

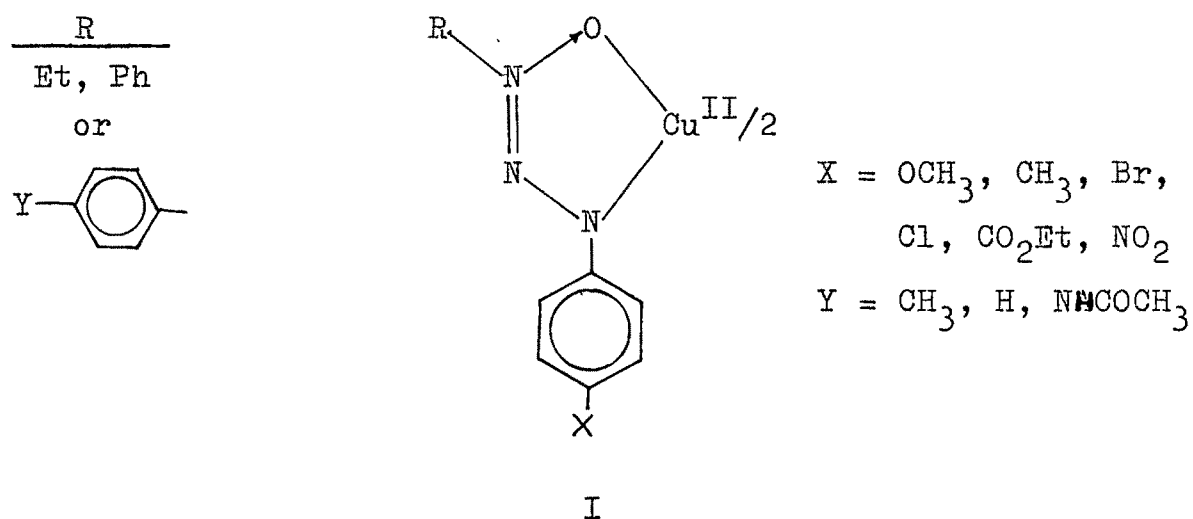
CHAPTER III

ELECTRON TRANSFER IN GROUPS OF COPPER  
TRIAZENE 1-OXIDES

## CHAPTER III

### ELECTRON TRANSFER IN GROUPS OF COPPER TRIAZENE 1-OXIDES

Abstract: The electron transfer properties of four coordinated grossly planar bis-copper(II) triazene 1-oxides of type  $\text{CuT}_2$  (I) are described.

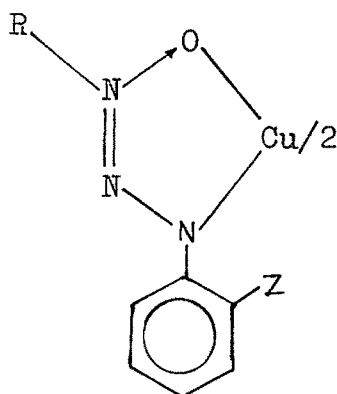


An one-electron process  $[\text{CuT}_2] + e^- \rightleftharpoons [\text{CuT}_2]^-$  is identified at mercury or platinum working electrode. At mercury electrode, the metal-centered reduction is nearly reversible in dimethylformamide and acetonitrile but quasireversible in dichloromethane. At platinum electrode, in general, the electrode reaction becomes quasireversible.

The  $E_{298}^0$  values are sensitive to R and X. The  $E_{298}^0$  values (vs SCE) fall in the ranges: -0.46 to -0.84V (R=Et) and -0.37 to -0.66V (R=Ph). The  $E_{298}^0$  values linearly correlate with Hammett substituent constants. The  $\rho$  values are: 0.17V (R=Et) and 0.13V (R=Ph).

The electron transfer properties of ortho substituted  $CuT_2$  complexes and cis planar copper(II) complexes of tetradentate ligands are also studied. Each of these complexes exhibit an one-electron copper(II)-copper(I) couple.

In ortho substituted complexes (II) the  $E_{298}^0$  values are



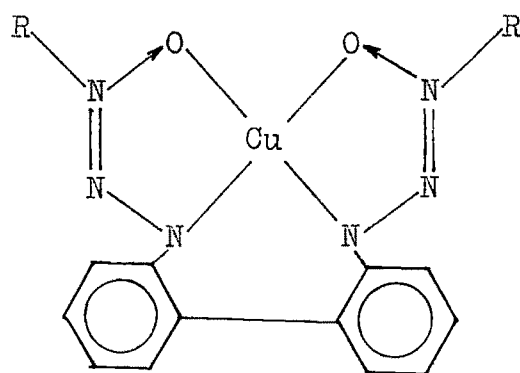
R = Et

Z = OCH<sub>3</sub>, CH<sub>3</sub>, Cl

II

more negative (-0.81 to -0.91V) than that of type I complexes corresponding to a higher value of the ortho substituent constants. The  $E_{298}^0$  values correlate linearly with Taft ortho substituent constants,  $\sigma_o$  ( $\rho = 0.10V$ ).

Complexes of tetradentate ligands (III) have the most



R = Et, Ph

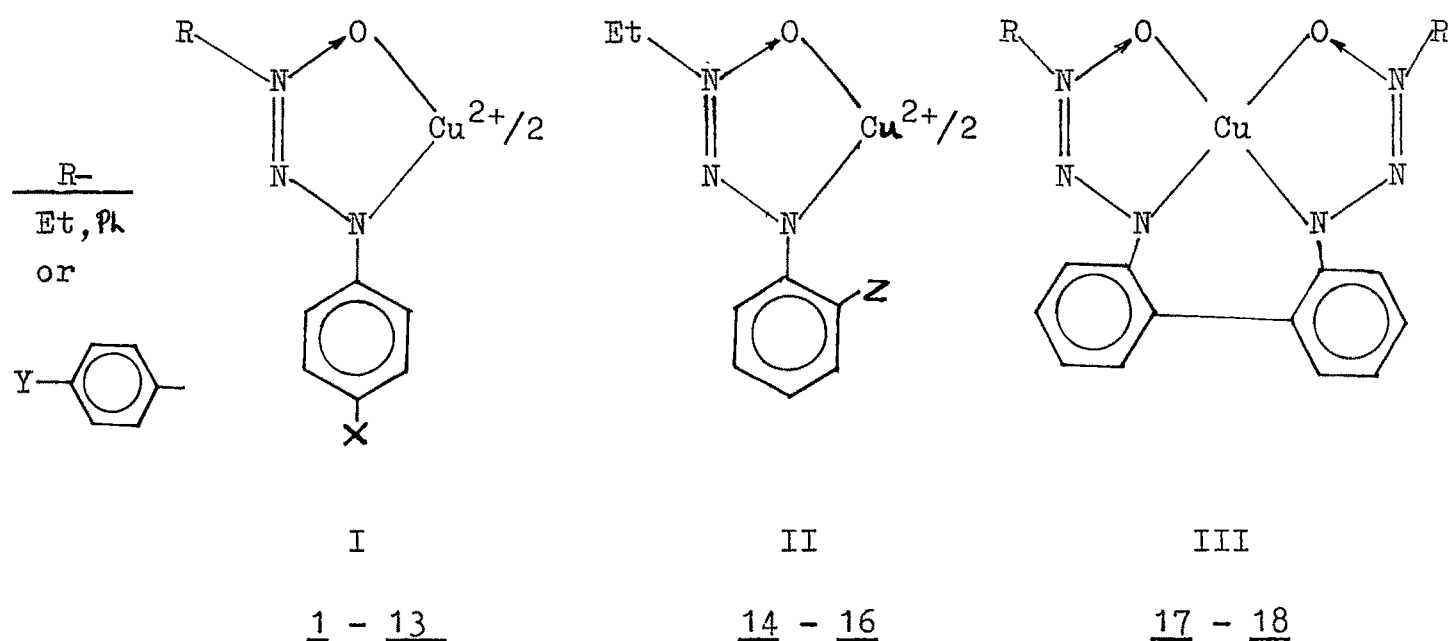
III

negative  $E_{298}^0$  values (-1.07V, R = Et and -0.86V, R = Ph). This could be partly due to ligand fixedness with relation to copper(I) stereochemistry.

These copper(II) complexes display a ligand field band at  $\sim 900$  nm. The position of the band maxima shifts with the substituents.

### III.1 INTRODUCTION

The work described in the last chapter demonstrates that the substituents present at the remote site of the ligand measurably affect the metal-centered redox potentials in pseudooctahedral iron(III) and cobalt(III) triazene 1-oxides. In this chapter, we investigate the corresponding electron transfer properties of a large group of four coordinated grossly planar bis copper(II) triazene 1-oxides using cyclic voltammetry. Species studied are of type I, II and III. Of these I with para-substituents is



analogous to  $\text{FeT}_3$  and  $\text{CoT}_3$  of last chapter. In II an ortho-substituent is present and a study of the ortho-substituent effect is made with II — a problem not considered for iron and cobalt complexes. Lastly in III, the ligand is tetradentate and this allows us to make an

assessment of the effect of augmented chelate effect and ligand fixedness on redox thermodynamics. Unlike  $\text{FeT}_3$  and  $\text{CoT}_3$ , the copper(II) complexes display a ligand field transition in the visible region. The position of the band maxima for this transition shifts with the substituent.

### III.2 RESULTS AND DISCUSSION

#### A. Syntheses and Serial Number of Complexes

The general method of synthesis of triazene 1-oxides is already described in Chapter II. The complexes were synthesized<sup>1-4</sup> by direct reaction of the ligand with copper acetate in ethanolic solution. The purity of each complex was checked by elemental analysis (vide Experimental Section). For the sake of identification, a serial number is given to each of such complex as in the last chapter (Table III.1).

#### B. The Complexes and their Structure

This topic was already considered in Chapter I. For ready reference, salient features are recapitulated.

The magnetic moments of I, II and III lie<sup>2-4</sup> in the range 1.8-1.9 B.M. The  $\text{CuT}_2$  species, 1-13, have trans planar  $\text{MN}_2\text{O}_2$  coordination environment<sup>2,3</sup> as in analogous palladium<sup>5</sup> and nickel<sup>6</sup> complexes. The gross properties of II are akin to those of I and

Table III.1  
Serial Numbers of Complexes

	<u>Substituents</u>		Serial Number
	X or Z	R or Y	
<u>Complexes of</u> <u>type I</u>	OMe	Et	<u>1</u>
	Me	Et	<u>2</u>
	H	Et	<u>3</u>
	Br	Et	<u>4</u>
	Cl	Et	<u>5</u>
	CO <sub>2</sub> Et	Et	<u>6</u>
	NO <sub>2</sub>	Et	<u>7</u>
	OMe	Ph	<u>8</u>
	Me	Ph	<u>9</u>
	H	Ph	<u>10a</u>
	H	p-MeC <sub>6</sub> H <sub>4</sub>	<u>10b</u>
	H	p-MeCONHC <sub>6</sub> H <sub>4</sub>	<u>10c</u>
	Cl	Ph	<u>11</u>
CO <sub>2</sub> Et	Ph	<u>12</u>	
NO <sub>2</sub>	Ph	<u>13</u>	
<u>Complexes of</u> <u>type II</u>	OMe	Et	<u>14</u>
	Me	Et	<u>15</u>
	Cl	Et	<u>16</u>
<u>Complexes of</u> <u>type III</u>	-	Et	<u>17</u>
	-	Ph	<u>18</u>

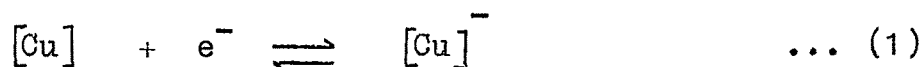
they are also given the trans planar geometry. In III, the ligand is tetradentate and as elaborated in Chapter I, this enforces both planarity and cis geometry for the  $\text{CuN}_2\text{O}_2$  coordination sphere<sup>4</sup>.

### C. Electrochemical Studies

All complexes display electrochemical response in the negative side of saturated calomel electrode (SCE). They were studied with an extensive use of cyclic voltammetry.

#### (a) The Electrode Reaction and Formal Potential

The complexes were studied primarily in dimethylformamide (DMF) because of lack of solubility in acetonitrile (AN). In the potential range  $-0.37\text{V}$  to  $-1.07\text{V}$  vs SCE all complexes exhibit one cathodic and a corresponding anodic response at HMDE with  $i_{pc}/i_{pa} \sim 1$ . Both peak currents increase linearly with the square root of the scan rate ( $v$ ). The current function  $i_p^{-1/2}$  is constant within the experimental error. Representative examples are in Fig. III.1. Electrochemical data at 298K are collected in Table III.2. At HMDE the peak to peak separations  $\Delta E_p$  generally lie in the range 60-70 mV for the majority of complexes, suggesting the presence of a nearly reversible one-electron process (1)



where  $[\text{Cu}]$  stands for I, II or III.



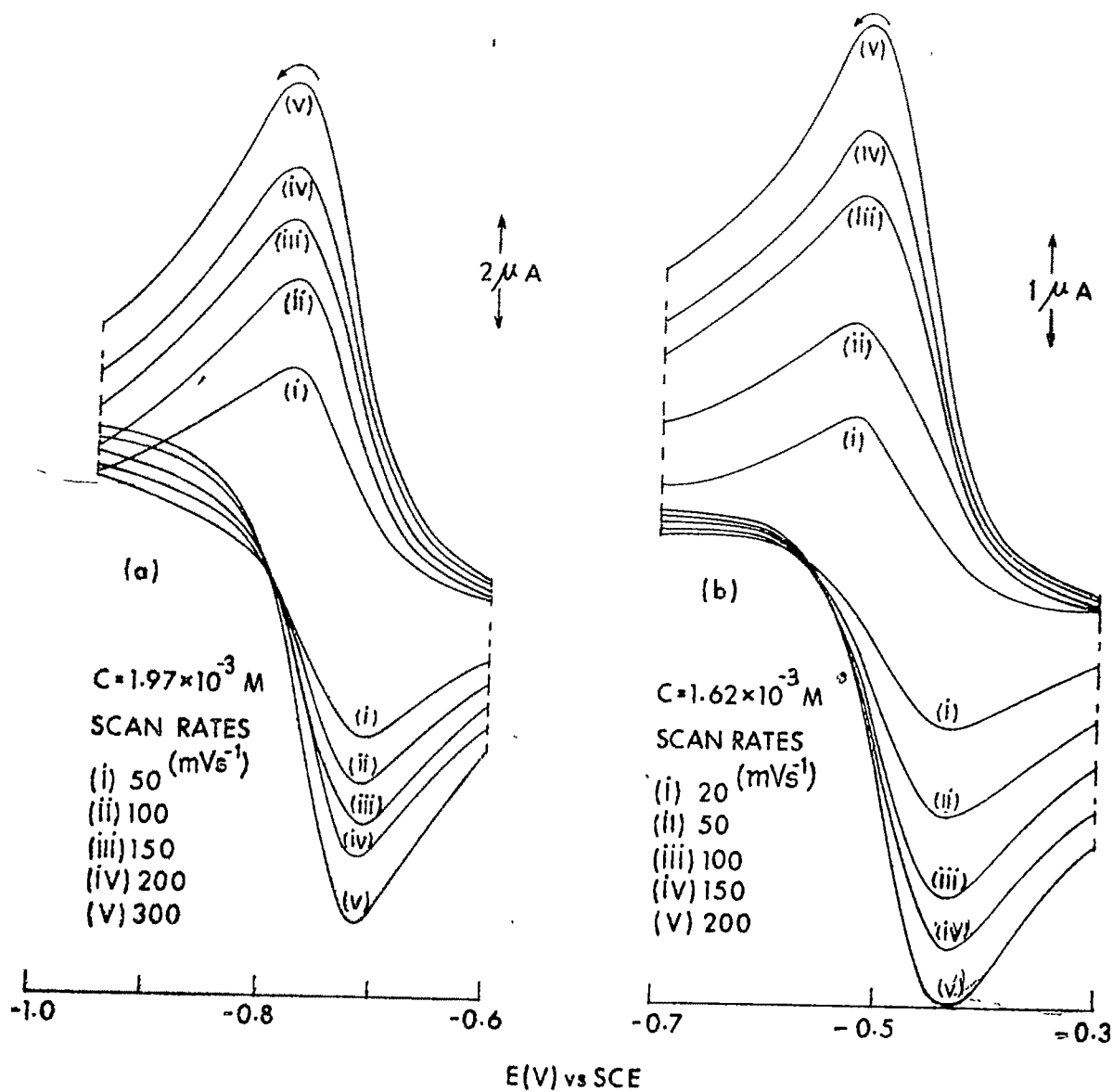


FIG. III.1. CYCLIC VOLTAMMOGRAMS OF (a) 3 AND (b) 12 IN DMF AT HMDÉ

Table III.2Electrochemical Data<sup>a-c</sup> at 298K using HMDE in Dimethylformamide

Serial Number	$v(\text{mVs}^{-1})$	$E_{pc}(\text{V})$	$E_{pa}(\text{V})$	$E_{298}^{\circ}(\text{V})$	$\Delta E_p(\text{mV})$
<u>1</u>	50	-0.940	-0.740	-0.84	200
	100	-0.962	-0.718	-0.84	244
<u>2</u>	50	-0.812	-0.747	-0.78	65
	100	-0.825	-0.755	-0.79	70
<u>3</u>	50	-0.782	-0.717	-0.75	65
	100	-0.782	-0.717	-0.75	65
<u>4</u>	50	-0.725	-0.655	-0.69	70
	100	-0.725	-0.655	-0.69	70
<u>5</u>	50	-0.737	-0.662	-0.70	75
	100	-0.737	-0.662	-0.70	75
<u>6</u>	50	-0.645	-0.575	-0.61	70
	100	-0.647	-0.570	-0.61	77
<u>7</u>	50	-0.495	-0.425	-0.46	70
	100	-0.495	-0.425	-0.46	70
<u>8</u>	50	-0.695	-0.625	-0.66	70
	100	-0.700	-0.620	-0.66	80
<u>9</u>	50	-0.662	-0.597	-0.63	65
	100	-0.667	-0.592	-0.63	75
<u>10a</u>	50	-0.630	-0.570	-0.60	60
	100	-0.630	-0.570	-0.60	60
<u>10b</u>	50	-0.632	-0.567	-0.60	65
	100	-0.632	-0.567	-0.60	65

Table III.2(contd)

Serial Number	$v(\text{mVs}^{-1})$	$E_{pc}(\text{V})$	$E_{pa}(\text{V})$	$E_{298}^{\circ}(\text{V})$	$\Delta E_p(\text{mV})$
<u>10c</u>	50	-0.642	-0.577	-0.61	65
	100	-0.642	-0.577	-0.61	65
<u>11</u>	50	-0.590	-0.530	-0.56	60
	100	-0.594	-0.526	-0.56	68
<u>12</u>	50	-0.540	-0.440	-0.49	100
	100	-0.540	-0.440	-0.49	100
<u>13</u>	50	-0.405	-0.335	-0.37	70
<u>14</u>	50	-0.955	-0.865	-0.91	90
<u>15</u>	50	-0.885	-0.812	-0.85	73
	100	-0.887	-0.812	-0.85	75
<u>16</u>	50	-0.850	-0.770	-0.81	80
	100	-0.852	-0.767	-0.81	85
<u>17</u>	50	-1.110	-1.030	-1.07	80
<u>18</u>	50	-0.895	-0.825	-0.86	70

<sup>a</sup> Meaning of units and symbols are the same as in text.

<sup>b</sup> Supporting electrolyte TEAP (0.1M).

<sup>c</sup> Coulometric data: 11, 6.55 mg reduced at -0.8V; Calcd.  $Q = 1.14$ ; Found  $Q = 1.24$ ; 13, 7.93 mg reduced at -0.57V; Calcd.  $Q = 1.10$ ; Found  $Q = 1.15$ .

The one-electron involvement was confirmed by constant potential coulometric reduction studies in selected cases (Table III.2).

For selected copper(II) complexes the electrode reaction (1) was also studied using platinum (Pt) as the working electrode. The peak potentials  $E_{pc}$  and  $E_{pa}$  get widely separated, i.e., the electrode reaction becomes quasireversible. The cyclic voltammetric data at Pt electrode are presented in Table III.3 and representative voltammograms are exhibited in Fig. III.2.

The formal potentials  $E_{298}^0$  for couple (1) were calculated as the average of the cathodic and anodic peak potentials eq (2) and are collected in Tables III.2, 3 and 4.

$$E_{298}^0 = \frac{1}{2} (E_{pc} + E_{pa}) \quad \dots (2)$$

Selected complexes were studied both in DMF and AN or dichloromethane (DCM). The complex 5 was examined in all the three solvents. The solvent dependence of the electrochemical response is discussed separately.

#### (b) Confirmation of Metal Reduction

The  $1e^-$  reduction in couple (1) is of the metal centre as is evidenced from the following observations. The electrochemical response of the free ligands are already discussed in Chapter II. The irreversible reduction appears at lower potentials.

Table III.3

Cyclic Voltammetric Data<sup>a,b</sup> at 298K using Pt Electrode in  
Dimethylformamide

Serial Number	$v(\text{mVs}^{-1})$	$E_{pc}(\text{V})$	$E_{pa}(\text{V})$	$E_{298}^{\circ}(\text{V})$	$\Delta E_p(\text{mV})$
<u>2</u>	50	-0.912	-0.687	-0.80	225
	100	-0.952	-0.667	-0.81	285
<u>3</u>	50	-0.910	-0.630	-0.77	280
<u>5</u>	50	-0.910	-0.550	-0.73	360
<u>9</u>	50	-0.835	-0.485	-0.66	350
<u>10a</u>	50	-0.722	-0.497	-0.61	225
	100	-0.747	-0.472	-0.61	275
<u>10b</u>	50	-0.785	-0.475	-0.63	310
	100	-0.837	-0.462	-0.65	375
<u>10c</u>	50	-0.645	-0.555	-0.60	90
	100	-0.652	-0.547	-0.60	105
<u>11</u>	50	-0.842	-0.337	-0.59	505

<sup>a</sup> Meaning of units and symbols are the same as in text.

<sup>b</sup> Supporting electrolyte TEAP (0.1M).

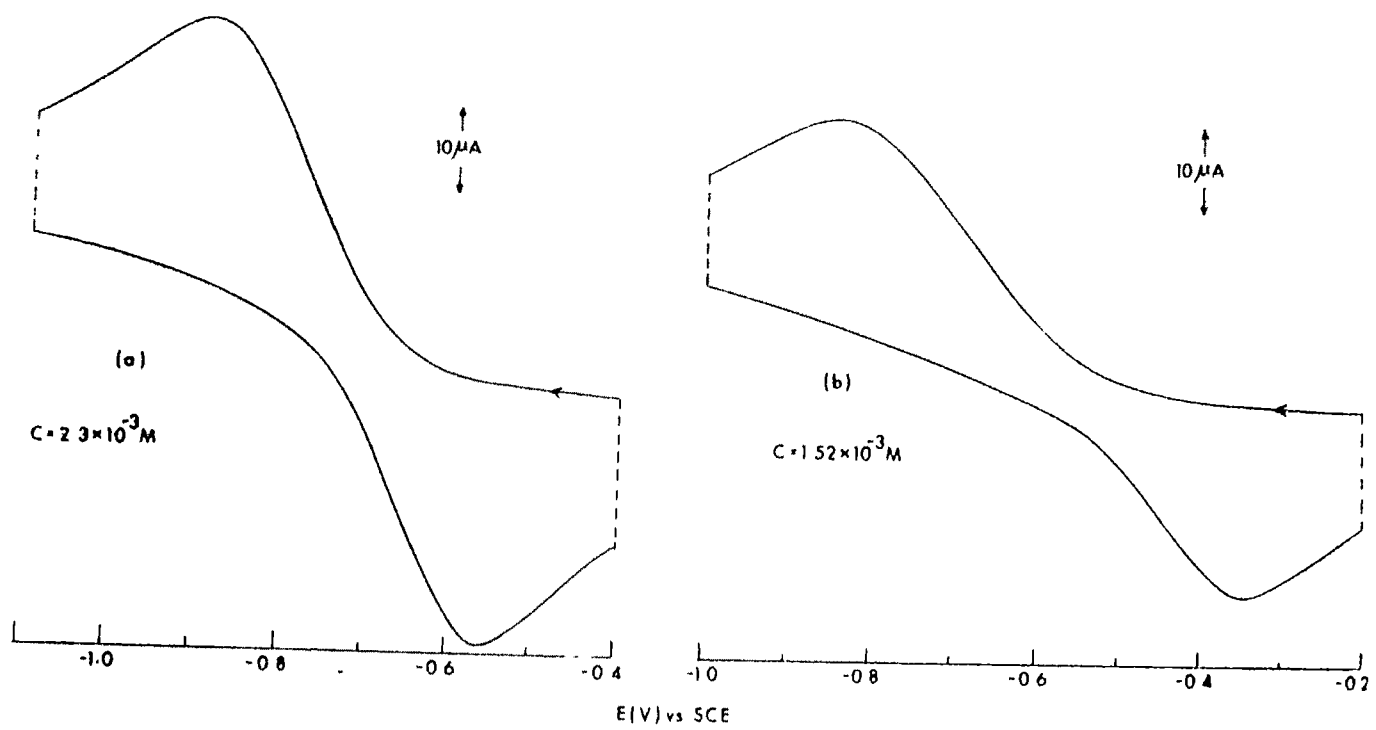


FIG III 2 CV RESPONSE OF (a) S AND (b) I IN DMF AT Pt ELECTRODE ( $v = 50 \text{ mVs}^{-1}$ )

Further, planar  $\text{NiT}_2$  does not display any metal reduction peak; an irreversible ligand reduction peak is observed at a potential less than  $-1.0\text{V}$  (e.g.,  $-1.03\text{V}$  in the nickel(II) analogue of 13). This is displayed in Fig. III.3. This is understandable since the nickel(I) state is not expected<sup>7</sup> to be accessible in combination with a ligand of type HT. On coulometric reduction of  $\text{CuT}_2$ , the colour changes to reddish brown and the characteristic ligand field band<sup>2-4</sup> near  $900\text{ nm}$  (see below) disappears as expected. In air the reduced species  $[\text{CuT}_2]^-$  is rapidly reconverted to  $\text{CuT}_2$ . In summary, couple (1) is essentially a copper(II)-copper(I) couple. In this background we believe that in  $\text{FeT}_3$  and  $\text{CoT}_3$  the electrochemical reduction response is also of the metal origin.

(c) The Effect of Solvent

The couple (1) behaves in a nearly reversible manner in DMF and AN while in DCM it is quasireversible (Table III.4) as is evidenced from the  $\Delta E_p$  values. In DCM the  $\Delta E_p$  values are found to be  $\sim 160\text{ mV}$  compared to  $\sim 70\text{ mV}$  at  $v = 50\text{ mVs}^{-1}$  in AN and DMF using the same working electrode HMDE. The poorer electrochemical reversibility in DCM may be due to the low dielectric constant of this solvent (8.93) compared to that of AN (37.50) and DMF (36.71). The charge separation is hindered in low dielectric medium.

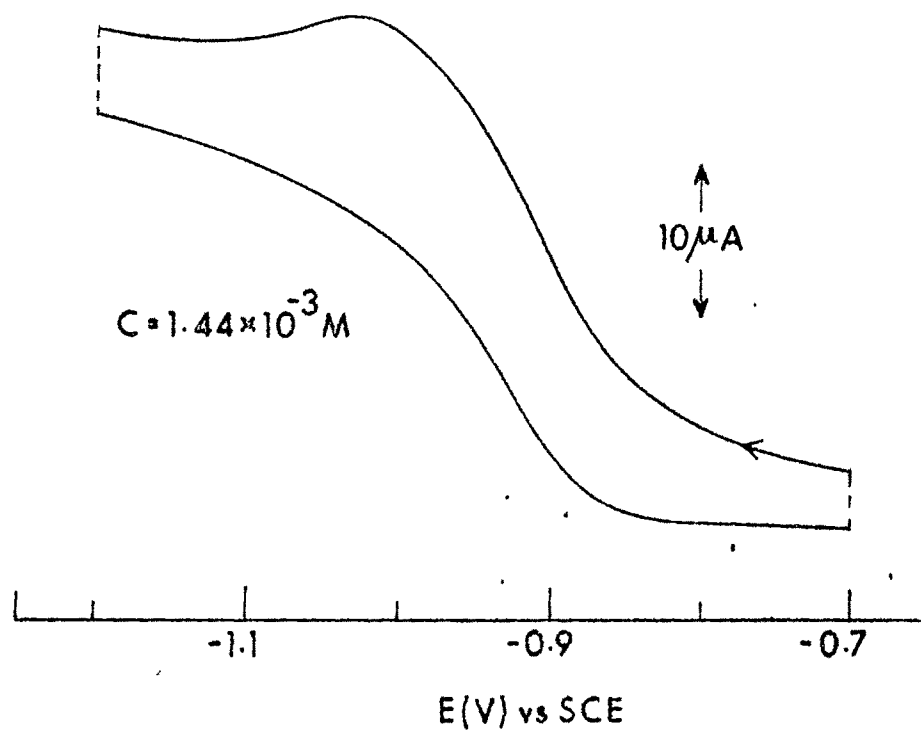


FIG. III. 3. CV RESPONSE OF  $\text{NiT}_2$  (HT =  $\text{PhN}(\text{O})=\text{N}-\text{NHAr}$ ,  
 $\text{Ar} = \text{p-NO}_2\text{C}_6\text{H}_4$ ) IN  $\text{CH}_3\text{CN}$  AT Pt ELECTRODE  
 $(v = 50 \text{ mVs}^{-1})$



Table III.4  
Cyclic Voltammetric Data<sup>a,b</sup> at 298K in Different  
Solvents using HMDE

Serial Number	Solvent	$v(\text{mVs}^{-1})$	$E_{pc}(\text{V})$	$E_{pa}(\text{V})$	$E_{298}^{\circ}(\text{V})$	$\Delta E_p(\text{mV})$
<u>2</u>	AN	50	-0.835	-0.765	-0.80	70
		100	-0.835	-0.765	-0.80	70
	DMF	50	-0.812	-0.747	-0.78	65
		100	-0.825	-0.755	-0.79	70
<u>3</u>	AN	50	-0.827	-0.752	-0.79	75
		100	-0.840	-0.760	-0.80	80
	DMF	50	-0.782	-0.717	-0.75	65
		100	-0.782	-0.717	-0.75	65
<u>5</u>	AN	50	-0.765	-0.695	-0.73	70
		100	-0.766	-0.694	-0.73	72
	DMF	50	-0.737	-0.662	-0.70	75
		100	-0.737	-0.662	-0.70	75
<u>6</u>	DCM	50	-0.877	-0.702	-0.79	175
	DMF	50	-0.645	-0.575	-0.61	70
		100	-0.648	-0.571	-0.61	77
	DCM	50	-0.780	-0.620	-0.70	160
<u>7</u>	DMF	50	-0.495	-0.425	-0.46	70
		100	-0.495	-0.425	-0.46	70
	DCM	50	-0.640	-0.480	-0.56	160
		100	-0.655	-0.465	-0.56	190

<sup>a</sup> Meaning of units and symbols are the same as in text.

<sup>b</sup> Supporting electrolyte TEAP (0.1M).

The  $E_{298}^0$  of a couple (3) depends among other factors



(vide Chapter V) on the difference in free energy of solvation<sup>8</sup> between ox and red. The difference will be positive if the red is better solvated than ox. In our case, red =  $[\text{Cu}]^-$  bears a unit negative charge and the ox =  $[\text{Cu}]$  is neutral. Therefore changes in the solvational free energies in going from one solvent to another are likely to be dominated by changes in the solvation energy of the charged species viz.  $[\text{Cu}]^-$  in our case. Since the dielectric constant of AN and DMF are nearly the same and are much higher than that of DCM, we expect  $E_{298}^0(\text{DCM}) < E_{298}^0(\text{AN}, \text{DMF})$  as observed (Table III.4). Small differences are observed between  $E_{298}^0(\text{AN})$  and  $E_{298}^0(\text{DMF})$  as also reported by others<sup>9</sup>. The solvent dependence of  $\bar{u}$  for the electrode reaction (1) is shown in Fig. III.4.

#### D. Linear Free Energy Relationships

In the complexes, 1-13, the formal potentials are quite responsive to the inductive properties of the phenyl ring's para substituent and also to the group R (Table III.2). When  $\text{NO}_2$  group is replaced by OMe group, the  $\text{Cu}^{\text{II}}-\text{Cu}^{\text{I}}$  reduction potential is increased by 380 mV for R=Et (Table III.2). In general, electron releasing groups are found to make reduction more difficult as in the changing of R from Ph to Et for a given X. When X is systematically varied for a constant R, the relationship (4) is applicable.

$$\Delta E_{298}^0 = 2\sigma\rho \quad \dots (4)$$

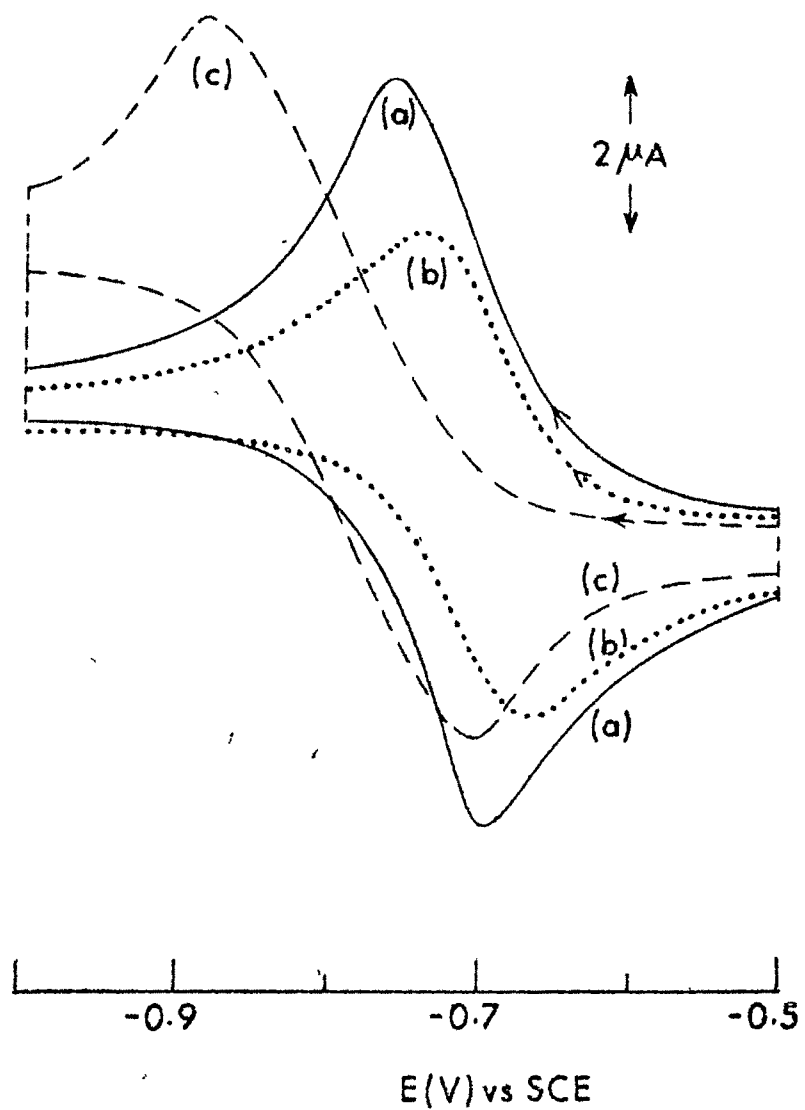
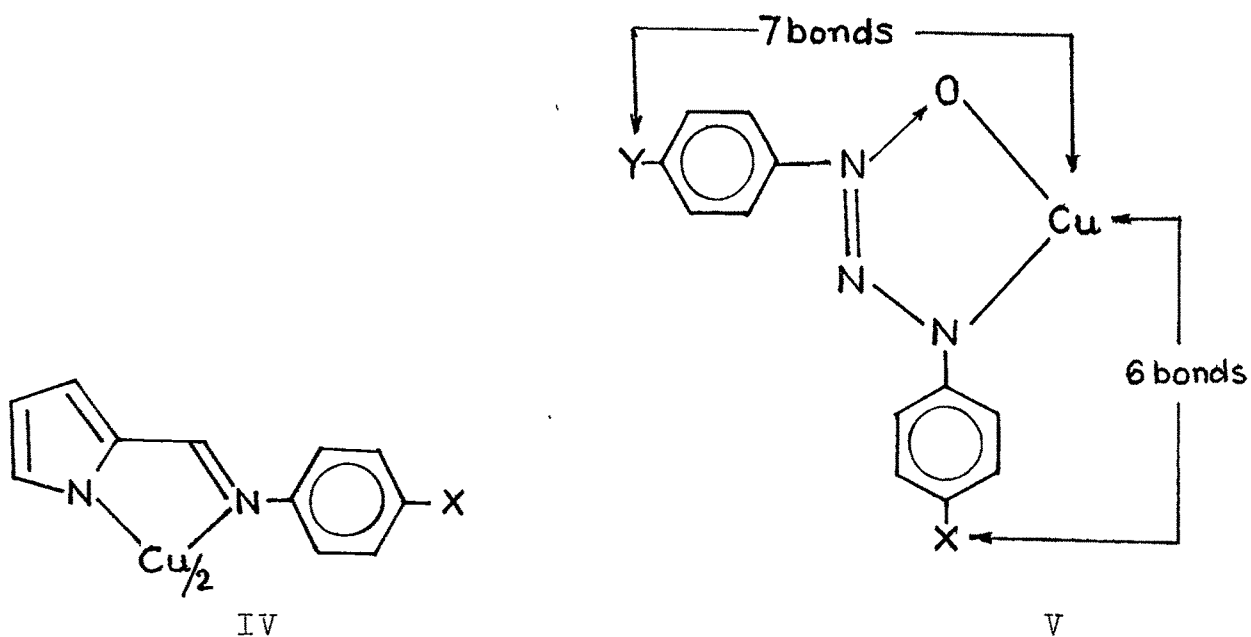


FIG. III. 4. CYCLIC VOLTAMMOGRAMS  
 OF 5 IN (a)  $\text{CH}_3\text{CN}$   
 —,  $C = 2.98 \times 10^{-3} \text{ M}$  (b) DMF  
 .....  $C = 2.30 \times 10^{-3} \text{ M}$  (c) DCM  
 ---,  $C = 3.97 \times 10^{-3} \text{ M}$  AT HMDE ( $v = 50 \text{ mV s}^{-1}$ )

The  $\sigma$  values used in the correlation are those of Chapter II. As before,  $\Delta E_{298}^{\circ}$  is the shift of  $E_{298}^{\circ}$  from the standard complex having  $X=H$  and  $2\sigma$  is the weighted Hammett substituent constant for two chelate rings carrying the substituents and  $\rho$  is the reaction constant. The  $E_{298}^{\circ}-2\sigma$  lines are satisfactorily linear (Fig. III.5). As in the case of  $FeT_3$  and  $CoT_3$  (Chapter II),  $\rho$  changes on replacing  $R$  from Et to Ph. The  $\rho$  values are: 0.17V ( $R=Et$ ) and 0.13V ( $R=Ph$ ).

In  $Cu(pyr)_2^{10}$  (IV) the bond sequence is the same as in  $CuT_2$  (structure V) for substituent X. In both cases X is six bonds



away from the copper(II) centre but the redox potential in  $CuT_2$  is more susceptible to substituent effects as is evidenced from the  $\rho$  value (0.08V) of  $Cu(pyr)_2$ .

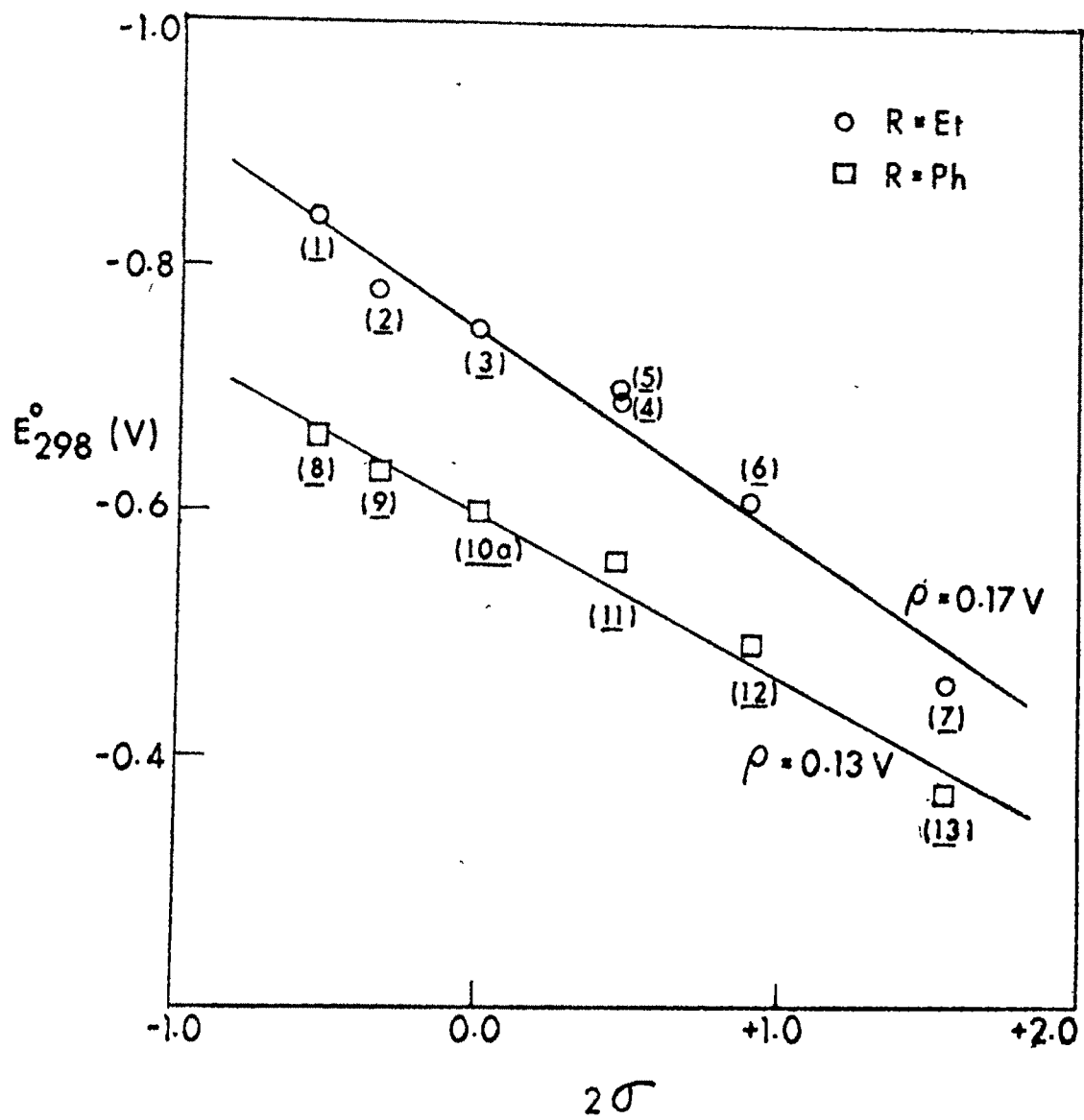


FIG. III.5.  $E_{298}^{\circ} - 2\sigma$  PLOT FOR TWO GROUPS OF  $CuT_2$

In the  $\text{CuT}_2$  group, 10a-10c, the substituent Y changes. The  $E_{298}^0$  values of 10a and 10b are identical which manifests the mildness of the Y substituent which is seven bonds away (V) (vide Chapter II).

The fitting of the  $\text{CuT}_2$  data with Taft (Chapter II) is in Fig. III.6. The corresponding  $\rho$  parameters thus derived are the same within experimental error ( $\pm 0.01$ ) with those obtained using Hammett constants. As expected, the behaviour of  $\text{FeT}_3$ ,  $\text{CoT}_3$  and  $\text{CuT}_2$  are parallel in this regard.

#### E. Ortho Substituted Copper Complexes of Type II

Each of the complexes, 14-16, has an ortho substituent (Z). Their  $E_{298}^0$  values are systematically more negative (Table III.2) than those of the corresponding para-substituted compounds (1-13). The observed data can be fitted to the  $\text{CuT}_2$  line (R=Et) of Fig. III.5 if it is assumed that the substituent constants for Z are: OMe, -0.46; Me, -0.26; Cl, -0.15 (This fit corresponds to  $\rho = 0.17V$ ). These constants are much more negative than the Taft ortho substituents<sup>11</sup>  $\sigma_o$ : OMe, -0.39; Me, -0.17; Cl, + 0.20. If, on the other hand, we insist that Taft  $\sigma_o$  values are to be used, the  $E_{298}^0$  of 3 and 14-16 still correlates with  $2\sigma_o$  (Fig. III.7) with  $\rho = 0.10V$ .

Steric factors play a major part in the peculiar effects of ortho-substituents<sup>11</sup>. In the electrochemical measurements the factors include steric hindrance to solvation and the approach to the electrode surface. The main approach to understand the ortho-effect is to separate steric effects from polar effects. The combination of steric with polar effects vitiates the meaningful correlation.

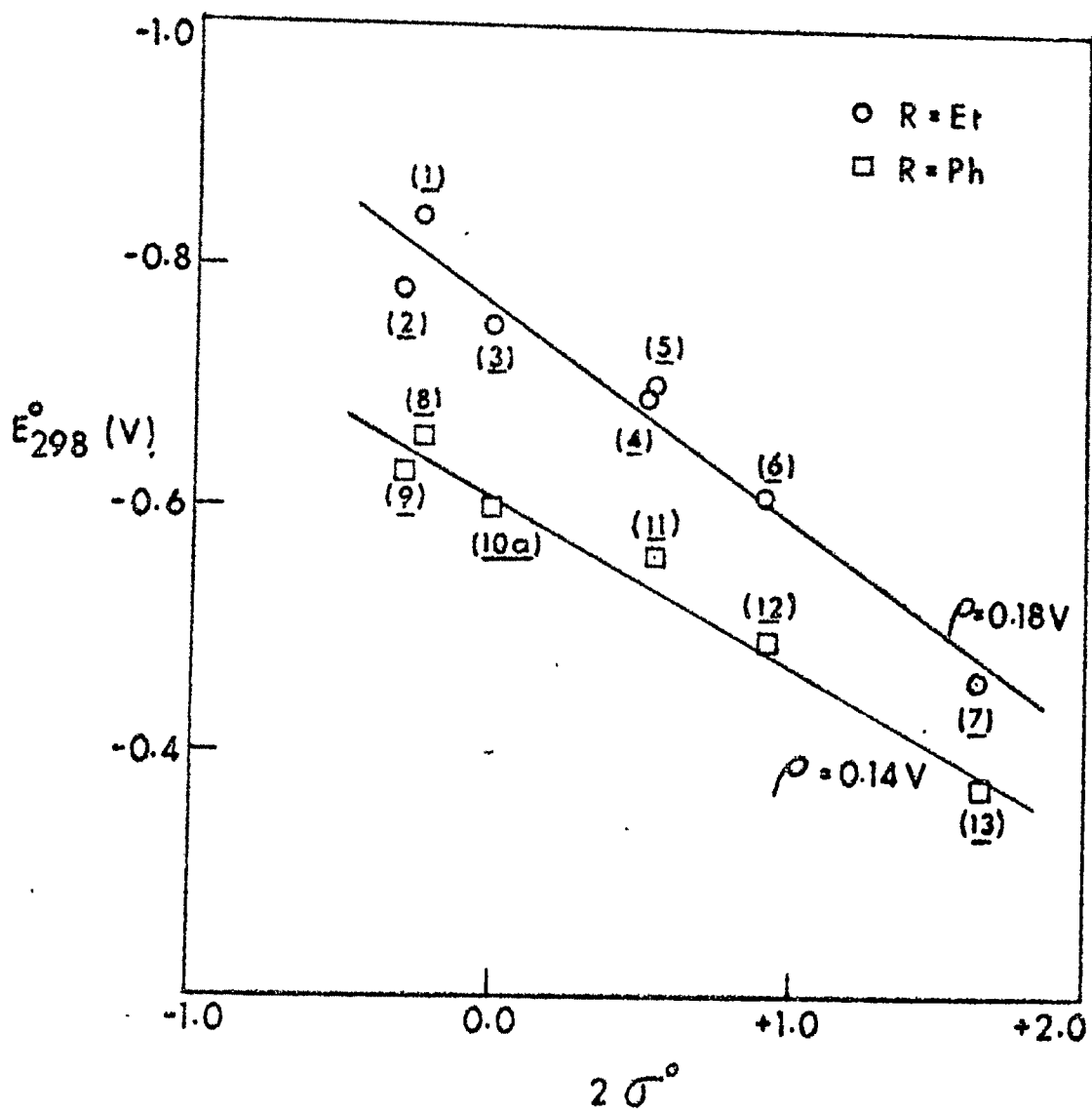


FIG. III.6.  $E_{298}^\circ - 2\sigma^\circ$  PLOT FOR TWO GROUPS OF  $CuT_2$

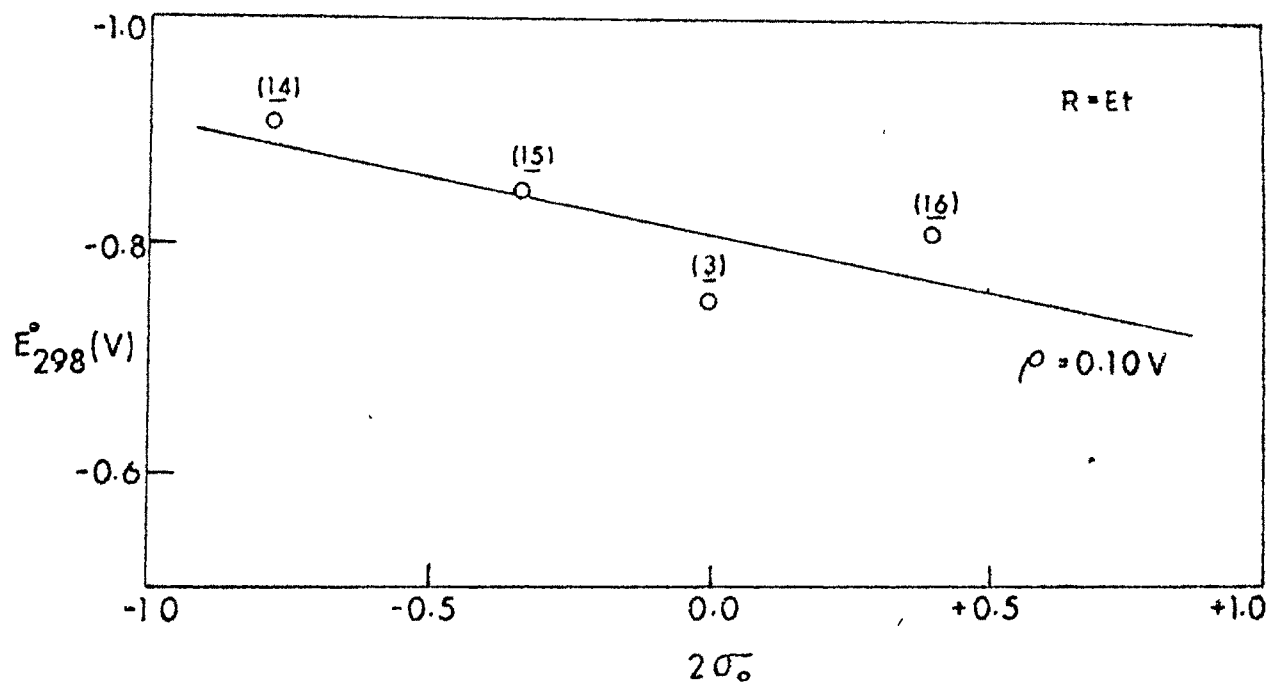


FIG. III.7.  $E_{298}^{\circ} - 2\sigma_{\circ}$  PLOT FOR  $\text{CuT}_2$



#### F. Tetradentate Complexes, Type III

Among all the copper complexes (R=Et) reported here, 17 has the most negative  $E_{298}^0$ ; a similar comment applies to 18 among copper complexes with R=Ph (Table III.2). The potentials of 17 and 18 are  $\sim 300$  mV more negative than those of 3 and 10a respectively.

The tetradentate ligands in 17 and 18 enforce both planarity and cis geometry for  $\text{CuN}_2\text{O}_2$  coordination sphere. The bis complexes 1-16 are probably trans and grossly planar. Since a bis complex with cis geometry is not known, an analysis of the origin of the low potentials in III becomes difficult. However, we wish to draw attention to one possible factor. The reduced species  $[\text{Cu}]^-$  contains copper(I) and planar tetracoordination is not a favourable geometry for this oxidation state<sup>12</sup> — a distortion towards tetrahedral structure can remove this difficulty. Such a distortion is possible in bis complexes I and II. The tetradentate ligand is sterically more demanding and distortion would be harder to come by. This may contribute towards the more negative  $E_{298}^0$  values of III.

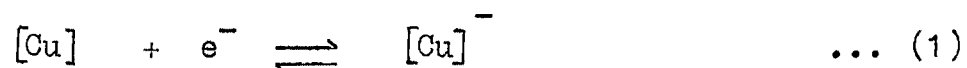
#### G. Spectral Correlation in Copper Complexes

As already stated in Chapter I, the copper(II) complexes show a ligand field band near 900 nm. Representative spectra and data taken in benzene (BZ) and DMF solution for the extensive

series considered by us are in Fig. III.8 and Table III.5. A slight shift ( $\sim 200 \text{ cm}^{-1}$ ) to lower energy occurs in going from BZ to DMF which may be due to axial coordination<sup>2</sup>. In grossly planar copper(II) complexes, several ligand field bands are expected<sup>13</sup>, but often a broad envelope is all that is observed<sup>14,15</sup>. This is true in the present complexes. The position of the band maximum ( $\lambda_{\text{max}}$ ) of the envelope shifts with substituent X (Table III.5). This question in the broader context of the thermodynamics of electrode reactions will be considered in Chapter V.

#### H. Conclusions

1. The copper complexes of type I, II and III uniformly display the electrode reaction



where reduction occurs at the metal centre. The reaction is nearly reversible in DMF and AN but quasireversible in DCM. In summary, iron(III), cobalt(III) and copper(II) complexes of triazene 1-oxides all display a good metal reduction response.

2. Among complexes of type I, the  $E_{298}^0$  of couple (1) correlates linearly with Hammett substituent constant. The  $\rho$  values are: 0.17V (R=Et) and 0.13V (R=Ph).

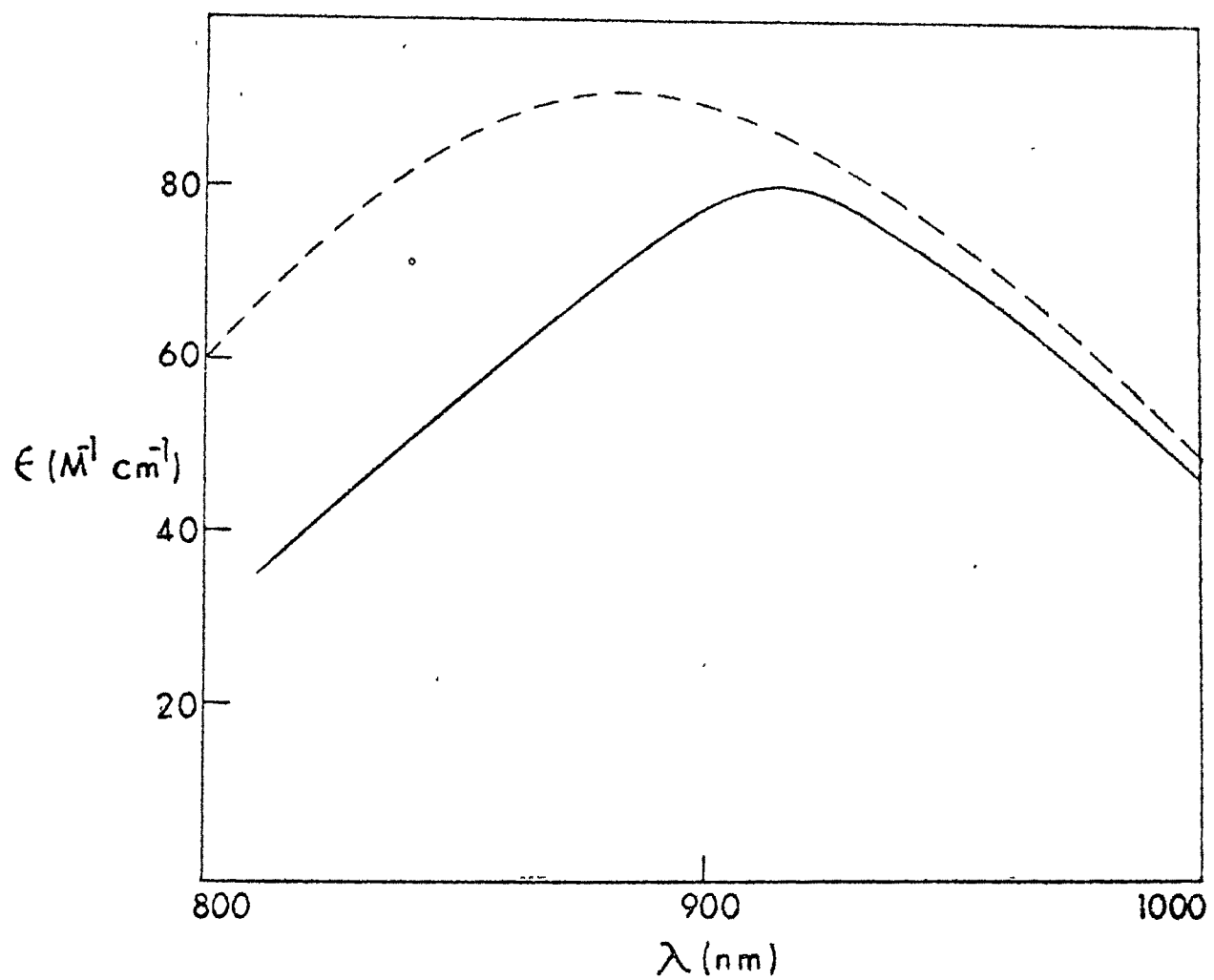


FIG. III. 8. LIGAND FIELD SPECTRA OF 2 (—) AND 7 (---) IN BENZENE SOLUTION

Table III.5

Band Maximum ( $\lambda$ , nm) and Extinction Coefficient ( $\epsilon$ ,  $M^{-1}cm^{-1}$ )  
in Benzene and Dimethylformamide Solution

Serial Number	In benzene	$\lambda(\epsilon)$	In dimethylformamide
<u>2</u>	915 (81)		945 (92)
<u>3</u>	908 (70)		930 (88)
<u>4</u>	905 (72)		925 (79)
<u>5</u>	908 (79)		915 (80)
<u>6</u>	905 (92)		-
<u>7</u>	885 (91)		-
<u>8</u>	900 (95)		920 (85)
<u>10a</u>	895 (86)		910 (68)
<u>11</u>	890 (97)		905 (82)
<u>12</u>	885 (95)		-
<u>14</u>	930 (96)		-
<u>15</u>	910 (94)		-
<u>16</u>	960 (96)		-
<u>18</u>	890 (77)		-

3. In ortho substituted complexes (type II),  $E_{298}^0$  is more negative than that of I, corresponding to a higher value of the ortho substituent constant.
4. Complexes of tetradentate ligands (type III) have the most negative  $E_{298}^0$  values. This could be partly due to ligand fixedness with relation to copper(I) stereochemistry.
5. The ligand field  $\lambda_{\max}$  of the complexes shifts with the substituents.

### III.3 EXPERIMENTAL SECTION

#### A. Preparation of Compounds

##### a. Preparation of ligands

(i) The bidentate triazene 1-oxides were prepared as described in Chapter II.

(ii) Tetradentate triazene 1-oxide (R=Ph) was prepared as follows:

2-iodonitrobenzene was prepared by following a published procedure<sup>16</sup> for 4-iodonitrobenzene. 2,2'-dinitrodiphenyl was prepared from 2-iodonitrobenzene by the method<sup>17</sup> of Gore and Hughes. 2,2'-diaminodiphenyl was prepared by reduction of 2,2'-dinitrodiphenyl with stannous chloride dihydrate in presence of concentrated hydrochloric acid and 95% ethyl alcohol according to the prescription<sup>18</sup> of Everett and Ross. Tetrazotisation of 2,2'-diaminodiphenyl was carried out by the method<sup>19</sup> of Sandin and Cairns.

To a solution of 1.96g N-phenylhydroxylamine in 100 ml (1:1) water-alcohol mixture was added a solution of tetrazotized 2,2'-diaminodiphenyl (prepared from 1.75g of 2,2'-diaminodiphenyl, 23.6 ml 2N hydrochloric acid, 24 ml water and 1.3g of sodium nitrite at 0°C) with mechanical stirring. During this addition a solution of 10g sodium acetate in 30 ml water was also added slowly such that the pH of the solution remained in the range 3-5 and the temperature remained in the range 0-5°C. Stirring was continued for 0.5h after completion of additions. The yellow crystalline product was filtered and was recrystallised from 95% ethanol (Yield, 40%).

This general procedure was used for the preparation of ligand with R=Et.

b. Preparation of Complexes<sup>1-4</sup>

Copper(II) Chelates of Type II and III

To a hot alcoholic solution of the triazene 1-oxide (0.02 mol) was added aqueous copper(II) acetate monohydrate (0.01 mol) with magnetic stirring. The crystals thus obtained were recrystallized from acetone.

Bis(1-phenyl 3-p-nitrophenyl triazene 1-oxidato)nickel(II)

To a hot alcoholic solution of the triazene 1-oxide (0.02 mol) was added a solution of sodium hydroxide (0.02 mol).

To this was then added aqueous nickel(II) acetate tetrahydrate (0.01 mol) with magnetic stirring. The crystals thus obtained were recrystallized from acetone.

### Copper(II) Chelates of Type III

To a hot alcoholic solution of the ligand (R=Ph) (130 mg in 50 ml 95% ethanol) was added a hot solution of copper(II) acetate monohydrate (70 mg in 10 ml water) with magnetic stirring. The red compound was recrystallized from acetone.

#### c. Tetraethylammonium Perchlorate (TEAP)

TEAP was prepared according to the method described in Chapter II.

### B. Characterization of the Complexes

This was done by C, H, N microanalyses. Data of all complexes prepared during the present work are collected in Table III.6.

### C. Solvents

Acetonitrile was purified according to the procedure of Chapter II. A.R. grade dimethylformamide was used without any further purification.

Table III.6

## Characterization Data of Complexes

Serial Number	Formula	% C		% H		% N	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
<u>1</u>	$C_{18}H_{24}N_6O_4Cu$	47.84	47.81	5.31	5.30	18.60	18.63
<u>2</u>	$C_{18}H_{24}N_6O_2Cu$	51.48	51.45	5.72	5.70	20.02	20.55
<u>3</u>	$C_{16}H_{20}N_6O_2Cu$	49.04	49.42	5.11	5.24	21.45	21.71
<u>4</u>	$C_{16}H_{18}N_6O_2Br_2Cu$	34.94	34.92	3.27	3.28	15.28	15.26
<u>5</u>	$C_{16}H_{18}N_6O_2Cl_2Cu$	41.69	41.69	3.91	3.89	18.24	18.20
<u>6</u>	$C_{22}H_{28}N_6O_6Cu$	49.30	49.20	5.23	5.30	15.68	15.70
<u>7</u>	$C_{16}H_{18}N_8O_6Cu$	39.87	39.86	3.74	3.72	23.26	23.27
<u>8</u>	$C_{26}H_{24}N_6O_4Cu$	56.98	56.96	4.38	4.34	15.34	15.32
<u>9</u>	$C_{26}H_{24}N_6O_2Cu$	60.52	60.51	4.65	4.63	16.29	16.26
<u>10a</u>	$C_{24}H_{20}N_6O_2Cu$	59.07	59.38	4.10	4.15	17.23	17.15
<u>10b</u>	$C_{26}H_{24}N_6O_2Cu$	60.52	60.53	4.65	4.67	16.29	16.26
<u>10c</u>	$C_{28}H_{26}N_8O_4Cu$	55.86	55.92	4.32	4.34	18.62	18.61
<u>11</u>	$C_{24}H_{18}N_6O_2Cl_2Cu$	51.75	51.75	3.23	3.25	15.09	15.06



Table III.6(contd)

Serial Number	Formula	% C		% H		% N	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
<u>12</u>	$C_{30}H_{28}N_6O_6Cu$	57.00	57.02	4.43	4.51	13.30	13.28
<u>13</u>	$C_{24}H_{18}N_8O_6Cu$	49.87	49.89	3.12	3.13	19.39	19.37
<u>14</u>	$C_{18}H_{24}N_6O_4Cu$	47.84	47.82	5.31	5.30	18.60	18.62
<u>15</u>	$C_{18}H_{24}N_6O_2Cu$	51.48	51.47	5.72	5.62	20.02	20.04
<u>16</u>	$C_{16}H_{18}N_6O_2Cl_2Cu$	41.69	41.67	3.91	3.92	18.24	18.20
<u>17</u>	$C_{16}H_{18}N_6O_2Cu$	49.29	49.27	4.62	4.60	21.56	21.54
<u>18</u>	$C_{24}H_{18}N_6O_2Cu$	59.31	59.30	3.71	3.70	17.30	17.28

### Dichloromethane (DCM).

250 ml of commercial dichloromethane was thoroughly washed three times with 100 ml of 5% sodium carbonate solution. Then it was washed thoroughly with water and kept over enough calcium chloride. The fraction at 40-41°C was collected. The voltage window of the purified solvent at platinum electrode was + 1.5V to -1.5V and the same at the HMDE was + 0.2V to -1.5V.

### D. Physical Measurements

Electronic spectra and electrochemical measurements which include cyclic voltammetric and coulometric techniques have been done as described in Chapter II.

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