

## Cyclic voltammetric studies of copper(II) complexes with *N,N,N',N'*-tetramethylethylenediamine in dimethylsulfoxide

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**Abstract :** The electrochemical behaviour of  $[\text{Cu}(\text{tmen})\text{X}_2]$  (where  $\text{tmen} = N,N,N',N'$ -tetramethylethylenediamine and  $\text{X} = \text{Cl}$  or  $\text{Br}$ ) has been studied in dimethylsulfoxide (DMSO) solution containing 0.1 M tetrabutylammoniumperchlorate (TBAP) as supporting electrolyte at a platinum working electrode. The diffusion-controlled reduction of both the complexes occurred in two stages; the first one at  $E^{0'}$  = 342 to 352 and second at  $E^{0'}$  = 16 to 24 mV vs Ag/AgCl. The anodic to cathodic peak current ratio is greater than unity for the first redox couple while it is less than 1.0 for the second couple, suggesting that the electrogenerated  $\text{Cu}^{\text{I}}$ -complex species is weakly adsorbed in the former case while the second step involves electron transfer followed by a chemical reaction (EC mechanism). The two redox processes observed may be because of chemical equilibrium between the two complex species in DMSO medium.

**Keywords :** Copper, tetramethylethylenediamine, electrochemistry, cyclic voltammetry.

### Introduction

Chelating diamine ligands form a variety of binary as well as mixed-ligand complexes with transition metal ions. Diamine complexes of divalent metal ions have received great attention due to their biological activity. The dichloro complex  $\text{cis-Pt}(\text{en})\text{Cl}_2$ , like  $\text{cis-Pt}(\text{NH}_3)_2\text{Cl}_2$ , is also known for its antitumor activity<sup>1</sup>. The biological<sup>2</sup> as well as catalytic<sup>3</sup> activity of copper(II) complexes having diamine as a ligand has also been reported. During past decades, diamines and their derivatives are investigated for important applications as stable complexes in diverse fields like biotechnology, environmental science and biochemistry, etc.<sup>4-6</sup>. In this paper, we report the electrochemical properties of two complexes, viz.  $[\text{Cu}(\text{tmen})\text{Cl}_2]$  and  $[\text{Cu}(\text{tmen})\text{Br}_2]$  complexes.

### Results and discussion

The electrochemical redox behaviour of  $[\text{Cu}(\text{tmen})\text{Cl}_2]$  and  $[\text{Cu}(\text{tmen})\text{Br}_2]$  complexes has been investigated in deoxygenated DMSO containing 0.1 M TBAP as supporting electrolyte at a platinum working electrode employing cyclic voltammetry (CV). A typical voltammogram of 2 mM solution of  $[\text{Cu}(\text{tmen})\text{Br}_2]$  initiated in the negative direction in the potential range from +0.69 to -0.20

V vs Ag/AgCl at a scan rate of 100 mV s<sup>-1</sup> is depicted in Fig. 1. The electrochemical data of  $[\text{Cu}(\text{tmen})\text{X}_2]$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) complexes are summarized in Table 1. Both these complexes exhibit similar cyclic voltammogram. As is evident from Fig. 1, the voltammogram consists of two reduction waves  $\text{Cu}^{2+/+}$  (labelled as processes,  $c_1$  and  $c_2$  in Fig. 1) with cathodic peak potentials :  $E_{pc1} = +275$  mV and  $E_{pc2} = -53$  mV vs Ag/AgCl at scan rate 100 mV s<sup>-1</sup>. The corresponding oxidation waves (labelled as processes,  $a_1$  and  $a_2$  in Fig. 1) are found upon the reversal of the potential scan with anodic peak potentials :  $E_{pa1} = +423$  mV and  $E_{pa2} = +93$  mV vs Ag/AgCl for complex  $[\text{Cu}(\text{tmen})\text{Br}_2]$ . Both the cathodic peak potentials ( $E_{pc1}/E_{pc2}$ ) shift cathodically and the value of  $\Delta E_p$  ( $=E_{pa} - E_{pc}$ ) progressively increases with increasing scan rate. The values of  $\Delta E_p$  for both the couples are greater than 60 mV corresponding to a quasi-reversible single-electron process (Table 1). These observations are indicative of the heterogeneous quasi-reversible single-electron transfer process<sup>7</sup>. The plots of  $I_{pc1}$  and  $I_{pc2}$  vs square root of the scan rate ( $v^{1/2}$ ) are linear with zero intercept, showing that the electrode process is diffusion-controlled<sup>7,8</sup>.

It is interesting to note that the magnitudes of cathodic

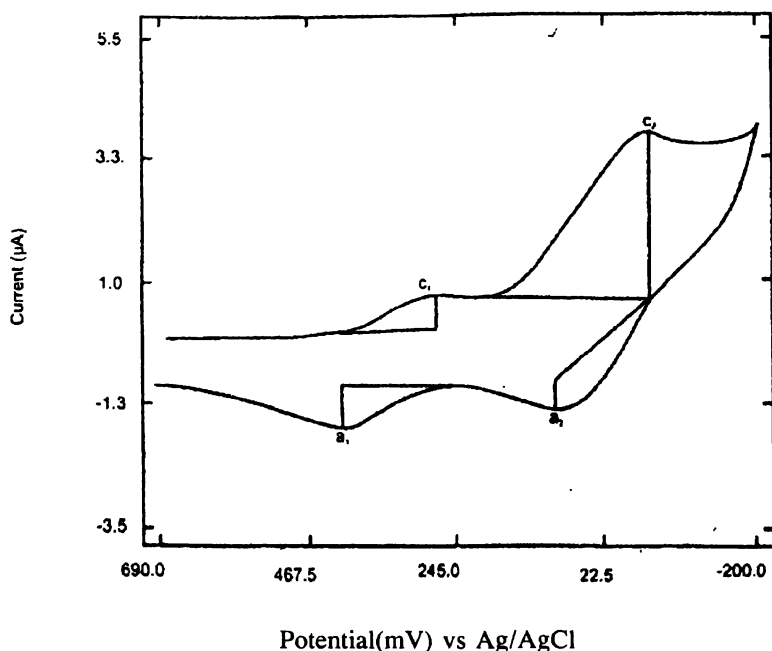


Fig. 1. Cyclic voltammogram of 2 mM  $[\text{Cu}(\text{tmen})\text{Br}_2]$  complex in DMSO/0.1 M TBAP at  $100 \text{ mV s}^{-1}$ .

Table 1. CV data for  $[\text{Cu}(\text{tmen})\text{X}_2]$  in DMSO/0.1 M TBAP (X = Cl or Br)

Scan rate ( $\text{mV s}^{-1}$ )	First step					Second step				
	$E_{pc1}$ (mV)	$E_{pa1}$ (mV)	$E_1^{0'}$ (mV)	$\Delta E_p$ (mV)	$I_{pa1}/I_{pc1}$	$E_{pc2}$ (mV)	$E_{pa2}$ (mV)	$E_2^{0'}$ (mV)	$\Delta E_p$ (mV)	$I_{pa2}/I_{pc2}$
For $[\text{Cu}(\text{tmen})\text{Cl}_2]$ :										
25	+310	+440	375	130	1.1	-44	+92	24	136	0.26
50	+300	+454	377	154	1.1	-54	+94	20	148	0.24
100	+290	+472	381	182	1.2	-66	+102	18	168	0.23
200	+270	+488	379	218	1.3	-82	+118	18	200	0.23
300	+250	+502	376	252	1.4	-90	+126	18	216	0.22
400	+240	+510	375	270	1.5	-99	+129	15	229	0.22
For $[\text{Cu}(\text{tmen})\text{Br}_2]$ :										
25	+288	+396	342	108	1.5	-52	+84	16	136	0.40
-50	+280	+408	344	128	1.5	-52	+90	19	142	0.28
100	+275	+423	349	148	1.5	-53	+93	20	146	0.27
200	+258	+442	350	184	1.5	-53	+99	23	152	0.23
300	+254	+450	352	196	1.6	-53	+101	24	153	0.23
400	+250	+454	352	204	1.9	-54	+102	24	156	0.23

peak currents  $I_{pc1}$  and  $I_{pc2}$  differ markedly, the former being smaller in the case of  $[\text{Cu}(\text{tmen})\text{X}_2]$  complexes (Table 1 and Fig. 1), showing that the reduction processes  $c_1$  and  $c_2$  are not due to the stepwise one-electron transfer reactions of the initial electroactive complex  $[\text{Cu}(\text{tmen})\text{X}_2]$

in DMSO/0.1 M TBAP medium. This may be due to the presence of more than one complex species<sup>9</sup> in coordinating DMSO solvent. The peak current ratio,  $I_{pa2}/I_{pc2}$  for the second redox process is less than unity, showing that the electron-transfer reaction is followed by chemical re-

action<sup>7,9</sup> (EC mechanism). It should be mentioned that the formal potentials  $E^{0'}_{(1)}$  and  $E^{0'}_{(2)}$  of  $[\text{Cu}(\text{tmen})\text{X}_2]$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) differ by approximately 30 mV and 15 mV, respectively (Table 1).

### Experimental

Cyclic voltammograms (CVs) were obtained using BAS Electrochemical system-Model EPSILON (USA) having an electrochemical cell with a three electrode system and a personal computer for data storage and processing. An Ag/AgCl reference electrode ( $E^0 = +199$  mV vs NHE), a Pt wire as auxiliary counter electrode and Pt as a working electrode were employed for the electrochemical studies. All the cyclic voltammetry experiments were done in an inert atmosphere achieved by purging the solution with pure nitrogen for about 20 min. An inert atmosphere of nitrogen was also maintained over the cell solution during recording of the voltammograms. Experiments were performed at 25 °C.

$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{CuBr}_2 \cdot 2\text{H}_2\text{O}$ , tetramethylethylenediamine (tmen), TBAP and DMSO of high purity were purchased from Sigma-Aldrich Chemicals Pvt. Ltd.  $[\text{Cu}(\text{tmen})\text{X}_2]$  complexes were prepared according to literature procedures<sup>10(a,b)</sup> and their purity was checked from chemical analyses. Freshly prepared  $2 \times 10^{-3}$  M solutions of these complexes in DMSO containing 0.1 M TBAP were used for electrochemical studies.

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