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Electrochemical investigations on copper(II) complexes with quardidentate Schiff bases with O_2N_2 donor set

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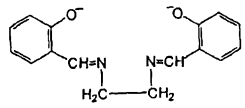
Abstract : The electrochemical investigations of Cu(salen), 1 and Cu(salophen), 2, where salen = *N,N'*-ethylenebis-(salicylaldiminato) dianion and salophen = *N,N'*-phenylenebis-(salicylaldiminato) dianion, have been carried out in dimethylformamide (DMF) containing 0.1 *M* sodium perchlorate ($NaClO_4$), 0.1 *M* tetrabutyl ammonium perchlorate (TBAP) and tetramethyl ammonium chloride (TMACl) as the supporting electrolyte using cyclic voltammetry at a platinum working electrode. Both these complexes show similar electrochemical behaviour under identical solution conditions. Complexes 1 and 2 revealed a diffusion-controlled, quasi-reversible one-electron transfer process ($Cu^{2+/+}$) at a more negative potential with $E^{0'}$ = -1235 to -970 mV vs SCE, suggesting a greater redox stability of these complexes. It is found that the reduction potential of 2 is more positive than that of 1, indicating easier reduction of the former. It is also observed that the redox potentials of both these complexes are influenced by the nature of the supporting electrolyte.

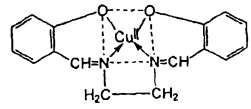
Keywords : Cyclic voltammetry, copper complexes, Schiff bases, electrochemistry.

Copper(II) complexes have found possible medicinal uses in the treatment of many diseases including cancer[1,2]. Salene complexes of transition metals attract considerable interest because of their physical and chemical (especially catalytic) properties[3]. Copper complexes have also been described as functional and structural models of several copper proteins, in a wide range of active centers, including superoxide dismutase Cu_2Zn_2SOD[4,5].

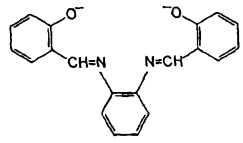
Mononuclear Cu^{II} complexes, [CuL] with quadridentate Schiff base chelating agents having extended π-delocalization, where L = salen and salophen (salen = *N,N'*-ethylenebis(salicylaldiminato) dianion, salophen = *N,N'*-*o*-phenylenebis(salicylaldiminato) dianion) selected for the present electrochemical investigation are neutral four-coordinate square planar chelate species[6,7] in which Cu^{II} is bound to two N and two O donor atoms as shown below.



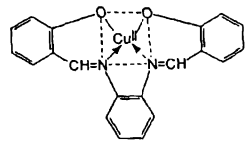
salen



Cu(salen), **1**



salophen



Cu(salophen), **2**

Results and discussion

The redox properties of 1 mM solutions of the mononuclear complexes, Cu(salen), **1** and Cu(salophen), **2** were examined in DMF containing 0.1 *M* $NaClO_4$, TBAP, or TMACl as a supporting electrolyte at a platinum working electrode in a scan rate range 25-300 mV s^{-1}. The CV results for these complexes are presented in Tables 1 and 2. Typical cyclic voltammograms for Cu(salophen), **2** in DMF containing 0.1 *M* $NaClO_4$ and 0.1 *M* TBAP are shown in Fig. 1a and b, respectively at a scan rate of 25 mV s^{-1}.

Fig. 1(a) shows that when the potential is swept from -0.75 to +0.75 V vs SCE and back to -0.75 V, practically no redox reaction is occurring in this potential region. However, a negative scan initiated at +0.75 to -1.4 V and back to +0.75 yielded a well-defined quasi-reversible[8,9] couple $Cu^{2+/+}$ at $E^{0'}$ = -1100 mV (E_{pc_1} = -1130 mV, E_{pa_1} = -1070 mV) with ΔE_p = 60 mV and I_{pa_1}/I_{pc_1} = 0.73) and an irreversible large anodic peak at $E_{pa_1'}$ = +90 mV, but its complementary cathodic wave did not appear even at higher scan rates up to 500 mV s^{-1}. This is characteristic of a dissolution process[10], as the

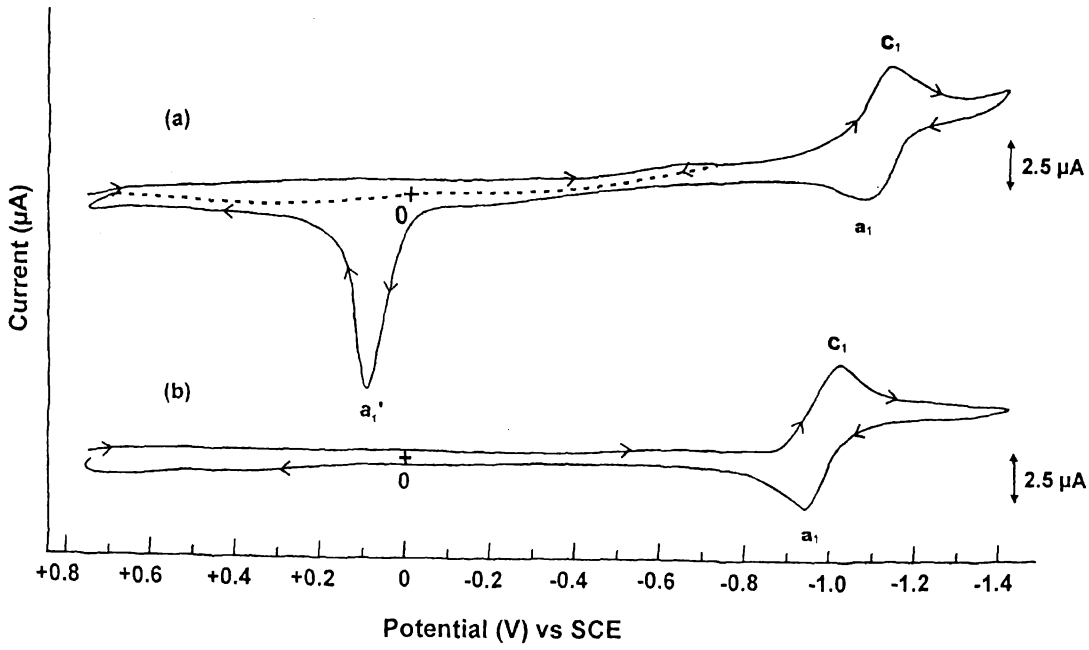


Fig. 1. Cyclic voltammograms of 1 mM of Cu(salophen) in DMF/0.1 *M* $NaClO_4$ (a) and in DMF/0.1 *M* TBAP (b) at a scan rate of 25 mV s^{-1}.

dissolution peak intensity is related to the amount of material deposited on electrode. It is noteworthy to mention that the anodic peak current $I_{pa_1'}$ decreases with increasing scan rate and that it completely disappeared at scan rate $\nu \geq 150$ mV s^{-1}. The plot of I_{pc_1} vs square root of the scan rate ($\nu^{1/2}$) gives a straight line passing through origin. Coulometry at -1.30 vs SCE has confirmed that the redox process involves a single electron per molecule of the complex. On the basis of these observations, it is concluded that the reduction of Cu^{II}(salophen) involves a diffusion-controlled quasi-reversible one-electron transfer followed by a slow chemical reaction[8,9]. Thus, the above electrode processes may be described by reactions (1) to (4) :

$$[Cu^{II}(salophen)] + e^- \underset{}{\overset{E}{\rightleftharpoons}} [Cu^{I}(salophen)]^- \qquad c_1/a_1 \quad (1)$$

$$2[Cu^{I}(salophen)]^- \xrightarrow[\text{CHEM}]{\text{slow}} Cu^0 + Cu^{II}(salophen) + salophen^{2-} \quad (2)$$

$$Cu^0 \xrightarrow{E} Cu^{2+} + 2e^- \qquad a_1' \quad (3)$$

$$Cu^{2+} + (salophen)^{2-} \xrightarrow[\text{CHEM}]{\text{fast}} [Cu^{II}(salophen)] \quad (4)$$

In each case the shapes of the CV waves for **1** and **2** are virtually the same under identical experimental conditions. The only significant difference between the electrochemical properties of these two complexes is that the complex **2** has reduction potentials more positive (or less negative) than the complex **1**. It is interesting to note that the anodic peak, a_1' is observed only in DMF/0.1 *M* $NaClO_4$ medium (Tables 1 and 2) indicating that reduction of both these complexes is presumably followed by a slow rearrangement of the product, reaction (**2**). However, the redox process of these complexes is found to be chemically reversible since $I_{pa_1}/I_{pc_1} = 1.0$, but electrochemically quasi-reversible ($\Delta E_p > 60$ mV) in DMF containing 0.1 *M* TBAP or TMACl as supporting electrolyte (Fig. 1(b)), which is further substantiated by the absence of anodic peak, a_1' ($Cu^0 \rightarrow Cu^{2+} + 2e^-$) (Tables 1 and 2).

A perusal of Tables 1 and 2 clearly shows that the redox potentials for both Cu(salen) and Cu(salophen) are influenced by the nature of the supporting electrolyte. It should be noted that the formal redox potential ($E^{o\prime}$) of both these complexes shifted anodically (i.e. towards less negative value) with increasing size of the cation of the supporting electrolyte : $NaClO_4 \rightarrow$ TMACl $\rightarrow$ TBAP (Tables 1 and 2).

Table 1. CV data for [Cu(salen)] in DMF containing different supporting electrolytes

Scan rate (mV s^{-1})	E_{pc_1} (mV)	E_{pa_1} (mV)	$E^{o\prime}$ (mV)	ΔE_p (mV)	$\frac{I_{pa_1}}{I_{pc_1}}$	$E_{pa_1\prime}$ (mV)	$I_{pa_1\prime}$ (μA)
In 0.1 *M* $NaClO_4$:							
25	-1180	-1120	-1150	60	0.80	+100	10.0
50	-1200	-1100	-1150	100	0.82	+100	4.0
100	-1210	-1090	-1150	120	0.82	+125	2.0
150	-1210	-1080	-1145	130	0.96	NA	
200	-1220	-1060	-1140	160	0.96	NA	
250	-1230	-1040	-1135	190	0.95	NA	
300	-1230	-1030	-1130	200	0.95	NA	
In 0.1 *M* TBAP :							
25	-1080	-1010	-1045	70	1.0		
50	-1090	-1000	-1045	90	1.0		
100	-1100	-990	-1045	110	1.0		
150	-1120	-980	-1050	140	1.0		
200	-1140	-960	-1050	180	1.0		
250	-1160	-940	-1050	220	0.98		
300	-1170	-930	-1050	240	0.98		
In 0.1 *M* TMACl :							
25	-1120	-1060	-1090	60	1.0		
50	-1120	-1050	-1085	70	1.0		
100	-1130	-1050	-1090	80	1.0		
150	-1140	-1050	-1095	90	1.0		
200	-1150	-1050	-1100	100	1.0		
250	-1150	-1040	-1095	110	0.96		
300	-1160	-1040	-1100	120	0.96		

$E^{o\prime} = 1/2\ (E_{pc_2} + E_{pa_2})$; $\Delta E_p = E_{pa} - E_{pc}$; NA, not appeared.

Table 2. CV data for [Cu(salophen)] in DMF containing different supporting electrolytes

Scan rate (mV s^{-1})	E_{pc_1} (mV)	E_{pa_1} (mV)	$E^{o\prime}$ (mV)	ΔE_p (mV)	$\frac{I_{pa_1}}{I_{pc_1}}$	$E_{pa_1\prime}$ (mV)	$I_{pa_1\prime}$ (μA)
In 0.1 *M* $NaClO_4$:							
25	-1130	-1070	-1100	60	0.73	+90	7.3
50	-1130	-1070	-1100	60	0.71	+100	3.9
100	-1140	-1060	-1100	80	0.70	+100	1.8
150	-1140	-1060	-1100	80	0.93	NA	
200	-1140	-1060	-1100	80	0.93	NA	
250	-1140	-1060	-1100	80	0.92	NA	
300	-1150	-1060	-1105	90	0.92	NA	
In 0.1 *M* TBAP :							
25	-1010	-930	-970	80	0.96		
50	-1020	-920	-970	100	0.96		
100	-1030	-910	-970	120	0.96		
150	-1050	-900	-975	150	0.96		
200	-1060	-900	-980	160	0.94		
250	-1070	-890	-980	180	0.94		
300	-1080	-880	-980	200	0.94		
In 0.1 *M* TMACl :							
25	-1080	-1030	-1055	50	1.0		
50	-1080	-1020	-1050	60	1.0		
100	-1090	-1020	-1055	70	1.0		
150	-1090	-1010	-1050	80	1.0		
200	-1090	-1000	-1045	90	1.0		
250	-1100	-1000	-1050	100	0.98		
300	-1100	-1000	-1050	100	0.98		

Furthermore, a comparison of formal redox potentials ($E^{o\prime}$) for **1** and **2** in DMF with given electrolyte reveals that $E^{o\prime}$ has shifted anodically by $\simeq$ 50 mV in $NaClO_4$ and TMACl and by 80 mV in TBAP for the latter complex **2** (Tables 1 and 2), suggesting that the reduction of salophen complex, **2** is easier than that of salen complex, **1**. This may be due to stronger σ- donor ability and/or poor π- acceptor ability[11] of salen as compared to that of salophen, causing larger electron density on the metal in complex **1** and thus its difficult reduction.

Experimental

All the experimental details have already been described in our previous papers[8].

Spectroscopic grade dimethylformamide (DMF), supplied by S.D. Fine Chemicals. Ltd. was used as such without further purification. Sodium perchlorate ($NaClO_4$) (E. Merck), tetrabutyl ammonium perchlorate (TBAP), and tetramethyl ammonium chloride (TMACl) were obtained from Fluka Chemika, Switzerland and were used as the supporting electrolytes in the present electrochemical investigation. Salicylaldehyde, ethylenediamine and *o*-phenylenediamine, copper acetate $Cu(CH_3COO)_2$ were purchased from Sigma-Aldrich Chemicals Private Limited.

The Schiff bases and their complexes with copper(II) were prepared according to literature procedures[6].

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