

# Correlation of Electrode Behaviour and Spectral Properties of Some Mixed-Ligand Complexes of Copper(II)

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Analyses of the electrode behaviour with regard to half-wave potential ' $E_{1/2}$ ', formal rate constant ' $K_1$ ', activation energy of rearrangement  $Q_e$  and activation energy of diffusion,  $Q_D$  *vis-a-vis* spectral behaviour of mixed-ligand complexes of Cu(II) with 2,2'-bipyridyl and 1,10-phenanthroline as primary ligands and some aliphatic, aromatic, amino acids and phenols as secondary ligands have been made. In aqueous potassium nitrate solution, the complexes containing bipyridyl as primary ligand give two-electron, single-step reduction wave while the complexes containing phenanthroline as primary ligand give two step electro-reduction wave at dme. All the systems are observed to be diffusion controlled and irreversible. A correlation of electrode behaviour with the spectral parameters has been attempted. It has been observed that the half-wave potential shifts towards more negative side as the ligand field shifts towards higher energy side. The rate constant shows a decreasing trend in conformity with this. A possible mechanism of electron transfer has been suggested on the basis of orientation of orbitals towards the electrode. The activation energy of diffusion shows a direct relationship with the energy difference between binary and ternary complexes in a particular series.

It is being increasingly realized that transition metal complexes behave characteristically at the dropping mercury electrode yielding information about the lowest vacant orbital. Considering that information about the highest occupied orbital may be gained from spectral behaviour of such a system, it should be possible to correlate redox properties of coordination compounds with their spectral properties. Following this idea, attempts<sup>1-3</sup> have been made in the last decade to seek correlation of the spectral characteristics *vis-a-vis* electrode behaviour of coordination compounds with some success. Work on mixed-ligand complexes, however, is very scanty.

In the work embodied in the present communication, such a correlation has been attempted by studying electrode behaviour of some mixed-ligand complexes of a biologically important transition metal like copper and important ligands such as 2, 2'-bipyridyl ( $C_8H_8N_2$ ) and 1, 10-phenanthroline ( $C_{12}H_8N_2$ ) as primary ligands and aliphatic acids, aromatic acids, amino acids and phenols as secondary ligands. Such mixed-ligand complexes are likely to be important as models for metallo-enzyme substrate complexes and also as components of the multi-metal-multi-ligand systems in biological fluids. The complexes studied are  $[Cu(bip)L]$  and  $[Cu(phen)L]$  in 1:1:1 and 1:2:1 ratio, where bip stands for 2, 2'-bipyridyl, phen stands for 1,10-phenanthroline and L stands for aliphatic acids [formic acid,  $HCOOH$ ; oxalic acid,  $(COOH)_2$ ; tartaric acid,  $(CH(OH)COOH)_2$ ; citric acid,  $(CH_2COOH)_2C(OH)COOH$ ; succinic acid,  $(CH_2COOH)_2$  abbreviated as (For), (Ox), (Tar), (Cit), (Suc) respectively], aromatic acids [benzoic acid,  $(C_6H_5COOH)$ ; phthalic acid,  $C_6H_4(COOH)_2$ ; salicylic acid,  $C_6H_4OH.COOH$ ; mandelic acid,

$C_6H_5CH(OH).COOH$ ; gallic acid,  $C_6H_2(OH)_3COOH$  abbreviated as (Ben), (Ph), (Sal), (Man), (Gal) respectively], amino acids [glycine,  $(NH_2CH_2COOH)$ ; valine,  $(CH_3)_2CHCH(NH_2)COOH$ ; serine  $HOCH_2CH(NH_2)COOH$ ; leucine  $(CH_3)_2CHCH_2CH(NH_2)COOH$  abbreviated as (Gly), (Val), (Ser), (Leu) respectively], and phenols [resorcinol,  $C_6H_4(OH)_2$  and catechol,  $C_6H_4(OH)_2$  abbreviated as (Res) and (Cat) respectively]. Spectral studies<sup>10-12</sup> on these complexes reveal that they are having distorted octahedral stereo-chemistry in water. A probable mechanism of electron transfer from the electrode to the complex depolarizer, based on the above correlation, has been attempted for these series of complexes.

Studies in uv region of these ternary complexes have also been made with a view to observe metal-ligand and ligand-ligand interaction. The polarographic behaviour has been compared with the charge transfer transitions.

## Experimental

Spectra of these complexes have been recorded on a Beckmann double beam with auto recording spectrophotometer Model 26, in the range of 400 to 900 nm for visible and 200 to 400 nm for uv regions.

Polarographic measurements have been made with a manual polarographic circuit recommended by Kolthoff and Lingane having Leeds and Northrup potentiometer and galvanometer assembly. All the potentials are measured against a Hume and Harris saturated calomel electrode (SCE). For the polarographic study, potassium nitrate of AnalaR grade has been used as a supporting electrolyte. Oxygen is removed from the solution with a stream

of oxygen-free nitrogen. Resistance of the system is measured by an ac wheatstone bridge. The resistance was between 700-800Ω. The characteristic of dme in aqueous medium (open circuit) has been determined for at least three heights. Result of one set is given below :

$$h=40 \text{ cm, } m=2.43 \text{ mgs}^{-1}, t=3.23 \text{ sec, } m^{2/3}t^{1/6} = 2.198 \text{ mg}^{2/3} \text{ sec}^{-1/2}.$$

All solutions are prepared in aqueous medium. 20 ml of total solution has been taken in the polarographic cell in each case.

**Results**

The polarographic characteristics of the systems studied here are described in detail elsewhere<sup>1,3</sup>. In 0.5M aqueous KNO<sub>3</sub> as supporting electrolyte, all these mixed-ligand complexes of bipyridyl produce single well-defined polarographic waves, except the complexes [Cu(bip)Gal], [Cu(bip)Leu] and [Cu(bip)-Cat] where double waves are observed. In the mixed ligand complexes of phenanthroline, double waves are obtained in every case. The nature of double wave can be explained on the basis of adsorption. All these electrode processes are found to be diffusion-controlled. The value of n, the number of electrons transferred, thus obtained from the Ilkovic equation was nearly equal to two for each of the bipyridyl mixed-ligand complexes except for the above three complexes as also the phenanthroline complexes where the value of n is lower. All the complexes are observed to undergo irreversible electroreduction under the present experimental conditions. Oldham and Parry's equation<sup>1,4</sup> has been used to calculate the formal rate constant K<sub>f</sub> and transfer coefficient value. The activation energy Q<sub>e</sub> and the activation energy of diffusion Q<sub>D</sub> have been calculated using the equation given by Vlček<sup>1,5</sup>.

The values of E<sub>1/2</sub>, K<sub>f</sub>, Q<sub>D</sub> and Q<sub>e</sub> for these systems are given in Tables 1, 2, 3 and 4.

All the mixed ligand complexes give one spectral band with ν<sub>max</sub> in the range of 600-700 nm as shown in Tables 1-4, for both the complexes of the type [Cu(bip)L] and [Cu(phen)L]. Data show the energy difference of the binary(1 : 1) and the ternary (1 : 1 : 1) and (1 : 2 : 1) complexes. Changes take place in the energy of ternary complexes according to their ligand-field strength. Perusal of data shows that in this series, complex [Cu(bip)Ox], [Cu(bip)Ben], [Cu(bip)Val] and [Cu(phen)Ox] give maximum absorption value (ν<sub>max</sub>). This leads to the conclusion that these secondary ligands (oxalic acid, benzoic acid and valine) have a very strong ligand-field strength. However, in case of complexes of the type (1 : 2 : 1), there is no marked energy difference in the binary (1 : 2) and ternary (1 : 2 : 1) complexes. The ν<sub>max</sub> values of ternary complexes [Cu(bip)Ox] and [Cu(phen)Ox] (1 : 2 : 1) have high energy values in comparison to the other ternary complexes. One may conclude that oxalic acid is a very strong ligand in comparison to the other ligands used which can affect the energy of the complex (1 : 2 : 1) while in others, energy is not affected by the addition of secondary ligand. Comparison of the polarographic and spectral data (visible) are given in Tables 1-4.

Spectral data of mixed ligand complexes of copper(II) in the uv range are given in Tables 5 and 6 including data on binary complexes [Cu(bip)] and [Cu(phen)] in 1 : 1 and of primary ligands alone.

Two bands are obtained in the case of bipyridyl and phenanthroline which further split in binary and ternary complexes.

TABLE 1—A CORRELATION OF SPECTRAL AND REDOX PROPERTIES OF COPPER : BIPYRIDYL WITH SECONDARY LIGANDS 1:1:1

Complex	E <sub>1/2</sub> V vs SCE	Formal Rate Constant "K <sub>f</sub> " 1 × 10 <sup>-4</sup> cm sec <sup>-1</sup>	ν <sub>max</sub> (cm <sup>-1</sup> )	Δν (cm <sup>-1</sup> )	Q <sub>D</sub> Kcal	Q <sub>e</sub> Kcal
Cu : Bipyridyl	-0.1065	1.557 × 10 <sup>-1</sup>	14285	0	3.25	6.72
Cu : bip : Formic acid	-0.0980	1.642	14285	0	2.32	5.82
Cu : bip : Oxalic acid	-0.1100	1.562	15625	-1340	3.82	5.52
Cu : bip : Tartaric acid	-0.0970	1.672	14925	-640	1.84	6.27
Cu : bip : Citric acid	-0.0920	1.795	14600	-315	1.74	5.56
Cu : bip : Succinic acid	-0.0920	1.748	14184	+101	1.52	7.12
Cu : bip : Benzoic acid	-0.1100	1.403	14700	-600	3.23	6.72
Cu : bip : Phthalic acid	-0.1000	1.516	14390	-105	2.14	5.70
Cu : bip : Salicylic acid	-0.0880	1.646	14490	-205	1.52	5.71
Cu : bip : Mandelic acid	-0.0900	1.566	14600	-315	1.82	5.82
Cu : bip : Gallic acid	-0.0530 } -0.2800 }	1.118 } 2.630 × 10 <sup>-1</sup> }	14285	0	2.32	
Cu : bip : Glycine	-0.1070	1.416	15640	-1355	6.8	9.79
Cu : bip : Valine	-0.1490	1.010	15837	-1505	7.8	9.88
Cu : bip : Serine	-0.1150	1.453	15790	-1552	8.5	10.23
Cu : bip : Leucine	-0.0105 } -0.3150 }	1.182 } 4.786 × 10 <sup>-1</sup> }	15267	-982	6.65	8.62
Cu : bip : Resorcinol	-0.0975	1.995	14285	0	2.10	5.73
Cu : bip : Catechol	-0.0880 } -0.3880 }	1.058 } 2.270 × 10 <sup>-1</sup> }	14184	+101	—	—

TABLE 2—A CORRELATION OF SPECTRAL AND REDOX PROPERTIES OF COPPER : BIPYRIDYL WITH SECONDARY LIGANDS 1:2:1

Complex	$E_{1/2}$ V vs. SCE	Formal Rate Constant "K <sub>f</sub> " $1 \times 10^{-4}$ cm sec <sup>-1</sup>	$\nu_{max}$ cm <sup>-1</sup>	$\Delta\nu$ cm <sup>-1</sup>	Activation energies	
					$Q_D$ Kcal	$Q_0$ Kcal
Cu : Bipyridyl	-0.2000	0.5679	13927	0	7.83	10.21
Cu : bip : Formic acid	-0.1420	1.5030	13927	0	7.00	9.21
Cu : bip : Oxalic acid	-0.2000	1.0920	15625	-1698	6.80	8.00
Cu : bip : Tartaric acid	-0.1730	1.0310	13927	0	7.32	10.12
Cu : bip : Citric acid	-0.1600	1.1530	13927	0	6.56	7.87
Cu : bip : Succinic acid	-0.1620	1.3850	13927	0	6.12	7.77
Cu : bip : Benzoic acid	-0.2000	0.7162	13700	+ 227	9.52	11.23
Cu : bip : Phthalic acid	-0.1600	1.3730	13800	+ 127	9.20	10.71
Cu : bip : Salicylic acid	-0.1360	1.5730	13700	+ 227	8.72	10.21
Cu : bip : Mandelic acid	-0.1440	4.5900	13940	- 13	8.51	9.23
Cu : bip : Gallic acid	-0.2120	1.0350	13800	+ 127	6.23	9.02
Cu : bip : Glycine	-0.2570	1.1140	13927	0	9.20	12.28
Cu : bip : Valine	-0.2650	1.2620	13927	0	9.70	12.56
Cu : bip : Serine	-0.2600	1.1680	13927	0	9.80	13.26
Cu : bip : Leucine	-0.2420	1.1690	13927	0	8.50	11.26
Cu : bip : Resorcinol	-0.1840	1.5320	13927	0	6.92	10.30
Cu : bip : Catechol	-0.1100 } -0.4050 }	0.9298 } 0.3710 }	13927	0	7.82	10.87

TABLE 3—A CORRELATION OF SPECTRAL AND REDOX PROPERTIES OF COPPER : PHENANTHROLINE WITH SECONDARY LIGANDS 1:1:1

Complex	$E_{1/2}$ V vs. SCE	Formal Rate Constant "K <sub>f</sub> " $1 \times 10^{-4}$ cm sec <sup>-1</sup>	$\nu_{max}$ cm <sup>-1</sup>	$\Delta\nu$ cm <sup>-1</sup>	Activation energies	
					$Q_D$ Kcal	$Q_0$ Kcal
Cu : Phenanthroline	+0.0120	0.7925	13927	0	4.20	7.65
Cu : phen : Formic acid	-0.3100	0.4298	14490	- 563	3.72	7.23
Cu : phen : Oxalic acid	+0.0020	1.0640	15625	-1698	5.32	9.12
Cu : phen : Tartaric acid	-0.1960	1.9630	15433	-1506	4.60	8.83
Cu : phen : Citric acid	+0.0100	1.1550	14925	- 998	4.12	8.78
Cu : phen : Succinic acid	-0.1670	1.2910	15151	-1224	3.29	8.12
Cu : phen : Benzoic acid	-0.0050	0.9183	15625	-1698	5.05	9.25
Cu : phen : Phthalic acid	-0.1918	1.3740	14285	- 358	5.24	9.92
Cu : phen : Salicylic acid	-0.0015	1.2290	14285	- 358	5.13	10.56
Cu : phen : Mandelic acid	-0.2085	1.0730	14285	- 358	5.31	10.23
Cu : phen : Gallic acid	0.0000	0.9629	13927	0	6.23	10.56
Cu : phen : Glycine	-0.1930	1.2210	16130	-2203	9.20	11.50
Cu : phen : Valine	-0.1960	1.0750	16390	-2463	9.85	12.67
Cu : phen : Serine	+0.0105	1.9630	16390	-2463	9.56	11.82
Cu : phen : Leucine	-0.1800	1.1790	16130	-2203	9.12	12.32
Cu : phen : Resorcinol	-0.1930	1.6900	15870	-1943	7.12	13.21
Cu : phen : Catechol	0.0000	1.2170	16130	-2203	7.84	14.04
	-0.1930	1.1030				
	-0.0050	2.1020				
	-0.2050	1.7020				
	-0.0900	0.2520				
	-0.3400	3.8230				
	-0.0015	0.7982				
	-0.2050	2.3790				
	-0.0080	0.4410				
	-0.1900	3.6040				
	-0.0045	4.1820				
	-0.2090	2.8790				
	-0.0020	0.4808				
	-0.2100	1.3320				
	+0.0035	1.2210				
	-0.1680	1.3030				
	+0.0090	1.0250				
	-0.1850					

TABLE 4—A CORRELATION OF SPECTRAL AND REDOX PROPERTIES OF COPPER : PHENANTHROLINE WITH SECONDARY LIGANDS 1:2:1

Complex	$E_{1/2}$ V vs SCE	Formal Rate Constant "K <sub>f</sub> " $1 \times 10^{-4}$ cm sec <sup>-1</sup>	$\nu_{max}$ cm <sup>-1</sup>	$\Delta\nu$ cm <sup>-1</sup>	Activation energies	
					Q <sub>D</sub> Kcal	Q <sub>o</sub> Kcal
Cu : Phenanthroline	+0.0180	2.1510	13927	0	6.80	10.90
Cu : phen : Formic acid	-0.3080	0.0755	13927	0	5.72	9.99
Cu : phen : Oxalic acid	+0.0065	1.8320	15151	-1224	6.21	10.97
Cu : phen : Tartaric acid	-0.3650	0.3850	13927	0	5.94	10.67
Cu : phen : Citric acid	+0.0015	1.9370	13927	0	5.50	9.23
Cu : phen : Succinic acid	-0.3750	0.2061	13927	0	5.50	9.45
Cu : phen : Benzoic acid	+0.0045	1.9369	13927	0	6.23	9.72
Cu : phen : Phthalic acid	-0.4200	0.3109	13927	0	7.88	10.84
Cu : phen : Salicylic acid	+0.0050	1.9560	13927	0	7.77	10.74
Cu : phen : Mandelic acid	-0.4360	0.3543	13927	0	7.99	10.47
Cu : phen : Gallic acid	0.0000	1.9560	13927	0	8.47	11.23
Cu : phen : Glycine	-0.4300	0.2291	13927	0	11.04	19.56
Cu : phen : Valine	-0.4000	0.2291	13927	0	11.47	18.23
Cu : phen : Serine	-0.0030	1.7970	14660	-733	10.25	17.14
Cu : phen : Leucine	-0.3600	0.2368	13927	0	11.23	16.21
Cu : phen : Resorcinol	-0.0060	1.9110	13927	0	8.20	18.40
Cu : phen : Catechol	-0.0120	1.7860	13927	0	9.20	
	-0.4650	0.3038				
	-0.0560	2.5840				
	-0.4905	0.1141				
	-0.0040	1.8660				
	-0.4500	0.4560				
	-0.0015	3.4100				
	-0.3880	0.8511				
	+0.0030	2.6000				
	-0.3915	0.6621				
	-0.0030	3.0140				
	-0.3630	0.1035				
	-0.0010	1.9190				
	-0.3900	0.1480				
	-0.0040	2.3090				
	-0.4500	0.2528				

TABLE 5—SPECTRAL DATA OF MIXED LIGAND COMPLEXES OF Cu(II) WITH BIPYRIDYL IN ULTRAVIOLET REGION

Secondary ligands	Complex	1:1:1 $\lambda_{max}$ (nm)		1:2:1 $\lambda_{max}$ (nm)	
		1st Peak	2nd Peak	1st Peak	2nd Peak
	Bipyridyl	176	228	276	228
	Cu : bip	296,306	216	294,306	218
Aliphatic acids	Cu : bip : Formic acid	294,304	234 (sh)	290,—	228
	Cu : bip : Oxalic acid	294,304	244	292,—	—
	Cu : bip : Tartaric acid	294,304	240 (sh)	292,304 (sh)	230
	Cu : bip : Citric acid	294,304	238	280,304 (sh)	228
	Cu : bip : Succinic acid	294,304	—	294,304	236 (sh)
	Cu : bip : Benzoic acid	294,304	218 (sh)	293,304	—
Aromatic acids	Cu : bip : Phthalic acid	294,304	200	293,304	230 (sh)
	Cu : bip : Salicylic acid	294,304	200	293,304	236 (sh)
	Cu : bip : Mandelic acid	294,304	200	293,304 (sh)	236 (sh)
	Cu : bip : Gallic acid	294,304	200	293,304	220
	Cu : bip : Glycine	294,304	234	—	—
Amino acids	Cu : bip : Valine	294,304	236	294,304	—
	Cu : bip : Serine	294,304	233	294,304	—
	Cu : bip : Leucine	294,304	234	294,304	—
Phenols	Cu : bip : Resorcinol	294,304	210	268 —	—
	Cu : bip : Catechol	294,304	214	276 —	—

TABLE 6—SPECTRAL DATA OF MIXED LIGAND COMPLEXES OF Cu(II) WITH PHENANTHROLINE IN ULTRA-VIOLET REGION

Secondary ligands	Complex	$\lambda_{max}$ (nm) 1:1:1		$\lambda_{max}$ (nm) 1:2:1	
		1st Peak	2nd Peak	1st Peak	2nd Peak
Aliphatic acids	Phenanthroline	258	220,—	—	—
	Cu : phen	268	218,198	264	219,197,—
	Cu : phen : Formic acid	266	218,—	266	218,197,—
	Cu : phen : Oxalic acid	266	218,184	265	218,198,—
	Cu : phen : Tartaric acid	266	218,196	264	218(sh),182
	Cu : phen : Citric acid	266	210,183	265	218,194,183
	Cu : phen : Succinic acid	266	210,196,184	265	218,194,183
Aromatic acids	Cu : phen : Benzoic acid	266	218,188	263	218,190
	Cu : phen : Phthalic acid	266	218,190	263	218,—
	Cu : phen : Salicylic acid	266	218,198	263	218,—
	Cu : phen : Mandelic acid	266	218,196,184	262	218,194,184
	Cu : phen : Gallic acid	266	218,200	261	218,194
Amino acids	Cu : phen : Glycine	266	216,198,—	265	218,197
	Cu : phen : Valine	266	218,198,183	266	218,197
	Cu : phen : Serine	266	218,196,182	265	218,197
	Cu : phen : Leucine	266	218,198,—	265	218,197
Phenols	Cu : phen : Resorcinol	266	—,190	266	216(sh),190
	Cu : phen : Catechol	266	—,192	266	218(sh),—

### Discussion

In the simple ligand field description of metal ion complexes, one is concerned with the effect of ligands on the energies of the d levels of metal ions. Since octahedral, square-planar and tetrahedral fields cause different splitting of the five d orbitals, geometry will have a pronounced effect upon the d-d transitions in a metal ion complex and spectral data for these transitions should provide information about the structure of complexes.

Copper complexes have a distorted octahedral structure in aqueous solution<sup>16</sup>, with four short-ligand bonds in one plane (XY) and two longer metal-ligand bonds lying along the Z axis above and below the plane. Such complexes give rise to one absorption band<sup>17</sup> in the visible region near 16000  $\text{cm}^{-1}$ . The relative order of these transitions will depend upon the extent of axial metal-ligand interaction.

In a six-coordinated complex of Cu(II) (distortion along Z direction) the nine d electrons are accommodated in different orbitals as follows :

$$(d_{xy})^2(d_{yz})^2(d_{zx})^2(\sigma_{xz}^*)^2\sigma_{x^2-y^2}^*$$

Postulating that the complex is oriented<sup>18</sup> at the electrode surface such that the square plane (XY-plane) is perpendicular to the electrode surface, the  $(\sigma_{x^2-y^2}^*)$  orbital as also the  $d_{xy}$  orbital point toward the electrode. The two electrons, needed for electro-reduction and coming from the electrode, shall be accommodated in the lowest lying vacant orbitals. The  $\sigma_{x^2-y^2}^*$  is incapable of receiving the incoming electrons due to its low electron affinity. Out of the two suitably oriented orbitals, namely  $d_{xy}$  and  $\sigma_{x^2-y^2}^*$ , the former is low lying and this must be vacated prior to the electron transfer. Under strong influence of the electrode field, two electrons are promoted to the next higher vacant orbitals. This promotion energy required for the process will naturally depend upon the energy

difference between the non-bonding  $T_{2g}$  orbitals and the antibonding  $E_g^*$  and  $A_{1g}^*$  orbitals and hence the ease of the reduction of the depolarizer may be correlated with the ligand field strength.

$E_{1/2}$  and  $\nu_{max}$  : For the sake of correlation of the redox properties of these complexes with their spectral behaviour, the polarographic characteristics

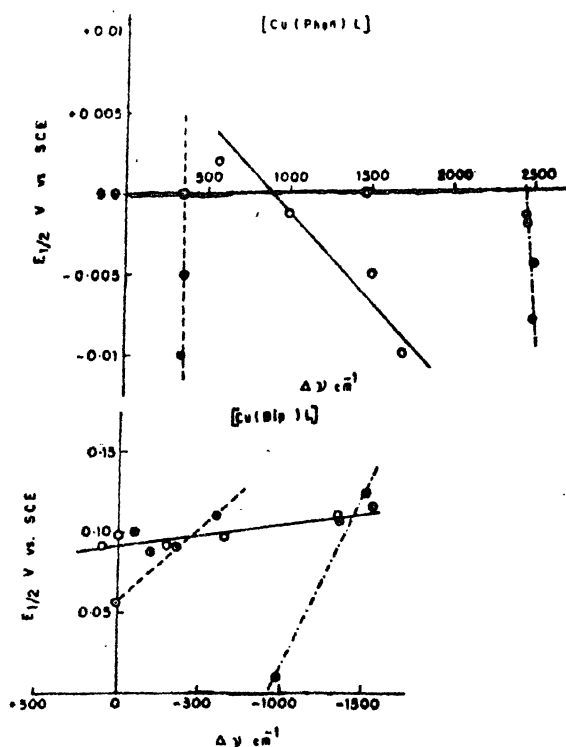


Fig. 1. Plot of  $E_{1/2}$  vs spectral shift of absorption band for Cu(II) complexes of the type  $[\text{Cu}(\text{bip})\text{L}]$  and  $[\text{Cu}(\text{p.h.a.})\text{L}]$ ; L = — aliphatic acids, - - - aromatic acids, - · - · - amino acids.

( $E_{1/2}$  and  $K_f$ ) have been tabulated along with the ligand field band of the complexes concerned in Tables 1-4. It will be seen that in the ternary complexes involving aliphatic acids, aromatic acids and phenols with the exception of those involving oxalic and benzoic acid, the half-wave potential shifts towards comparatively more positive values and the rate constant increases. This means that the ease of reduction increases. In case of ternary complexes involving amino acids, the  $E_{1/2}$  shifts towards more negative values while the value of rate constant decreases or the rate of electron transfer decreases. A further observation is that the ease of reduction as evidenced by  $E_{1/2}$  values also decreases with increasing ligand field-strength. A plot of half-wave potentials against the difference of the energy of the ternary complex and the parent binary complex gives a straight line (Fig. 1) for this series of complexes lending support to the above statement. Vlček<sup>1</sup> made similar observations in case of  $\text{Fe}(\text{phen})_2\text{X}_3$ ,  $\text{Fe}(\text{phen})_2\text{X}_2$  series,  $\text{NiL}_2^-$ ,  $\text{NiL}_3^-$  series and for cobalt and chromium complexes.

Reduction is regarded as comprising the acceptance of an electron into the lowest unoccupied, or singly occupied orbital of the depolarizer<sup>19,20</sup>. For reduction process, the rate and mechanism of the overall process will be dictated by the localization and energy of the lowest orbital. If the orbital in question has a high electron affinity, it may be possible for depolarizer particle to react directly with the electrode with only slight changes in configuration. A rearrangement will be necessary if the orbital has a low electron affinity since direct reduction in this instance will require a very large negative applied potential. The complexes of these series of the type  $[\text{Cu}(\text{bip})\text{L}]$  and  $[\text{Cu}(\text{phen})\text{L}]$  have confirmed essential correctness of the foregoing arguments. In such complexes, the lowest unoccupied orbital is an antibonding  $e_g^*$  orbital of very low electron affinity (much lower than that of the  $T_{2g}$  orbitals) so that direct reaction with the electrode is impossible. A configuration change, to give a structure capable of direct reaction with the electrode, must therefore take place whose energy may be regarded as a function of the difference between the ground and excited states i.e. the energy of the transition state depends on the ligand field strength of the complex.

A perusal of data on  $\text{Cu}(\text{II})$  phenanthroline series (Tables 3 and 4) of mixed ligand complexes shows that it does not confirm fully to the conclusion arrived at for the corresponding bipyridyl series of mixed-ligand complexes of  $\text{Cu}(\text{II})$ . In fact, the ease of reduction seems to be a composite of several structure and non-structural factors<sup>21</sup>. At least one factor which may cause this difference in behavioural pattern is prominently the delicate balance between two opposing forces of  $\sigma$  and  $\pi$  donation character of the ligands. The back bonding may reduce the electron density on the metal ion and thus facilitate the electron transfer and hence easier reduction of the depolarizer. The  $\pi$ -bond character of phenanthroline is much greater

compared to that of the bipyridyl as a ligand and hence flow of electron density from the filled metal orbitals into the  $\pi^*$  antibonding orbitals of the aromatic ring system of phenanthroline is much more facile.

$Q_D$  and  $\nu_{max}$ : An important condition governing all electrode processes follows from the Frank-Condon principle which states that electron transfer process takes place much more rapidly than configurational changes. Electron transfer may thus be regarded as occurring adiabatically and with negligible activation energy<sup>22</sup>. It follows that the electronic states of the reactants (electrode and depolarizer) must be equal before electron transfer takes place, i.e. the energy necessary to abstract one electron from its initial position must be exactly supplied by the energy with which it is bound in its final position in the depolarizer. If this occurs, the electronic energy of the depolarizer is changed prior to reduction and the formation of the transition state requires considerable energy (rearrangement activation energy) which forms a large part of the total activation energy for the process as a whole. Estimated values of  $Q_D$  give a straight line relationship with  $\Delta\nu$  (Fig. 2) supporting the above statement. Vlček made similar observations with following series of complexes:  $\text{Co}(\text{NH}_3)_6\text{X}^{n+}$ ,  $\text{Co}(\text{CN})_6\text{X}^{n-}$ ,  $\text{CoOX}_n(\text{am})_m^n$ ,  $\text{Rh}(\text{NH}_3)_6\text{X}^{n+}$ ,  $\text{Co}(\text{NH}_3)_4\text{X}_2^{n+}$ ,  $\text{Cr}(\text{NH}_3)_6\text{X}^{n+}$ ,  $\text{CrOX}_n(\text{am})_m^n$  and  $\text{Rh}(\text{en})_3\text{X}_2^{n+}$ .

*UV spectra*: In the uv region two transitions are observed for primary ligands alone indicating  $\pi\pi^*$  and  $n\pi^*$  transitions according to Robert D. McAlpine<sup>23</sup>. In the present conditions, bipyridyl absorbs at 228 nm and 276 nm indicating the transition  $\pi\pi^*$  and  $n\pi^*$ , respectively. The  $\pi\pi^*$  transition seems to be stronger than the  $n\pi^*$  transition. A similar spectra have been obtained in the case of phenanthroline molecule i.e. phenanthroline molecule absorbs at 220 nm and 258 nm indicating the  $\pi\pi^*$  and  $n\pi^*$  transitions, respectively. But in this case the  $\pi\pi^*$  transition seems to be stronger than the  $n\pi^*$  transition.

In the spectra of binary complexes,  $[\text{Cu}(\text{bip})]$  1:1 and 1:2, there is a bathochromic shift in  $\pi\pi^*$  transition and also splitting (296 nm and 306 nm) is observed on complexation due to the possibility of metal-ligand interaction. Back donation from metal filled-orbitals to vacant low-lying anti-bonding  $\pi^*$  orbitals of bipyridyl cause hypsochromic shift in  $\pi\pi^*$  (218 nm) transition. But in the binary complex,  $\pi\pi^*$  transition seems to be stronger than  $n\pi^*$  transition. In case of phenanthroline complexes, on complexation with metal ion bathochromic shift in  $\pi\pi^*$  (267 nm) and hypsochromic shift and splitting in  $\pi\pi^*$  (218 nm, 197 nm) are observed. In the case of 1:1 complex,  $\pi\pi^*$  transition is not split properly but a shoulder is observed at 218 nm. In the 1:2 complex, split band at 218 nm is stronger than the band at 197 nm.

A very small bathochromic shift is observed in  $\pi\pi^*$  transition on addition of secondary ligands

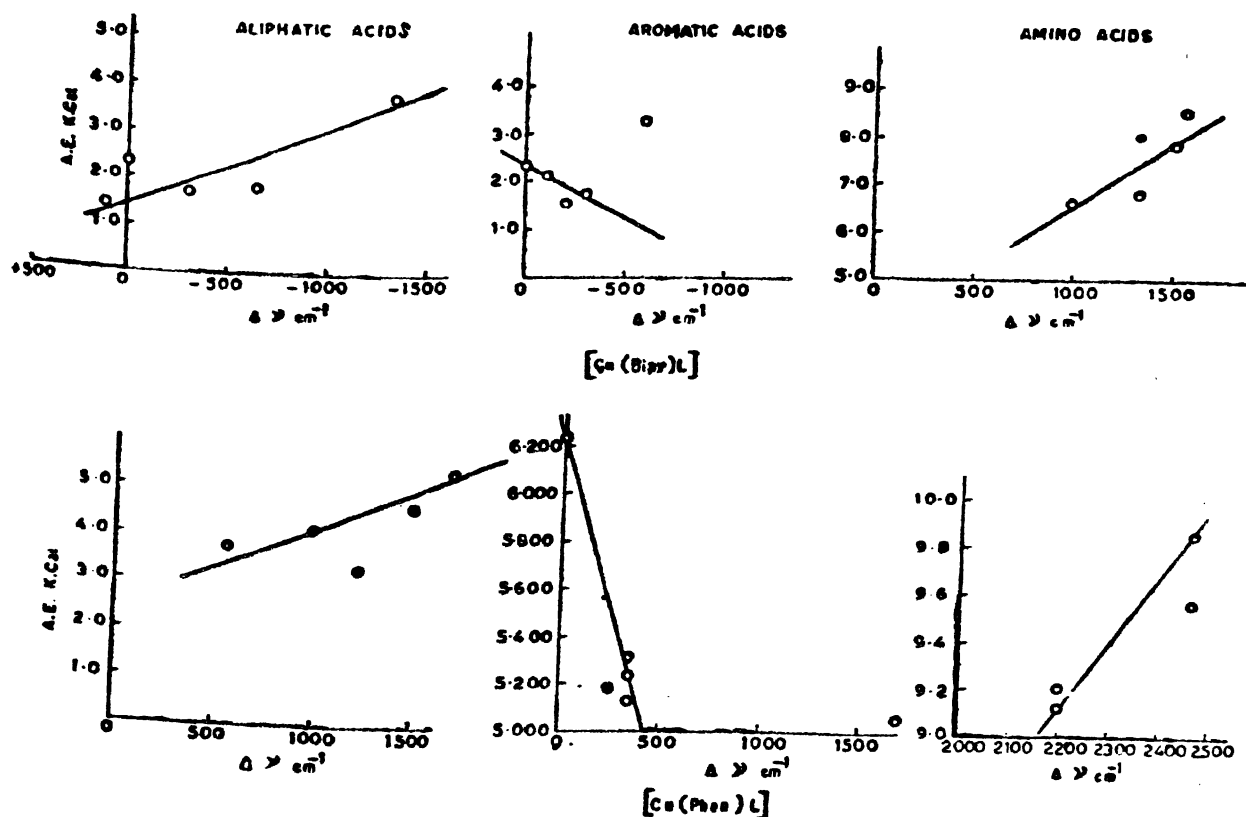


Fig. 2. Dependence of activation energy of the electrode process upon the absorption band shift of complexes  $[\text{Cu}(\text{bip})\text{L}]$  and  $[\text{Cu}(\text{phen})\text{L}]$ .

in 1 : 1 : 1 mixed ligand complexes. In aliphatic series, peak of  $\pi\pi^*$  is obtained only in the case of  $[\text{Cu}(\text{bip})\text{Ox}]$  and  $[\text{Cu}(\text{bip})\text{Cit}]$  complexes. A shoulder is obtained in  $[\text{Cu}(\text{bip})\text{Tar}]$  complexes and no  $\pi\pi^*$  band is observed in the case of  $[\text{Cu}(\text{bip})\text{Suc}]$  complex. In amino acid series, shoulder of  $\pi\pi^*$  band is observed. Further observation shows that the presence of secondary ligands possessing a ring e.g. phenols cause further hypsochromic shift in  $\pi\pi^*$  band. A shoulder is obtained in the case of  $[\text{Cu}(\text{bip})\text{Ben}]$  complex. But in other complexes of aromatic acid series, a hypsochromic shift in  $\pi\pi^*$  band (200 nm) is observed perhaps, due to the possibility of ligand-ligand interaction. But in the case of aliphatic acids and amino acids, there is no possibility of  $\pi\pi^*$  interaction due to the absence of ring. In the case of 1 : 2 : 1 ternary complexes of  $[\text{Cu}(\text{bip})\text{L}]$  the splitting of  $\pi\pi^*$  band (296 nm and 306 nm) is observed in each complex but there is no  $\pi\pi^*$  band except in the case of  $[\text{Cu}(\text{bip})\text{Tar}]$ ,  $[\text{Cu}(\text{bip})\text{Cit}]$  and  $[\text{Cu}(\text{bip})\text{Gal}]$ . In the case of phenanthroline mixed-ligand complexes 1 : 1 : 1 and 1 : 2 : 1, the presence of secondary ligands (possessing ring) causes further hypsochromic shift in  $\pi\pi^*$  indicating ligand-ligand interaction, while in the case of aliphatic and amino acids there is no further split showing their inability for ligand-ligand interaction. Possibility of metal-metal interaction is not indicated.

On comparing the data on the complexes of bipyridyl and phenanthroline with Cu(II), opposite

results are observed. In bipyridyl, splitting is obtained in  $\pi\pi^*$  while in the case of phenanthroline  $\pi\pi^*$  splitting is observed. This behaviour can be explained on the basis of the structure of these ligands. The nature of phenanthroline can be attributed to the hindered rotation along the fused axis while in the case of bipyridyl, due to the free rotation along joining axis, the splitting of  $\pi\pi^*$  transition is observed. In the case of the mixed-ligand complexes of phenanthroline, the effect of secondary ligand is appreciable indicating that the phenanthroline is a better ligand than bipyridyl which is also confirmed by the polarographic studies of these complexes.

The results obtained on comparing the spectral characteristics with the polarographic behaviour are not very revealing. Plots of  $E_{\frac{1}{2}}$  vs  $\nu$  are given in

Fig. 3. A linear relationship is obtained only for the complexes  $[\text{Cu}(\text{bip})\text{aliphatic acids}]$ ,  $[\text{Cu}(\text{bip})\text{aromatic acids}]$  and  $[\text{Cu}(\text{phen})\text{aromatic acids}]$ . This relationship is not very surprising. A linear relationship between  $E_{\frac{1}{2}}$  and  $\nu$  shall be obtained

only when the complexes in the series fulfil a number of important conditions like (i) the interatomic distances in the reduced and oxidised forms do not differ much, (ii) the donor or acceptor part of the molecule remains almost the same throughout the series, (iii) the change of solvation energy accompanying the redox transition and the change of

[Ck : Bip] 1 : 1 With aliphatic acids (A) and aromatic acids (B)

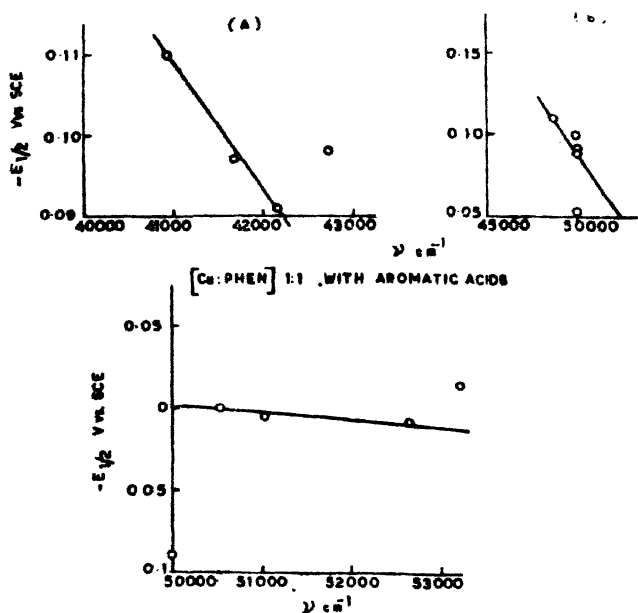


Fig. 3. Dependence of half wave potential on spectral studies (charge transfer spectra).

entropy for the redox couple remain constant throughout the series<sup>1</sup>.

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