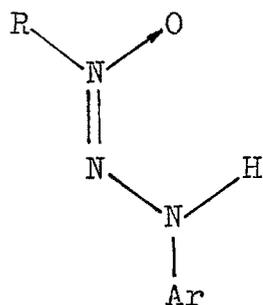


## SUMMARY

## SUMMARY

The primary concern of this thesis is a rational study of ligand substituent effects on metal-centered redox thermodynamics monitored electrochemically in related groups of transition metal complexes derived from triazene 1-oxides (HT) (1).



R = alkyl or aryl

Ar = aryl

1

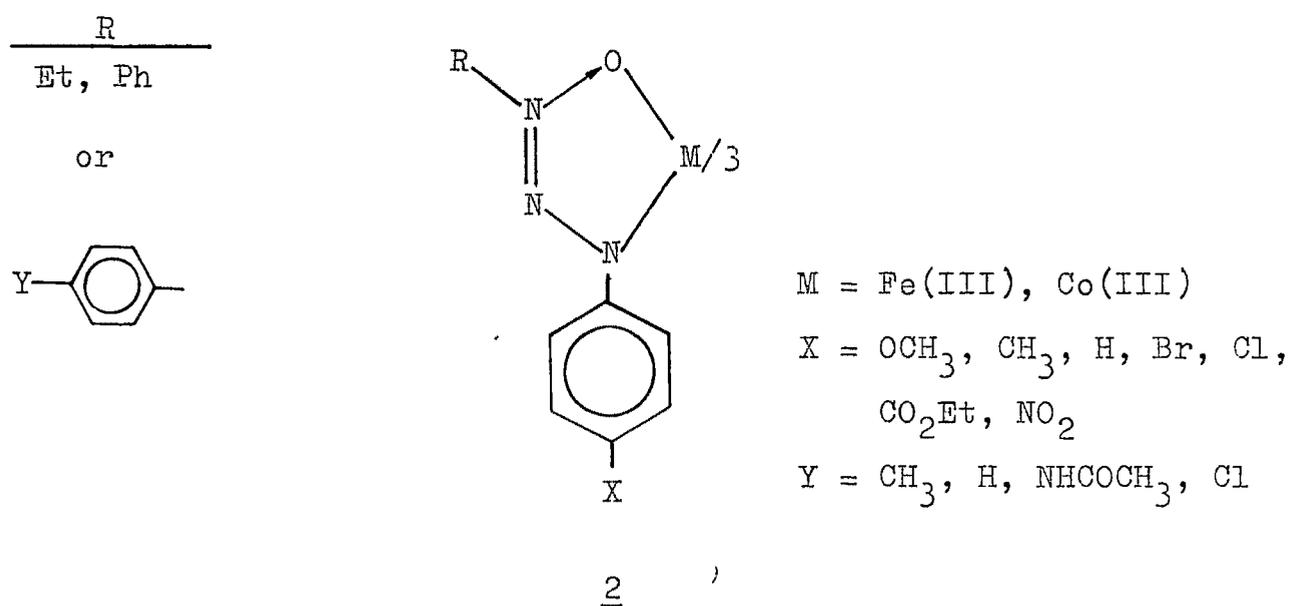
I

Aspects of the known chelate chemistry of triazene 1-oxides have been briefly reviewed in Chapter I. The basis of the various electrochemical techniques such as, cyclic voltammetry (CV), phase sensitive alternating current cyclic voltammetry (PSACV),

differential pulse voltammetry (DPV) and constant potential coulometry used by us are summarized. The purpose of the present investigation is outlined in this background.

## II

Chapter II deals with the electron transfer properties of iron(III) and cobalt(III) triazene 1-oxides ( $MT_3$ ) (2).



The  $FeT_3$  complexes are uniformly high-spin ( $t_{2g}^3 e_g^2$ ) and  $CoT_3$  complexes are diamagnetic ( $t_{2g}^6$ ).

A reversible to quasireversible electrochemical (CV) response in the negative side of SCE was found to occur in all

complexes. The  $E_{298}^0$  values (vs SCE) fall in the ranges:  $\text{FeT}_3$ , -0.14 to -0.76V;  $\text{CoT}_3$ , -0.08 to -0.56V. Constant potential experiments reveal it to be an one-electron reduction process as shown below.



In acetonitrile solution at hanging mercury drop electrode (HMDE) the  $\Delta E_p$  values generally lie in the range 65-90 mV at  $v = 50 \text{ mVs}^{-1}$  for the majority of complexes. Three  $\text{FeT}_3$  complexes were also studied in dimethylformamide solution. Electrochemical response then occurs at slightly less negative potential. In a number of cases the electrode reaction (1) was also studied using platinum working electrode. In general, the reversibility ( $\Delta E_p$  values) is much less compared to the results at HMDE. The rate of heterogeneous electron transfer is  $\text{FeT}_3 > \text{CoT}_3$  (for a given ligand). The reduction takes place at the metal centre. Free ligand are reduced irreversibly at more negative potentials.

The response for  $\text{FeT}_3$  complexes was further characterized by PSACV. The half band width ( $\delta$ ) values lie in the range 90-120 mV at slow scan rates ( $\ll 5 \text{ mVs}^{-1}$ ) indicating the general reversibility of the electrode process.

The formal potentials for the  $\text{MT}_3$  complexes are sensitive to R and six bonds away substituent X. The  $E_{298}^0$  values shift with the nature of the substituents. In general, electron-withdrawing

groups are found to make reduction easier ( $E_{298}^{\circ}$  less negative). When X is systematically varied keeping R fixed, linear Hammett relationship (2) holds

$$\Delta E_{298}^{\circ} = 3\sigma\rho \quad \dots (2)$$

Where  $\Delta E_{298}^{\circ}$  is the shift of  $E_{298}^{\circ}$  from the standard complex having X=H and  $3\sigma$  is the weighted Hammett substituent constant and  $\rho$  is the reaction constant measuring the susceptibility of the electron transfer process to polar effects. The  $\rho$  values obtained from the slope of the least square lines are as follows:  $\text{FeT}_3$ ,  $\rho = 0.16\text{V}$  (R=Et),  $\rho = 0.11\text{V}$  (R=Ph);  $\text{CoT}_3$ ,  $\rho = 0.17\text{V}$  (R=Et).

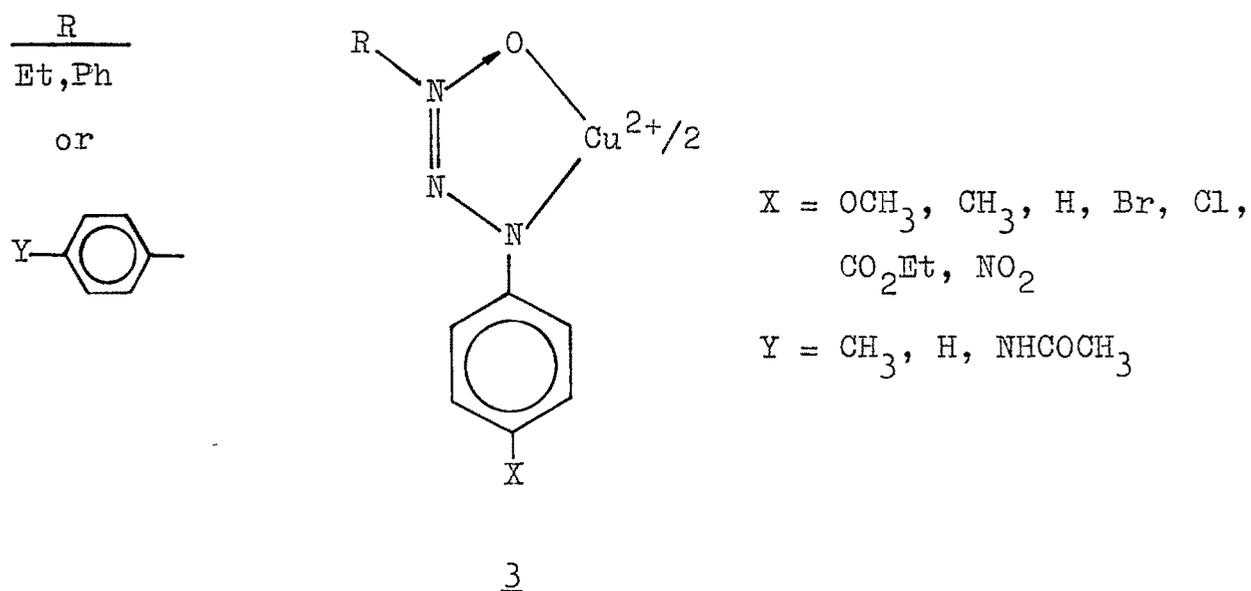
The  $\rho$  values of iron and cobalt lines (R=Et) are virtually equal. Thus for a given R the weighted change in  $E_{298}^{\circ}$  due to the X substituent is effectively independent of the metal ion, in this group of complexes.

For  $\text{FeT}_3$  complexes the  $\rho$  value decreases considerably when an extra bond (substituent Y) intervenes between the metal and substituent ( $\rho = 0.08\text{V}$ ).

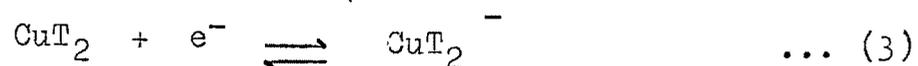
The iron(III) complexes exhibit two overlapping LMCT bands in the region 540–670 nm and cobalt(III) complexes exhibit such band at  $\sim 520$  nm. The LMCT band energies do not correlate with Hammett substituent constant.

## III

The electron transfer properties of four coordinated grossly planar bis-copper(II) triazene 1-oxides of type  $\text{CuT}_2$  (3) are described.



For all complexes at mercury or platinum working electrode a cyclic voltammetric response in the negative side of SCE was found to occur. The  $E_{298}^0$  values (vs SCE) fall in the ranges:  $-0.46$  to  $-0.84\text{V}$  ( $\text{R}=\text{Et}$ ) and  $-0.37$  to  $-0.66\text{V}$  ( $\text{R}=\text{Ph}$ ). Coulometric experiments confirmed the one-electron reduction behaviour of the electrode process (3).



At mercury electrode, the metal-centered reduction is nearly

reversible in dimethylformamide and acetonitrile ( $\Delta E_p$  lies in the range 60-70 mV at  $v = 50 \text{ mVs}^{-1}$ ) but quasireversible in dichloromethane. At platinum working electrode, in general, large deviation from reversibility occurs ( $\Delta E_p \sim 250-350 \text{ mV}$  at  $v = 50 \text{ mVs}^{-1}$ ).

The solvent dependence of the electrode reaction (3) was verified in a representative case. As the dielectric constant of the solvent decreases, the  $E_{298}^0$  values become more negative. The changes in solvational free energies in going from one solvent to another are likely to be dominated by changes in the solvation energy of the reduced charged species  $[\text{CuT}_2]^-$ .

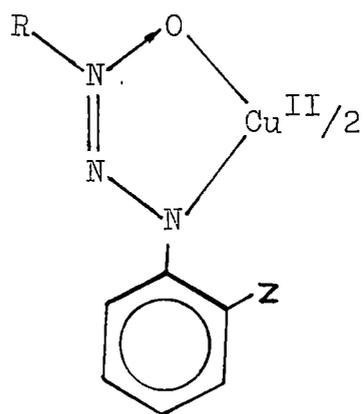
The  $E_{298}^0$  values are sensitive to R and X. As in the case of  $\text{MT}_3$  complexes (Chapter II), in general, electron donating groups are found to make reduction more difficult ( $E_{298}^0$  more negative). The  $E_{298}^0$  values correlate with Hammett substituent constant according to the relation (4).

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

The  $\rho$  values are: 0.17V (R=Et) and 0.13V (R=Ph).

The electron transfer properties of  $\text{CuT}_2$  complexes (4) having an ortho substituent Z and cis planar copper(II)

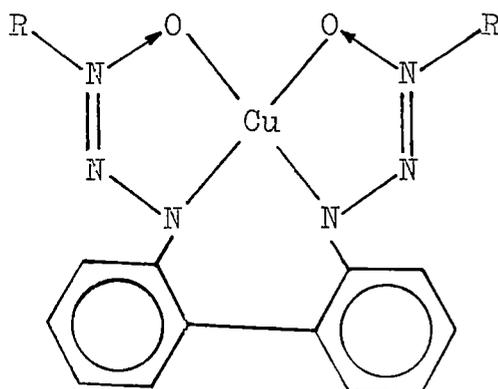
complexes (5) of tetradentate ligands were also studied. Each of



R = Et

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

4



R = Et, Ph

5

these complexes exhibit an one-electron redox process<sup>of</sup> type (3).

The  $E_{298}^0$  values of each of the complexes (4) are systematically more negative (-0.81 to -0.91V) than those of the corresponding para substituted compounds (3). The  $E_{298}^0$  values correlate linearly ( $\rho = 0.10V$ ) with Taft ortho substituted constants,  $\sigma_o$ .

Complexes of tetradentate ligands (5) have the most negative  $E_{298}^0$  values (-1.07V, R=Et; -0.86V, R=Ph). This could be partly due to ligand fixedness with relation to copper(I) stereochemistry.

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

## IV

The formation of mixed ligand complexes through ligand redistribution reactions in iron, cobalt and copper triazene 1-oxides are described. The mixture of two or three different  $\text{FeT}_3$  complexes, two different  $\text{CoT}_3$  and  $\text{CuT}_2$  complexes were examined. The dynamic electrochemical techniques have been shown to provide a powerful and sensitive tool for identification of these species in solution.

The  $E_{298}^0$  values of the mixed complexes are the weighted sum of the pure complexes. An additivity rule of type (5) is obeyed.

$$E_{298}^0[\text{MT}_q^a \text{T}_r^b \text{T}_s^c \dots] = \frac{q}{p} E_{298}^0[\text{MT}_q^a] + \frac{r}{p} E_{298}^0[\text{MT}_r^b] + \dots \quad (5)$$

where  $p = q + r + s + \dots$

The parent complexes and mixed species constitute a group which obey the Hammett relationship (6)

$$\Delta E_{298}^0 = (\Sigma \sigma) \dots \quad (6)$$

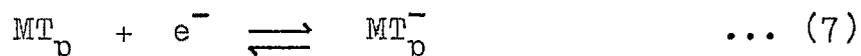
where in  $(\Sigma \sigma)$ , the weighted contribution of all substituted ligands are included.

In  $\text{CuT}_2$  mixtures the redistribution is statistical. In  $\text{FeT}_3$  and  $\text{CoT}_3$  mixtures the random situation is violated. This may arise from a catalytic effect.

A probable mechanism of redistribution is proposed. It is assumed that a transient dimer is formed in bimolecular collision which then leads to ligand scrambling.

## V

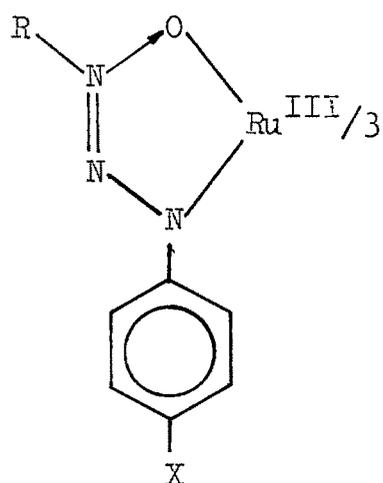
Various thermodynamic parameters such as, metal ionization potential, metal-ligand complexation energy and solvation energy responsible for the free energy change in metal-centered electron transfer reactions are considered. The free energy change for the general reaction (7) controlling the trends of  $E_{298}^0$  values



is of interest of this chapter. An attempt is made to assess the relative importance of spherical and nonspherical parts of the crystal, fields. Among complexes of the same metal ion, it is possible to express the shift of  $E_{298}^0$  in terms of the crystal field splitting parameter. The shift of  $E_{298}^0$  between iron and cobalt couples is controlled by metal ionization potential and nearly equally important spherical and nonspherical crystal field contributions. The energy of the ligand field band in copper(II) complexes linearly correlates with  $E_{298}^0$ .

## VI

In the Chapters VI-VIII, the syntheses along with spectral and electrochemical properties of new ruthenium-triazene 1-oxide systems are described. In Chapter VI, tris ruthenium(III) triazene 1-oxides of type  $\text{RuT}_3$  (6) are reported.



R = Et, Ph

X = CH<sub>3</sub>, H, Cl, CO<sub>2</sub>Et,  
NO<sub>2</sub>

6

Green crystals of the complexes are obtained by the reaction between  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  and HT in presence of  $\text{K}_2\text{CO}_3$ .

These nonelectrolytic complexes are uniformly paramagnetic with  $t_{2g}^5$  ( $S = \frac{1}{2}$ ) ground configuration and have  $\text{RuN}_3\text{O}_3$  (probably trans) coordination environment. In acetonitrile solution,  $\text{RuT}_3$

complexes display one or more LMCT band(s) in the region 600-700 nm.

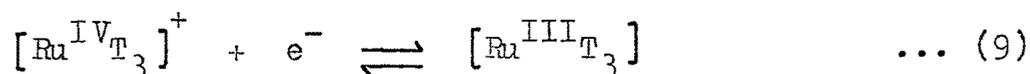
These complexes are redox active in acetonitrile solution at platinum working electrode. The occurrence of both oxidation to  $[\text{Ru}^{\text{IV}}\text{T}_3]^+$  (in the positive side of SCE) and reduction to  $[\text{Ru}^{\text{II}}\text{T}_3]^-$  (in the negative side of SCE) are observed.

At slow scan rates ( $v = 20\text{-}50 \text{ mVs}^{-1}$ ) the cathodic response for the reduction of  $\text{RuT}_3$  (8) is associated with either a diminished



or nonexistent anodic response. The diminished anodic response becomes observable when the scan rate is made high ( $> 50 \text{ mVs}^{-1}$ ). An irreversible and fast removal of  $[\text{Ru}^{\text{II}}\text{T}_3]^-$  species by some chemical reaction is implicated. An EC mechanism is operative in such cases. When both the responses are observable,  $\Delta E_p$  lies in the range 110-180 mV at  $v = 100 \text{ mVs}^{-1}$ , implicating the quasireversible nature of the electrode process (8). The  $E_{298}^0$  values (vs SCE) fall in the ranges: -0.69 to -1.20 (R=Et); -0.66 to -0.83V (R=Ph). The involvement of one electron

in the process (8) is confirmed from coulometric studies. In the positive side of SCE,  $\text{RuT}_3$  complexes undergo an one-electron redox process (9).



The electrode process (9) is nearly reversible ( $\Delta E_p$  lies in the range: 60–80 mV). The  $E_{298}^0$  (vs SCE) values fall in the ranges: 0.24 to 0.60V (R=Et), 0.45 to 0.66V (R=Ph).

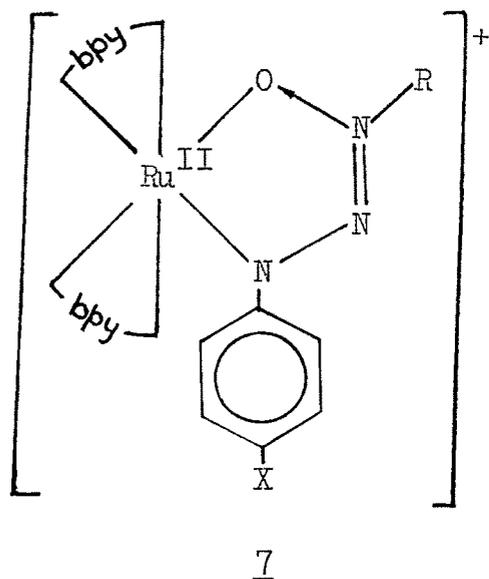
The formal potentials  $E_{298}^0$ , are sensitive to R and X. For the ruthenium(III)-ruthenium(II) couple, the ease of reduction increases ( $E_{298}^0$  values become more positive) as the electron-releasing power of substituents decreases. For the ruthenium(IV)-ruthenium(III) couple, the oxidation becomes difficult as the electron-withdrawing power of substituents increases. The  $E_{298}^0$  values for both the couples linearly correlate with Hammett substituent constants. The experimental  $\rho$  values lie in the ranges: 0.10 to 0.18V (Ru(III)/Ru(II) couple) and 0.11 to 0.13V (Ru(IV)/Ru(III) couple).

Coulometrically reduced species  $[\text{Ru}^{\text{II}}\text{T}_3]^-$  are unstable but the oxidized species  $[\text{Ru}^{\text{IV}}\text{T}_3]^+$  are quite stable in acetonitrile

solution (0.1M in TEAP). The oxidized species  $[\text{Ru}^{\text{IV}}\text{T}_3]^+$  display LMCT band at a lower energy ( $\sim 900$  nm) than those of  $\text{RuT}_3$ .

## VII

In this chapter, binding of triazene 1-oxides with cis-bis(2,2'-bipyridine)ruthenium(II) moiety  $\text{Ru}(\text{bpy})_2^{2+}$  giving rise to tris bidentate heterochelates of type  $[\text{Ru}(\text{bpy})_2\text{T}]^+$  (7) are reported.



R = Et, Ph

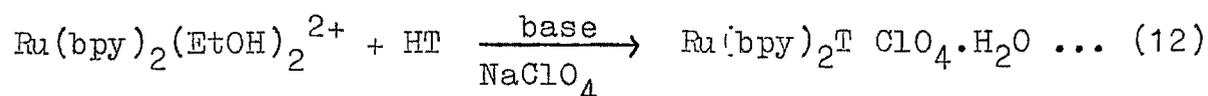
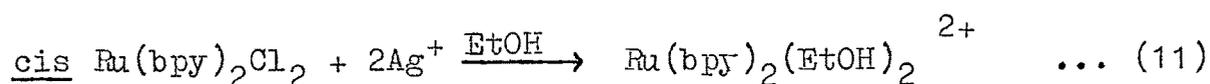
X = CH<sub>3</sub>, H, Cl, CO<sub>2</sub>Et,  
NO<sub>2</sub>

Brown crystalline perchlorate salts were prepared following either of the two routes: (i) decarbonation of the violet coloured  $\text{Ru}(\text{bpy})_2\text{CO}_3$  with HT (eq 10)



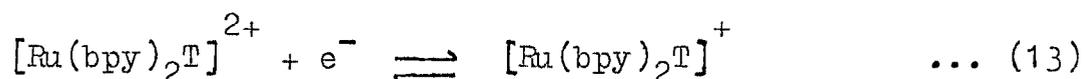
and (ii) nucleophilic halide displacement from violet coloured

cis-Ru(bpy)<sub>2</sub>Cl<sub>2</sub> with AgClO<sub>4</sub>·H<sub>2</sub>O and then reaction of disolvento species with HT in presence of a base NaOH or K<sub>2</sub>CO<sub>3</sub> (eq 11) and (eq 12).



The complexes [Ru(bpy)<sub>2</sub>T]ClO<sub>4</sub>·H<sub>2</sub>O have RuN<sub>5</sub>O coordination sphere. These are uniformly 1:1 electrolyte in acetonitrile solution and diamagnetic with t<sub>2g</sub><sup>6</sup> ground state configuration. In the visible region, three MLCT bands (~ 450, ~ 500, ~ 600 nm) are observed.

The presence of a nearly reversible (ΔE<sub>p</sub> values in the range: 60-80 mV at v = 50 mVs<sup>-1</sup>) one-electron couple (13)



is observed in all complexes. The E<sub>298</sub><sup>0</sup> values (vs SCE) fall in the ranges: 0.16 to 0.36V (R=Et); 0.25 to 0.44V (R=Ph).

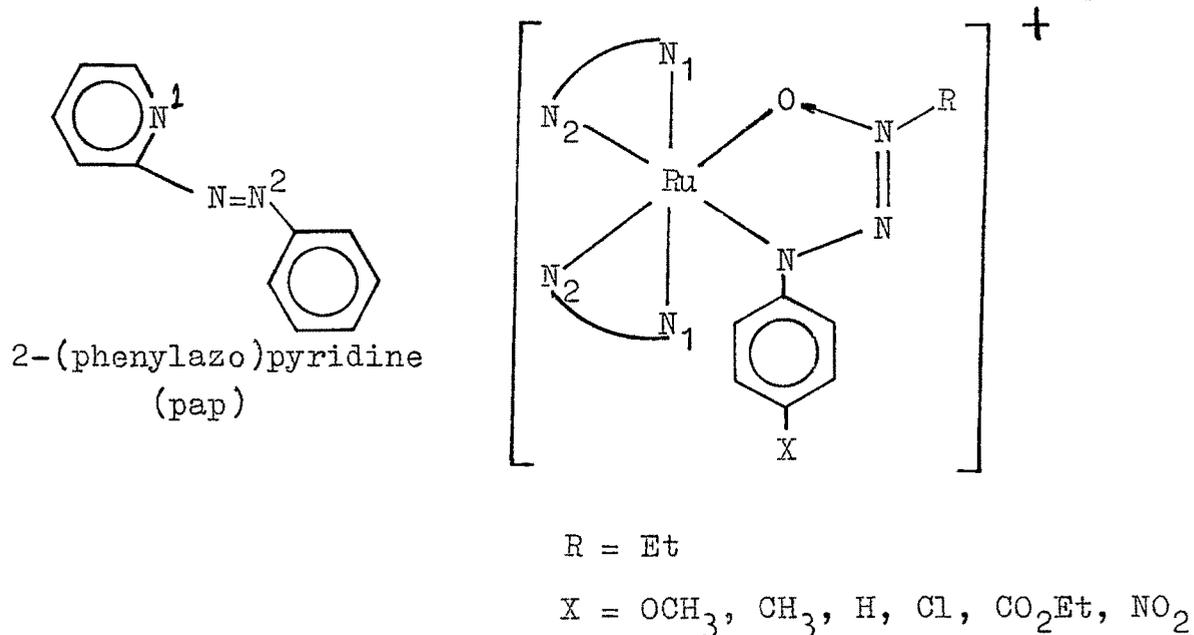
The formal potentials are sensitive to R and X. The [Ru(bpy)<sub>2</sub>T]<sup>+</sup> species have the lowest E<sub>298</sub><sup>0</sup> values among complexes of type [Ru(bpy)<sub>2</sub>(LL')]<sup>n+</sup> (LL' = two monodentate or one bidentate ligand). This is related to the low Dq of T. Ligand reduction is observed on the negative side of SCE (less than -1.0V). A

linear correlation between  $E_{298}^0$  (Ru(III)/Ru(II) couple) and Hammett substituent constant  $\sigma$  has been made. The  $\rho$  values are: 0.19V (R=Et) and  $\rho = 0.21V$  (R=Ph).

Coulometrically oxidized species  $[\text{Ru}(\text{bpy})_2\text{T}]^{2+}$ , show an intense band in the region 630-740 nm. This is assigned as  $\pi(\text{T}) \rightarrow t_{2g}(\text{Ru})(\text{LMCT})$ .

## VIII

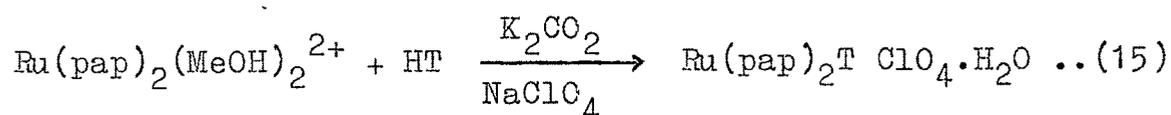
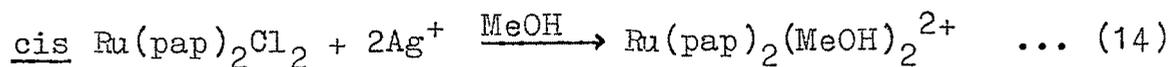
In this chapter, binding of triazene 1-oxides with cis bis(2-phenylazopyridine)ruthenium(II) moiety abbreviated as  $\text{Ru}(\text{pap})_2^{2+}$  analogous to cis  $\text{Ru}(\text{bpy})_2^{2+}$  (Chapter VII) is reported. Tris bidentate heterochelates of general type  $[\text{Ru}(\text{pap})_2\text{T}]^+$  (8)



8

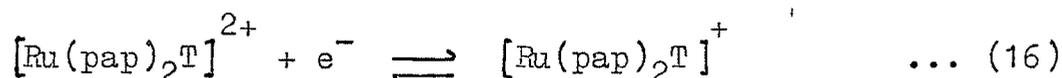
are isolated as red-violet crystalline perchlorate salt from

nucleophilic halide displacement reaction as described in eqs (14) and (15)



The complexes  $[\text{Ru(pap)}_2\text{T}]\text{ClO}_4 \cdot \text{H}_2\text{O}$  have  $\text{RuN}_5\text{O}$  coordination sphere. In acetonitrile solution 1:1 electrolytic nature was observed. These are uniformly diamagnetic  $t_{2g}^6$ . In the visible region, they exhibit two MLCT bands at  $\sim 720$  nm and  $\sim 550$  nm.

In acetonitrile solution, all complexes display an one-electron nearly reversible ( $\Delta E_p \sim 70$  mV at  $v = 50$  mVs $^{-1}$ ) redox process (16) in the positive side of SCE.



The  $E_{298}^0$  values (vs SCE) fall in the range: 0.71 to 0.93V.

The  $E_{298}^0$  values shift with the nature of substituent X. The  $E_{298}^0 - \sigma$  plot is satisfactorily linear ( $\rho = 0.19\text{V}$ ).

The complexes display multiple reduction of the azo function of the pap moiety ( $-0.4$  to  $2.3\text{V}$  vs SCE). The  $E_{298}^0$  values of the couples  $\sim -0.5\text{V}$  and  $\sim -1.0\text{V}$  shift with substituent present at the triazene 1-oxide frame. A fair to good linear Hammett correlation is observed ( $\rho = 0.09\text{V}$ , couple  $\sim -0.5\text{V}$ ;  $\rho = 0.13\text{V}$ , couple  $\sim -1.0\text{V}$ ).

The species  $\text{Ru(pap)}_2\text{T}^{2+}$  generated by coulometric oxidation exhibit, in the visible region, three bands at  $\sim 740$ ,  $\sim 550$  and  $\sim 500$  nm. The lowest energy band is assigned as  $\pi(\text{T}) \rightarrow t_2(\text{Ru})$  and the other two bands due to  $\pi(\text{pap}) \rightarrow t_2(\text{Ru})$  (LMCT).