldithiocarbamate at a glassy carbon electrode in water and water-organic mixtures in the presence of KCl and NaOH was investigated by Basova *et al.*⁹ using cyclic square-wave voltammetry and rotated electrode voltammetry.

Nicotinic acid is used as an intermediate for agrochemicals, feed additives, pharmaceuticals and animal food enrichments. Nicotinic acid is a biologically significant ligand, which forms useful metal complexes, due to their physiological properties¹⁰. Electrochemical reduction in metal ion was observed by Tan *et al.*¹¹ using proper electrochemical techniques, such as cathodic stripping voltammetry and pulse voltammetry.

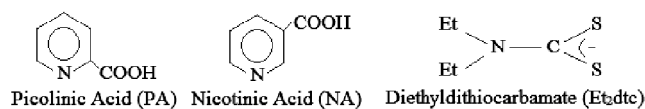
There are so many solid states copper(II) complexes of picolinic acid and nicotinic acid were synthesized and characterized by the spectroscopic techniques and elemental analysis^{12–15}, but the details cyclic voltammetric studies of their mixed ligand complexes are rare. Cyclic voltammetry is one of the best electrochemical techniques, because of its low cost, high sensitivity, easy operation and ability of analyzing the redox behavior of complexes compound. Rahman *et al.*¹⁶ studied the voltammetry behaviors of lead(II) ion in the presence of nicotinic acid ligand on hanging dropping mercury electrode.

The electrochemical behavior of the $[\text{Cu}(\text{pic})_2] \cdot 2\text{H}_2\text{O}$ complex was investigated by cyclic voltammetry in dimethylformamide solutions, showing that its reduction occurs through a quasi-reversible one-electron process¹⁴. Peter Comba *et al.*¹⁷ studied the synthesis, coordination chemistry and electrochemistry of hexadentate picolinic acid based bispidine ligands. Peter Comba *et al.*¹⁸ investigated the properties of a picolinic acid-based bispidine ligand for stable copper(II) complexation. Bolzán¹⁹ studied the electro-deposition of copper on glassy carbon electrodes in the presence of picolinic acid (PA) by means of voltammetric, chronoamperometric and electrochemical impedance spectroscopy measurements complemented by UV-Visible spectroscopy and SEM imaging. Fazary *et al.*²⁰ investigated the nicotine-metal ion interactions in solutions and characterized by potentiometric, cyclic voltammetry and quantum chemical calculations. Portela²¹ studied about the copper electrodeposition on platinum electrodes from slightly acidic solutions of copper sulphate containing nicotinic acid.

Tatlıdil and Biçer²² declared that the addition of NA to the Cu(II) solution caused a decreases in the peak current of free Cu(II)-Cu(0) reduction and also appearance of new peaks. Moreover, the currents of these peaks increased by increasing NA concentration. These peaks at more positive and negative potentials than that of free Cu(II)-Cu(0) reduction could be attributed to the complexed Cu(II)-Cu(I) and Cu(I)-Cu(0) reductions, respectively²².

Here we report the electrochemical and spectral behavior of Cu(II):PA (1:1); Cu(II):NA (1:1); Cu(II):Et₂dtc:PA (1:1:1) and Cu(II):Et₂dtc:NA (1:1:1) complexes in acetone on platinum working electrode by means of cyclic voltammetry and UV-Visible spectroscopy.

The chemical structures of ligands are as follows:



Results and discussion

Cyclic voltammetry (CV) of ligands and complexes:

The CV behaviour of PA and NA ligands were examined in the potential range +1000 mV to -1100 mV at scan rate 25 mV s⁻¹ to 200 mV s⁻¹. The CV data and voltammograms of these ligands are given in Table 1 and Fig. 1 respectively. In the voltammogram of PA ligand, the forward scan was initi-

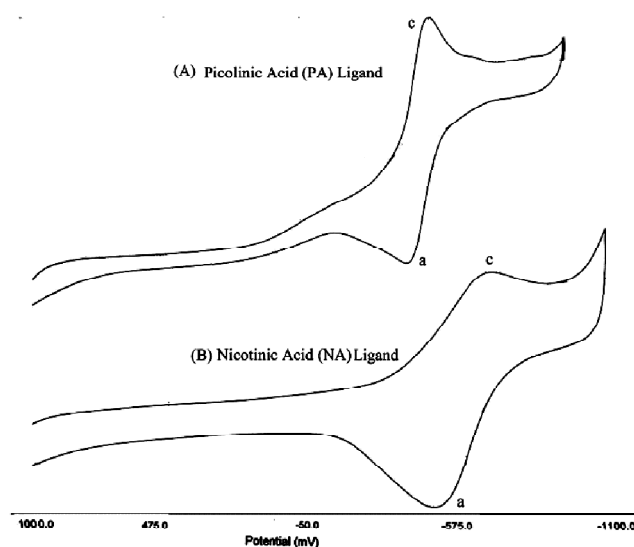


Fig. 1. Cyclic voltammograms of (A) picolinic acid (PA) ligands at 50 mV/s scan rate; (B) nicotinic acid (NA) ligands at 50 mV/s scan rate.

ated from +1000 mV and completed at -1100 mV in which one reduction peak (E_{pc}) appeared at -567 mV due to the reduction of PA ligand while in reverse scan from -1100 mV to +1000 mV one corresponding anodic peak displayed at -456 mV at scan rate 50 mV/s (Fig. 1A). The peak potential difference (ΔE_p) values were observed between the range of 111 mV to 125 mV (Table 1) indicated towards irreversible nature of the redox reaction. The values of anodic to cathodic peak current ratio I_{pa}/I_{pc} are less than unity. The graph plotted between I_{pc} or I_{pa} vs scan rate ($\nu_{1/2}$) gave straight line passing through origin, suggested the diffusion controlled followed by chemical reaction²³. The E_{pc} values at all scan

Table 1. CV data for 1 mM picolinic and nicotinic acid ligands containing 0.2 M NaClO₄ at Pt/Ag/AgCl electrode in acetone

Scan rate (mV s ⁻¹)	E_{pc} (mV)	E_{pa} (mV)	I_{pc} (μ A)	I_{pa} (μ A)	ΔE_p (mV)	$E_{0'}$ (mV)	I_{pa}/I_{pc} (μ A)
Picolinic acid							
25	-569	-457	2.4	1.8	112	513.0	0.75
50	-567	-456	3.1	2.5	111	514.5	0.80
100	-568	-450	4.2	3.3	118	513.0	0.78
200	-567	-442	5.6	4.8	125	504.0	0.85
Nicotinic acid							
25	-576	-448	1.4	1.5	128	512.0	1.0
50	-573	-420	2.2	2.0	153	501.5	0.9
100	-573	-416	2.9	2.7	157	494.5	0.9
200	-570	-414	3.7	3.4	156	492.0	0.9

rates are almost similar while the E_{pa} values shifted positively with increasing scan rate, indicated towards difficult oxidation of picolinic acid with increasing scan rate.

In the case of NA ligand, the cathodic peak E_{pc} was observed at -573 mV in forward scan, while in reverse scan an anodic peak was observed at -420 mV with scan rate 50 mV/s (Fig. 1B). The cathodic peak potential (E_{pc}) values were nearly stable at all scan rates. The E_{pc} was varies from -576 mV to -570 mV with scan rate 25 to 200 mV/s (Table 1). The anodic peak potentials (E_{pa}) shifted positively (-448 mV < -420 mV < -416 mV < -414 mV) with scan rate (25, 50, 100 and 200 mV/s). The ΔE_p was more than 120 mV indicated towards the irreversible redox nature of NA ligand. The similar results have been observed in both PA and NA ligands. The reduction of PA and NA ligands was not more affected by the scan rate while the oxidation reactions were going to more difficult with increasing scan rate. Both PA and NA ligands showed irreversibility in acetone medium. CV behavior of the ligands, PA and NA, showed a large peak separation owing to shift toward positive potential of E_{pa} with scan rate. This may indicated proton-coupled electron-transfer.

Rodriguez-Amar *et al.* studied the electrochemical reduction of nicotinic acid at a mercury electrode. In very strong media it involves two electron transfers followed by a protonation step yielding the corresponding nicotinic aldehyde. Two waves observed in the pH range 0.5 to 5.0²⁴.

The electrochemical studies of PA, NA and different pyridine dicarboxylic acid ligands such as 2,3-pdc, 2,4-pdc, 2,5-pdc, 2,6-pdc, 3,4-pdc, and 3,5-pdc (pdc = pyridine dicarboxylic

acid) have been carried out in dimethylsulfoxide medium. PA and NA ligand exhibits only one reduction peak in negative potential region between -1297 to -1520 mV in DMSO medium²⁵. But in acetone medium (present study) the redox behavior of PA and NA ligands are totally different.

The potential limit for the CV experiment of binary complex Cu(II):PA in 1:1 molar ratio was 0.0 mV to +900 mV to -1300 mV to 0.0 mV. In forward scan from 0.0 to +900 mV one sharp oxidation peak was observed at 330 mV with scan rate 100 mV/s due to Cu^{2+/3+} electrochemical reaction. The sharpness of the peak may be due to the some absorption on the surface of electrode. In reverse scan from +900 to -1300 one small reduction peak was observed at 75 mV due to the Cu^{3+/2+} change, one another broad reduction peak was observed at -700 mV due to Cu^{2+/+} electrochemical reaction while a corresponding broad anodic peak was observed at -649 mV because of the Cu^{+/2+} electrode reaction at scan rate 100 mV/s (Fig. 2a). When scan rates were increased the second reduction potential shift negatively.

In the case of binary complex Cu(II):NA (1:1), the CV studies were carried out in potential limits +900 mV to 50 mV because only within this potential limits its exhibits redox peaks. A broad reduction peak E_{pc1} showed at +149 mV in the forward scan while a sharp oxidation peak E_{pa1} displayed at +338 mV with scan rate 100 mV/s. The previous one was due to the reduction of Cu(III) to Cu(II) while later one sharp anodic peak may be due to the Cu^{2+/3+} with some adsorption on the surface of electrode (Fig. 2).

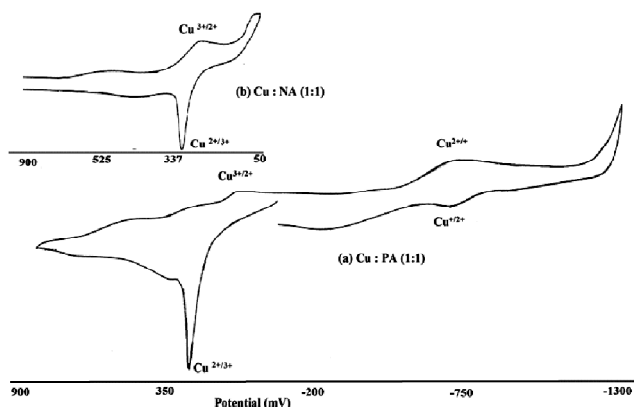


Fig. 2. Cyclic voltammograms of (a) Cu:picolinic acid (PA) 1:1 at 100 mV/s scan rate; (b) Cu:nicotinic acid (NA) 1:1 at 100 mV/s scan rate.

The CV data for complex Cu(II):Et₂dtc:PA and Cu(II):Et₂dtc:NA in 1:1:1 molar ratios are summarized in Table 2 and their voltammograms are given in Fig. 3.

The CV behavior of Cu(II):Et₂dtc:PA (1:1:1) was carried out in the potential range 0.0 mV to 900 mV to -1300 mV to 0.0 mV at 25 to 200 mV/s scan rate. In forward scan from 0.0 mV to +900 mV an oxidation peak E_{pa1} was observed at +644 mV because of the Cu^{2+/3+} electrode reaction while in the reverse scan from +900 to -1300 mV, a reduction peak E_{pc1} was observed at +461 mV with scan rate 50 mV/s due to the reduction of Cu(III) to Cu(II) (Fig. 4a). Two another reduction peaks E_{pc2} and E_{pc3} were also observed in negative potential region at -473 mV and -960 mV respectively at the scan rate 50 mV/s (Fig. 3a). The reduction peak E_{pc2} was the result of Cu(II) to Cu(I) but another reduction peak E_{pc3}

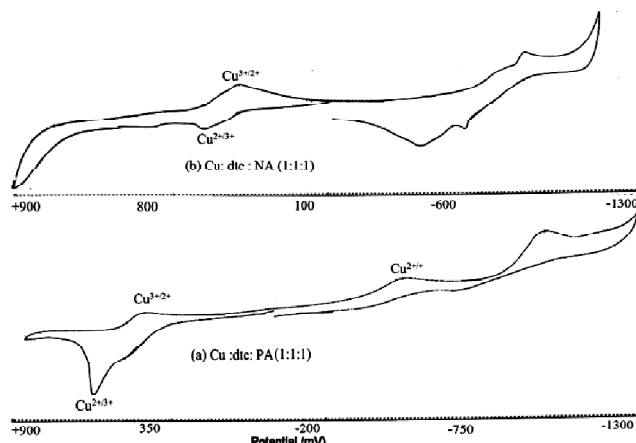


Fig. 3. Cyclic voltammograms of (a) Cu:Et₂dtc:PA 1:1:1 at 50 mV/s scan rate; (b) Cu:Et₂dtc:NA 1:1:1 at 50 mV/s scan rate.

was due to the reduction of free ligand or other new species generated in the solution. When the voltammetric scan was further reversed from -1300 mV to 0.0 mV, there were not a single peak was observed. The anodic peak potential E_{pa1} shifted positively viz. 549 mV < 644 mV < 679 mV < 692 mV with increasing scan rates 25 mV/s < 50 mV/s < 100 mV/s < 200 mV/s. The positive shifting of E_{pa1} with increasing scan rates is clearly indicating towards the difficult oxidations. The cathodic peak potential E_{pc1} was near about stable with increased scan rate. At slow scan rate 25 mV/s the peak potential difference ΔE_p observed at 93 mV because of the quasi-reversible nature of the redox reaction (Table 2). But when scan rate increased up to 200 mV/s the quasi-reversible natures were converted to irreversible, because the ΔE_p values increased with scan rate (Table 2). The anodic to ca-

Table 2. CV data for mixed ligand complexes formed in 1:1:1, Cu (ClO₄).6H₂O:Et₂dtc:picolinic/nicotinic acid containing 0.2 M NaClO₄ at Pt/Ag/AgCl electrode in acetone

Scan rate (mV s ⁻¹)	E_{pa1} (mV)	E_{pc1} (mV)	E_{pc2} (mV)	E_{pc3} (mV)	$E_{pa2'}$ (mV)	$E_{pa2''}$ (mV)	I_{pa1} (μA)	I_{pc1} (μA)	I_{pc2} (μA)	I_{pc3} (μA)	$I_{pa2'}$ (μA)	$I_{pa2''}$ (μA)	ΔE_p (mV)	E_0' (mV)	I_{pc1}/I_{pa1} (μA)
Mixed ligand complexes formed in 1:1:1, Cu (ClO ₄).6H ₂ O:Et ₂ dtc:picolinic acid:															
25	549	456	-510	-1022	Nil	Nil	1.1	1.0	2.6	4.4	Nil	Nil	93	502.5	0.90
50	644	461	-473	-960			1.3	1.1	4.2	6.4			183	552.5	0.84
100	679	455	-476	-950			4.6	3.2	5.0	9.3			224	567.0	0.70
200	692	455	-486	-967			6.7	4.9	6.3	12.7			237	573.5	0.73
Mixed ligand complexes formed in 1:1:1, Cu (ClO ₄).6H ₂ O:Et ₂ dtc:nicotinic acid															
25	614	454	Nil	-925	-643	-435	1.6	1.5	Nil	8.0	0.8	2.9	160	534.0	0.93
50	616	455		-928	-646	-437	1.7	1.6		8.3	0.9	3.2	161	535.5	0.90
100	618	439		-945	-621	-451	1.9	1.8		14.3	2.2	2.5	179	515.5	0.93
200	622	410		-927	-608	-446	6.5	4.0		13.5	1.9	1.7	212	516.0	0.61

thodic current ratios I_{pc1}/I_{pa1} is less than unity, showed EC mechanism of the electrochemical reaction in the complex solution. Plot of I_{pc} or I_{pa} vs scan rate $\nu_{1/2}$ gave straight line passing through origin.

In the case of NA based mixed ligand complex, the potential limit and scan rate of both PA and NA mixed ligand complexes was similar. In the forward scan region one anodic peak E_{pa1} was observed at 616 mV with scan rate 50 mV/s due to the $Cu^{2+}/3+$ electrochemical reaction while in reverse scan region two cathodic peaks E_{pc1} and E_{pc3} were observed at +455 mV and -928 mV (at scan rate 50 mV/s) respectively in which the first one E_{pc1} was due to the reduction of Cu(III) to Cu(II) and second other reduction peak E_{pc3} because of the reduction of ligand or other new species in solution (Fig. 3b). When voltammogram's scan was further reverse from -1300 mV to 0.0 mV, two weak oxidation peaks $E_{pa2'}$ and $E_{pa2''}$ were observed may be due to the oxidation of free ligand species or other new species present in the complex solution. The anodic peak potential E_{pa1} was near about similar in all scan rates. It was varies from 614 mV to 622 mV with scan rate 25 to 200 mV/s (Table 2) while the cathodic peak potential E_{pc1} shifts negative region with in-

creasing scan rate from 25 to 200 mV/s. The ΔE_p value was observed between 160 mV to 212 mV indicated that redox reaction was irreversible in nature. The anodic to cathodic peak potential ratios I_{pc1}/I_{pa1} is less than 1.0 which indicates that the electrochemical reaction is not reversible.

In our previous publication, the CV studies of Cu:Et₂dtc in 1:1 molar ratio in acetone medium have been carried out, in which the E_{pa1} values were observed at 542–548 mV and E_{pc1} values were observed at 450–444 mV for scan rate 25 to 200 mV/s²⁶. In present study, when the PA and NA ligands was mixed with Cu:Et₂dtc system, the Cu:Et₂dtc:PA (1:1:1) and Cu:Et₂dtc:NA (1:1:1) complexes were formed. At similar scan rate studies the E_{pa1} values in Cu:Et₂dtc:PA (1:1:1) complex were shifted positively and observed at 549–692 mV and E_{pc1} values also shifted in positive direction observed at 461–455 mV, while in case of Cu:Et₂dtc:NA (1:1:1) complex, the E_{pa1} values shifted positively and observed at 614–622 mV in compare to Cu:Et₂dtc (1:1) system. These shifting in peak potentials are due to the formation of mixed ligand complexes with PA and NA ligands in solution.

Electronic absorption spectral studies of binary and mixed ligand complex:

The UV-Visible spectral data of binary complex Cu(II):PA and Cu(II):NA in 1:1 molar ratios are given in Table 3 and spectra are given in Fig. 4. The electronic absorption spectra were carried out in 500 nm to 1000 nm range. The colour of the both complex solutions was clear and colorless. It was observed that Cu(II):PA complex solution showed a broad band at 746 nm and Cu(II):NA solution also showed a broad band at 790 nm due to the d-d transition. The complex did not show any band in UV region.

Bolzán¹⁹ carried out the UV-Visible spectra of $CuSO_4$ 0.02 M, $CuSO_4$ 0.02 M + PA 0.005 M and $CuSO_4$ 0.02 M + PA 0.01 M solutions and observed absorption band in visible

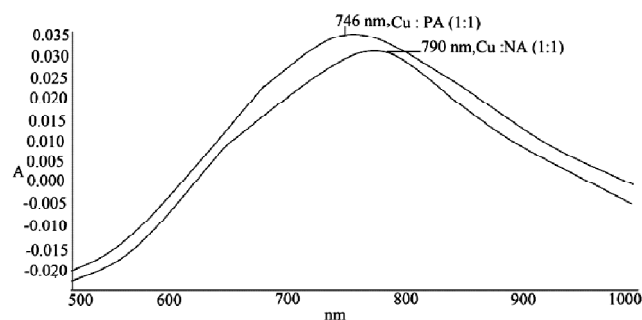


Fig. 4. Electronic absorption spectra of Cu:picolinic acid (PA) 1:1 and Cu:nicotinic acid (NA) 1:1.

Table 3. Electronic absorption data for 1 mM binary and mixed ligand complexes on acetone

Complexes formed in solution	Molar ratios	Colour	λ_{max} (nm)	Band
Cu(ClO ₄) ₂ .6H ₂ O:picolinic acid	1:1	Colourless	746	d-d
Cu(ClO ₄) ₂ .6H ₂ O:nicotinic acid	1:1	Colourless	790	d-d
Cu(ClO ₄) ₂ .6H ₂ O:Et ₂ dtc:picolinic acid	1:1:1	Dark green	415 641	CT d-d
Cu(ClO ₄) ₂ .6H ₂ O:Et ₂ dtc:nicotinic acid	1:1:1	Dark green	416 633	CT d-d

region only. The addition of PA shows, increase in the blue tinge of the 0.02 M CuSO₄ solution. The corresponding UV-Vis spectra show a blue-shift in the maximum absorption from 800 to 750 nm as the PA concentration is increased.

The colors of the both mixed ligand complex solutions were green. The spectral studies were performed between the limit of 300 nm to 1000 nm. It was found that mixed ligand complex Cu(II):Et₂dtc:PA (1:1:1) gave two absorption band, one band at 415 nm due to ligand to metal charge transfer while second other band observed at 641 nm due to the d-d transition (Table 3 and Fig. 5). In the case of nicotinic acid based mixed ligand complex solution two absorption band observed, one in UV region at 416 nm was charge transfer (CT) band and second other in visible region at 633 nm due to the d-d transition (Table 3 and Fig. 5).

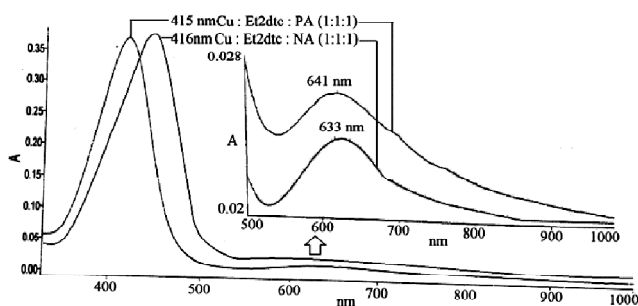


Fig. 5. Electronic absorption spectra of Cu:Et₂dtc:PA 1:1:1 and Cu:Et₂dtc:NA 1:1:1.

Experimental

The stock solutions of 0.01 M concentration of picolinic acid (PA), nicotinic acid (NA), diethyldithiocarbamate (Et₂dtc) ligands and copper perchlorate hexahydrate metal salt were freshly prepared separately in acetone. The binary complexes Cu(II):PA and Cu(II):NA were prepared in 1:1 metal to ligand molar ratio while the mixed ligand complexes i.e. Cu(II):PA:Et₂dtc and Cu(II):NA:Et₂dtc were formed in 1:1:1 metal to ligand PA/NA to ligand Et₂dtc molar ratios. The non-aqueous solutions of these complexes under investigation were freshly prepared in acetone. More dilute (0.001 M) solutions of complexes were prepared by accurate dilution for the CV studies. The similar complex solutions were used in both electrochemical studies as well as electronic absorption spectral studies.

Copper perchlorate hexahydrate (Cu(ClO₄)₂·6H₂O), picolinic acid (PA), nicotinic acid (NA), diethyldithiocarbamate (Et₂dtc), acetone and sodium perchlorate (NaClO₄) were purchased from Sigma Aldrich Chemicals Pvt. Ltd.

The BAS Electrochemical Systems, Model EPSILON (Bioanalytical Systems, Inc, USA) was used for all the electrochemical studies. The three electrode system were used for the CV studies of ligand and metal complexes, where the working electrode was platinum working electrode, the counter electrode was a 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 30 min before to analyze the solution. Great care was taken in the electrode pretreatment. The mechanical polishing of the working electrode was carried out with a drop of alumina suspension over a velvet microcloth. All the electrochemical experiments were performed at a constant temperature 25±0.5°C. IR compensation and back ground subtraction have been also done. All the cyclic voltammograms were recorded in acetone with 0.1 M NaClO₄ supporting electrolyte at platinum working electrode. The electronic absorption spectra of the similar complex solutions were measured in both UV and Visible region with a Perkin-Elmer UV-Visible spectrophotometer Model Lambda 35.

Conclusion

On the basis of above discussion it can be concluded that the oxidation of picolinic acid (PA) ligand was difficult with increasing scan rate and similar results were observed in case of nicotinic acid ligand. The CV behavior of Cu(II):PA and Cu(II):NA in positive potential region is similar but in negative potential region Cu(II):NA complex did not showed any electrochemical response. The mixed ligand complex solutions Cu(II):Et₂dtc:PA and Cu(II):Et₂dtc:NA showed an irreversible redox couple in positive potential region due to the Cu^{3+/2+} and Cu^{2+/3+} changes.

The binary complex Cu(II):PA and Cu(II):NA gives broad peaks in visible region at 746 nm and 790 nm respectively due to the d-d transition while mixed ligand complex solutions Cu(II):Et₂dtc:PA and Cu(II):Et₂dtc:NA gave sharp peak in UV region at 415 nm and 416 nm due to MLCT, and broad peak in visible region at 641 and 633 nm due to d-d transition.

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