ELSEVIER

Coordination Chemistry Reviews
168 (1998) 273–293

COORDINATION CHEMISTRY REVIEWS

# Properties and reactivities of polyaminopolycarboxylate (pac) complexes of ruthenium

Debabrata Chatterjee [1] *

*Catalysis and Silicate Group, Central Salt and Marine Chemicals Research Institute, Bhavnagar 364 002, India*

Received 11 April 1997; accepted 20 October 1997

**Contents**



## Abstract

The development and intriguing aspects of the chemistry of Ru–pac (pac = polyaminopolycarboxylate) complexes are reviewed in this article. Kinetics and mechanistic aspects of Ru–pac

* Tel: +91 27760 28694; fax: +91 278 26970.

[1] Present address: Chemistry Department, Central Mechanical Engineering Research Institute, Durgapur 713 209, India.


*PII* S0010-8545(97)00072-6

complexes towards substitution reactions are discussed with reference to the role of the uncoordinated pendant group of the pac ligands in the remarkable lability of Ru–pac complexes towards the aquo-substitution process. The catalytic ability of Ru–pac complexes in various organic transformations are highlighted, along with the mechanistic details. The recent development of electrocatalytic systems with Ru–pac complexes for activation of small molecules is addressed. Most current investigations on the mixed-ligand complexes of ruthenium-containing pac ligands are included in this article. Applications of these mixed-ligand complexes to some biochemical processes or in developing new inorganic materials are discussed. 

**Abbreviations**

| | |
|---|---|
| acac, | acetylacetonate |
| bipy, | 2,2′-bipyridyl |
| *o*-bqdi, | *ortho*-benzoquinoendiamine |
| *t*-BuOOH, | *tertiary*-butylhydroperoxide |
| dmg, | dimethylglyoximate |
| dms, | dimethylsulphide |
| dmso, | dimethylsulphoxide |
| DMTU, | dimethylthiourea |
| edta, | ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate |
| hedtra, | *N*-hydroxyethylethylenediamine-*N*,*N*,*N*′-triacetate |
| isn, | isonicotinamide |
| medtra, | *N*′-methylenediamine-*N*,*N*,*N*′-triacetate |
| *N*,*N*′-Me$_2$edda, | *N*,*N*′-dimethylethylendiaminediacetate |
| pac, | polyaminopolycarboxylate |
| pdta, | propylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate |
| *o*-pda, | *ortho*-phenylenediamine |
| py, | pyridine |
| pz, | pyrazine |
| *o*-phen, | *ortho*-phenanthroline |
| TU, | thiourea |
| TMTU, | tetramethylthiourea |
| ttha, | triethylenetetraaminehexaacetate |

## 1. Introduction

The chemistry of edta complexes of ruthenium has been developing for the last three decades [1–3]. Most of the work published in earlier periods was limited to the aqueous chemistry of these compounds, mainly concerning the substitution behaviour of Ru–edta complexes [4–6], along with some electrochemical studies [7–9]. In recent years, the catalytic ability of ruthenium polyaminopolycarboxylate (pac) complexes in various organic transformations has been demonstrated. Moreover, a number of mixed-ligand complexes of ruthenium-containing pac ligands have been synthesised, and among these complexes some are of biological impor-

tance. The aim of this article is to bring into focus the intriguing areas of this system which have not been reviewed hitherto. This review is mainly concerned with the kinetics and mechanistic aspects of Ru–pac complexes towards substitution reactions, various Ru(III/II)–pac catalysed reactions and current investigation of mixed-ligand complexes of ruthenium containing pac ligands.

## 2. Background chemistry

The pac ligands form very stable 1:1 metal complexes with ruthenium. It was shown earlier [1,5,6] and later established by crystallographic studies [10,11] that pac ligands function as pentadentate ligands (represented in Fig. 1) towards ruthenium. The sixth coordination site for the metal centre is occupied by a water molecule at low pH or by a hydroxide ion at high pH. The $pK_a$ values associated with the deprotonation of the uncoordinated carboxylic acid group and the uncoordinated water molecule for various Ru–pac complexes are summarised in Table 1. Electrochemical studies of Ru–pac complexes have shown that the electron transfer process is rapid and reversible for the $Ru^{III}pac(H_2O)/Ru^{II}pac(H_2O)$ couple. Some important spectral and electrochemical data for precursor $Ru^{III}pac(H_2O)$ complexes are summarised in Table 1.

## 3. Substitution of Ru(III)–pac complexes

The substitution reactions of ligands displacing the water molecule from $Ru^{III}(pac)(H_2O)$ complexes follow associative interchange [Ia] pathways, but

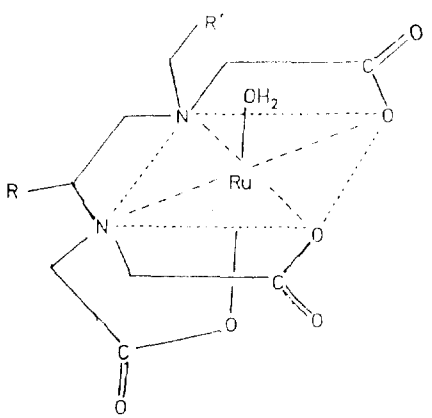



Fig. 1. Schematic representation of Ru–pap complexes. R=H, R'=–COOH: Ru(Hedta)($H_2O$); R=$CH_3$, R'=–COOH: Ru(Hpdta)($H_2O$); R=H, R'=–OH: Ru(hedtra)($H_2O$); R=H, R'=H: Ru(medtra)($H_2O$).

Table 1
Some important spectral, electrochemical and acid-dissociation constant data for $Ru^{III}(pac)(H_2O)$ complexes

| Complex | $\lambda_{max}$ ($\epsilon_{max}$) (in water) | $E_{1/2}$ (V)[c] | $pK_1$ | $pK_2$ | Ref. |
|---|---|---|---|---|---|
| $Ru^{III}(Hedta)(H_2O)$ | 280 (2800±50)<br>350[b] (680±30) | −0.04 | 2.4 | 7.6 | [6] |
| $Ru^{III}(Hpdta)(H_2O)$ | 282[a] (2890±50)<br>370[b] (940±50) | −0.05 | 2.3 | 8.1 | [11] |
| $Ru^{III}(hedtra)(H_2O)$ | 285[a] (1950±20)<br>350[b] (850±20) | −0.07 | | 4.9 | [17] |
| $Ru^{III}(medtra)(H_2O)$ | 290[a] (2400±30)<br>380[b] (920±60) | −0.10 | | 6.3 | [18] |

[a] Peak.
[b] Shoulder.
[c] $Ru^{III}/Ru^{II}$ couple vs. NHE, in water.

$Ru^{III}(edta)(H_2O)$ has an internal Ia pathway via its own pendant uncoordinated $-COO^-$ group which lowers $\Delta H^{\ddagger}$ by about 10 kJ mol$^{-1}$.

### 3.1. Substitution of the Ru(III)–edta complex with monodentate ligands

In 1979 Yoshino [5] reported that the reaction of $Ru(edta)(H_2O)^-$ with a variety of sulphur-containing ligands (cysteine, thiourea etc.) is too rapid to be followed by conventional mixing techniques, but thiosulphate reacts at a moderate rate [5]. This observation was in contrast to other ruthenium(III) complexes containing N and O donor atoms which were reported to be substitution-inert (i.e. react at a very slow rate) [12,13]. Matsubara and Creutz also observed the unusual lability of the $Ru^{III}(edta)(H_2O)^-$ complex towards substitution with various aromatic N-heterocycles [4,6]. The reaction was characterised by the rapid formation of a 1:1 (metal ligand) substituted product complex [Ru(edta)L]. However, formation of a 1:2 (metal ligand) product ($[Ru^{III}(edta)L_2]$) complex also takes place over a longer period when an excess of L is used. Stopped-flow kinetics of the aquo-substitution reaction revealed that under a pseudo-first-order condition of excess incoming ligand L, the values of the observed rate constant ($k_{obs}$) increase linearly with the concentration of entering ligand (L). The plots exhibited no meaningful intercepts, indicating an absence of reverse aquation under the conditions employed. The pH dependence of the process (Fig. 2) is associated with the substitution lability of the various edta complex species in equilibria (Eqs. (1) and (2)) and interpreted in terms of the following reaction paths (Eqs. (3)–(5))

$$Ru^{III}(edta\text{–}H)(H_2O) \overset{K_1}{\rightleftharpoons} Ru^{III}(edta)(H_2O)^- + H^+ \quad (1)$$

$$Ru^{III}(edta)(H_2O)^- \overset{K_2}{\rightleftharpoons} Ru^{III}(edta)(OH)^{2-} + H^- \quad (2)$$

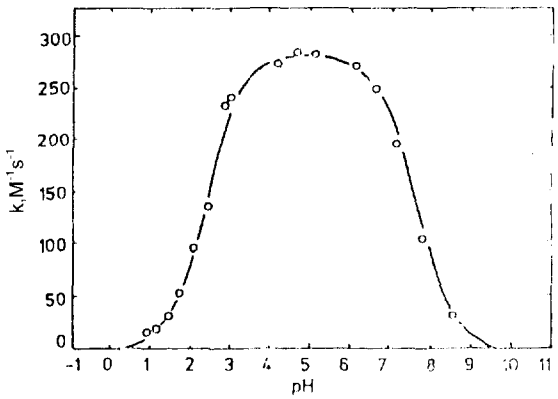



Fig. 2. Effect of pH on the second-order rate constant for the thiocyanate substitution of the Ru(III)–edta complex at 25 C (adapted from [6]).

$$Ru^{III}(edta\text{–}H)(H_2O)+L \overset{k_1}{\Rightarrow} Ru^{III}(edta\text{–}H)(L)+H_2O \quad (3)$$

$$Ru^{III}(edta)(H_2O)^- + L \overset{k_2}{\Rightarrow} Ru^{III}(edta)(L)^- + H_2O \quad (4)$$

$$Ru^{III}(edta)(OH)^{2-} + L \overset{k_3}{\Rightarrow} Ru^{III}(edta)(L)^- + OH^- \quad (5)$$

for which the following rate expression can be derived (Eq. (6))

$$k_{obs} = \{(k_1[H^+]^2 + k_2K_1[H^+] + k_3K_1K_2)/([H^+]^2 + K_1[H^+] + K_1K_2)\}[L] \quad (6)$$

The two inflections in the bell-shaped curve (Fig. 2) occur exactly at the $pK_1$ and $pK_2$ of the Ru(edta–H)($H_2O$) complex (Table 1). The maximum reactivity of the substitution reaction is observed in the pH range 4–6, where the values of the observed rate constant are practically independent of pH. The unusual lability of the Ru(edta)($H_2O$)$^-$ complex (which exists predominantly in the pH range 4–6) may be explained in terms of internal hydrogen bonding between an oxygen atom of the uncoordinated carboxylate group ($COO^-$) and the coordinated water molecule which creates either an open area for access to the entering ligand or labilises the coordinating water molecule by affecting the $Ru^{III}$–$OH_2$ bond strength.

A different mechanism involving transient coordination of a pendant group which assists the elimination of the coordinated water molecule in $Ru^{III}(edta)(H_2O)^-$ appeared in the literature [14,15]. Subsequently Bajaj and van Eldik, in a series of publications [16–18] reporting the effect of pressure on the substitution rate, established that it is neither hydrogen bonding nor transient coordination of the dangling

carboxylate group, but the carbonyl oxygen atom by virtue of its *syn* lone pair of electrons, which labilises the coordinated water molecule. Compelling evidence in favour of this was given in a recent report [19] where substitution of $[(NH_3)_5Ru^{III}(edta)Ru^{III}(H_2O)]^{2+}$ was carried out with TU. Although the incorporation of a pendant carboxylate group into the $[Ru^{III}(NH_3)_5]^{3+}$ moiety prevents the transient coordination as proposed by Ogino et al. [15], the rate of substitution was found to be higher than Ru(hedtra)($H_2O$) [17] and [Ru(medtra)($H_2O$)] [18] where chelate pac ligands do not contain any pendant carboxylic group. Results of the substitution of the Ru(edta)($H_2O$)$^-$ complex with various nucleophiles reported so far are summarised in Table 2. The data in Table 2 will be helpful in rationalising the nucleophilicity of various ligands towards substitution of $Ru^{III}$(edta)($H_2O$)$^-$.

### 3.2. Substitution of $Ru^{III}(edta)(H_2O)^-$ with bidentate ligands

The interaction of $Ru^{III}$(edta)($H_2O$)$^-$ with 2-mercaptopyridine [20] was characterised by a two step reaction. In the first step, rapid aquo-substitution takes place ($k = 1.05 \times 10^4 M^{-1} s^{-1}$ at 25 °C, pH = 5.0, $\mu = 0.1$ M) to produce a monosubstituted red ($\lambda_{max} = 550$ nm) product complex. This step is quite similar to those for other thio-ligands reported earlier [16]. The second step involves the ring-closure step in which a chelated green ($\lambda_{max} = 630$ nm) product is formed. The ring-closure step was found to be independent of ligand concentration, but dependent on the pH of the

Table 2
Rate and activation parameters for the reaction

$$Ru^{III}(edta)(H_2O)^- + L \underset{k_r}{\overset{k_f}{\rightleftarrows}} Ru^{III}(edta)L^- + H_2O$$

| Entering ligand (L) | $k_f^a$ ($M^{-1} s^{-1}$) | $k_r$ ($s^{-1}$) | $\Delta H_f^{\ddagger}$ (kJ $mol^{-1}$) | $\Delta S_f^{\ddagger}$ ((cal deg $C^{-1}$) $mol^{-1}$) | $\Delta V_f^{\ddagger}$ ($cm^3$ $mol^{-1}$) | Ref. |
|---|---|---|---|---|---|---|
| Pyrazine | 20000 ± 1000 | – | 24 ± 2 | −84 ± 13 | – | [6] |
| Pyridine | 6300 ± 500 | 2.0 ± 0.5 | – | – | – | [6] |
| Isonicotinamide | 8300 ± 600 | – | 28 ± 2 | −80 ± 14 | – | [6] |
| $CH_3CN$ | 30 ± 7 | 3.2 ± 0.2 | 35 ± 2 | −101 ± 16 | – | [6] |
| $SCN^-$ | 270 ± 27 | – | 37 ± 2 | −75 ± 6 | −9.5 ± 0.3 | [16] |
| Imidazole | 1860 ± 100 | – | – | – | – | [6] |
| Azide | 1885 ± 80 | – | 24.8 ± 1.4 | −99 ± 5 | −9 ± 0.6 | [6] |
| TU | 2970 ± 50 | – | 22.3 ± 1.4 | −105 ± 5 | −6.8 ± 0.6 | [16] |
| DMTU | 1450 ± 25 | – | 25.3 ± 1.3 | −107 ± 4 | −8.8 ± 0.2 | [16] |
| TMTU | 154 ± 5 | – | 28.9 ± 3.3 | −107 ± 11 | −12.2 ± 0.5 | [16] |
| $S_2O_3^{2-}$ | 2.94 ± 0.1 | – | – | – | – | [5] |
| DMSO | 11 ± 6 | 6 ± 2 | – | – | – | [85] |
| $Cl^-$ | 8.7 ± 1.1 | 27.2 ± 3.3 | – | – | – | [86] |
| $CN^-$ | 1.01 ± 0.5 | | 33 ± 4 | −126 ± 16 | – | [87] |
| $Fe(CN)_6^{4-}$ | 99 ± 5 | – | 28.3 | −112 ± 8 | – | [72] |

[a]Temperature = 25 °C, pH = 5.0.

medium. Similar kinetic behaviour was also observed in the reaction between $Ru^{III}(edta)(H_2O)^-$ and 4,6-dimethyl-2-mercaptopyrimidine [21]. The rate constant for the formation of monosubstituted product was found to be $7.8 \times 10^3 M^{-1} s^{-1}$ at 30 °C (pH = 5.1, $\mu$ = 0.2M). Detailed kinetic investigation on the pH dependence of the ring-closure step (Fig. 3) was carried out and the results interpreted in terms of the following acid-dissociation equilibrium (Eq. (7)) and chelate formation step (Eq. (8))

$$RH^+ + H_2O \overset{K_a}{\rightleftharpoons} R + H_3O^+ \tag{7}$$

$$R \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} V \tag{8}$$

(where $RH^+$ and R represent the protonated and deprotonated forms of a monosubstituted red complex, respectively, and V represents the violet chelate product) for which a rate expression is derived in Eq. (9)

$$k_{obs} = \frac{\{k_{-4}(K_a + [H_3O^+])\} + k_4 k_a}{K_a + [H_3O^+]} \tag{9}$$

As seen in Fig. 3, the $k'_{obs}$ values are independent of pH in low-acid ($K_a \gg [H_3O^+]$) and high-acid ($[H_3O^+] \gg K_a$) regions and go from $k'_{obs} = k_{-4}$ to $k'_{obs} = k_4 + k_{-4}$. The values of $k_4$ and $k_{-4}$ thus calculated are 0.91 and 0.41 $s^{-1}$, respectively. The apparent $pK_a$ (sum of $pK_a$ of $RH^+$ and log of chelation equilibrium) estimated by using the values of $k_4$ and $k_{-4}$, is 4.79 at 30 °C. The reaction of $Ru^{III}(edta)(H_2O)^-$ with a bidentate ligand is typically represented in Fig. 4.

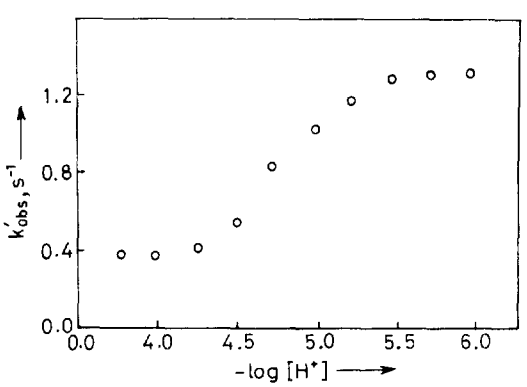



Fig. 3. pH versus rate constant. Profile for the ring-closure step of 30 °C (adapted from [21]).

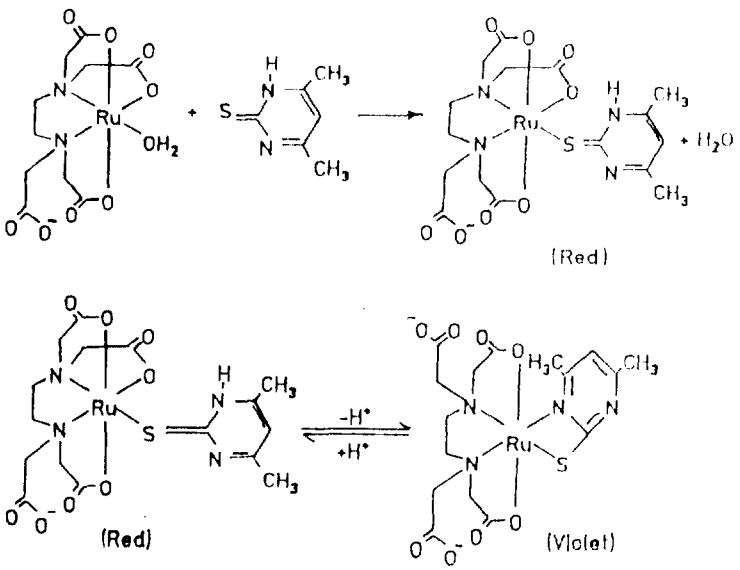



Fig. 4. Schematic representation of the reaction of $Ru(edta)(H_2O)^-$ with 4,6-dimethyl-2-mercaptopyrimidine (adapted from [21]).

### 3.3. Substitution reactions with the $Ru^{III}(pdta)(H_2O)^-$ complex

The coordination environments of $Ru^{III}(edta)(H_2O)^-$ and $Ru^{III}(pdta)(H_2O)^-$ are virtually identical in ligand-donor and steric effects. The substitution of $Ru^{III}(pdta)(H_2O)^-$ with TU and $SCN^-$ was carried out [11] as a function of ligand concentration, pH and temperature. The rate constant values ($k_2$) and activation parameters ($k_2 = 4170 \pm M^{-1} s^{-1}$, $\Delta H^{\ddagger} = 25 \pm 1$ kJ mol$^{-1}$, $\Delta S^{\ddagger} = -94 \pm 3$ J K$^{-1}$ mol$^{-1}$ for TU; $k_2 = 460 \pm 10 M^{-1} s^{-1}$, $\Delta H^{\ddagger} = 35 \pm 3$ kJ mol$^{-1}$, $\Delta S^{\ddagger} = -79 \pm 10$ J K$^{-1}$ mol$^{-1}$ for $SCN^-$) are quite comparable to those reported for the substitution of $Ru^{III}(edta)(H_2O)^-$ with TU and $SCN^-$. The slight extra lability of the pdta complex as compared to the edta complex may be attributed to the presence of an electron donating methyl group on the ethylene collar of the pdta ligand [11] which increases the electron density on the metal centre and causes an extra labilisation of the $Ru^{III}$–$OH_2$ bond.

### 3.4. Substitution reactions with the $Ru^{III}(hedtra)(H_2O)$ complex

Studies on the substitution of $Ru^{III}(hedtra)(H_2O)$ complex were necessary to evaluate the role of the pendant group on the substitution lability of the $Ru^{III}$–pac complex. In this regard, kinetic studies of substitution of $Ru^{III}(hedtra)(H_2O)$ with TMTU, DMTU, TU, $SCN^-$ and $N_3^-$ were carried out by Bajaj and Van Eldik [17]. The observed rate constant were found to increase linearly with increase of concentration of substituting ligands. The sigmoid-shape pH versus rate constant profile

showed limiting values of $k_{obs}$ ($=k_1[L]$) at low and high pH ($k_{obs}=k_2[L]$), respectively, with an inflection point at pH 4.7 ($=pK_a$). In another paper, Ogino and coworkers also reported the kinetic results of the substitution of [Ru(hedtra)($H_2O$)] with $Br^-$, $SCN^-$, py and $CH_3CN$ [15]. Although no basic difference in the kinetic behaviour of $Ru^{III}$(hedtra)($H_2O$) towards substitution was reported in those reports [15,17]. Ogino et al. retained to their postulate of the transient coordination of a pendant group ($-CH_2CH_2OH$). The useful kinetic data available so far for this particular system are summarised in Table 3.

### 3.5. Substitution reactions with the $Ru^{III}$(medtra)($H_2O$) complex

There seems to be only one report [18] available in the literature where the substitution of a [$Ru^{III}$(medtra)($H_2O$)] complex is described. The kinetics of the substitution of $Ru^{III}$(medtra)($H_2O$) with TMTU, DMTU, TU, SCN and $N_3^-$ were carried out as a function of entering ligand concentration, pH, temperature and pressure. The observed first-order rate constant again increased linearly with increasing ligand concentration. The pH dependence of the observed rate constant was interpreted in terms of the following acid-dissociation equilibrium (Eq. (10)) and reactions (Eqs. (11) and (12)).

$$Ru^{III}(medtra)(H_2O) \overset{K_a}{\rightleftharpoons} Ru^{III}(medtra)(OH)^- + H^+ \quad (10)$$

Table 3
Rate and activation parameters for the reaction

$$Ru^{III}(hedtra)(H_2O) + L \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Ru^{III}(hedtra)(L) + H_2O$$

| Ligand | $k_f^a$ ($M^{-1}s^{-1}$) | $k_r$ ($s^{-1}$) | $\Delta H_f^{\ddagger}$ (kJ $mol^{-1}$) | $\Delta S_f^{\ddagger}$ (J $mol^{-1}$ deg C) | $\Delta V_f^{\ddagger}$ | Ref. |
|---|---|---|---|---|---|---|
| $CH_3CN$ | $0.48 \pm 0.02$ | | | | | [15] |
| | | $3.0 \times 10^{-2}$ | | | | |
| Pyridine | $18 \pm 2$ | | | | | [15] |
| $Br^-$ | 0.13 | | | | | [15] |
| | | $1.9 \times 10^{-2}$ | | | | |
| $I^-$ | 0.08 | – | $63 \pm 2$ | $-54 \pm 7$ | | [88] |
| $SCN^-$ | $7.5 \pm 0.2$ | | $39 \pm 2$ | $-100 \pm 7$ | | [17] |
| | | $1.3 \times 10^{-2}$ | | | | |
| TU | $22.6 \pm 1.0$ | 0.03 | $34 \pm 1$ | $-105 \pm 2$ | $-4.1 \pm 0.7$ | [17] |
| DMTU | $9.4 \pm 2.0$ | 0.06 | $37 \pm 4$ | $-99 \pm 13$ | $-6.2 \pm 0.5$ | [17] |
| TMTU | $2.05 \pm 0.2$ | 0.1 | $39 \pm 2$ | $-100 \pm 7$ | $-7.3 \pm 0.6$ | [17] |
| $N_3^-$ | $18.5 \pm 2.6$ | – | $38 \pm 1$ | $-98 \pm 2$ | – | [17] |
| DMSO | $0.38 \pm 0.02$ | | $52 \pm 1$ | $-81 \pm 3$ | | [89] |
| Pyrazine | 50 | – | – | – | – | [6] |
| $Fe(CN)_6^{4-}$ | 2.6 | | – | – | – | [73] |

[a] Temperature = 25 °C.

$$Ru^{III}(medtra)(H_2O)+L \xrightarrow{k_1} Ru^{III}(medtra)(L)+H_2O \quad (11)$$

$$Ru^{III}(medtra)(OH)^- + L \xrightarrow{k_2} Ru^{III}(medtra)(L)+OH^- \quad (12)$$

A rate expression derived by considering the equilibrium (Eq. (10)) and reactions (Eqs. (11) and (12)) is outlined in Eq. (13)

$$k_{obs} = \{(k_1[H^+]+k_2K_a)/[K_a+H^+]\}[L] \quad (13)$$

The rate law (Eq. (13)) predicts a sigmoid-shaped curve for the plot of $k_{obs}$ versus pH with limiting values of $k_{obs}=k_1[L]$ and $k_{obs}=k_2[L]$ at low and high pH, respectively. The value of $pK_a$ calculated from the inflection point is 6.25 to the value estimated by potentiometry. A careful analysis of the rate data reveals that within the series of aquo/hydroxo complexes, the substitution rate constants decrease substantially along the series edta≫hedtra>medtra. This is accompanied by a general increase in $\Delta H^{\ddagger}$ and almost constant $\Delta S^{\ddagger}$. From this trend the highest lability is induced by the pendant group when $R=CH_2COO^-$, with significantly decreased lability for $R=CH_2CH_2OH$ and even further for $R=CH_3$ (Fig. 1). This substantiates the important role of the dangling pendant carboxylate group, as discussed earlier in the labilisation of the coordinated water molecule in the $Ru^{III}(edta)(H_2O)^-$ complex.

### 3.6. *Substitution of $Ru^{III}(edta)L$ with L′ (where L and L′ are ligands other than $H_2O$)*

The general reaction in this category can be represented in Eq. (14)

$$Ru(edta)L+L' \xrightarrow{k} Ru(edta)L'+L \quad (14)$$

Substitution of $Ru^{III}(edta)L$ (where $L=CH_3CN$, $SCN^-$) with L′ (pyrazine) was reported [6] to be independent of the concentration of substituting ligand L′. Moreover, for a particular $Ru^{III}(edta)L$, the rate of reaction was found to be independent of the nature of the substituting ligands. This suggests the operation of a dissociative mode of activation in the substitution process involving the formation of $Ru^{III}(edta)(H_2O)^-$ species in a rate-determining step. Arguments in favour of the proposed mechanism are supported as the rate constant data ($k$) obtained experimentally for reaction (Eq. (14)) are identical, within experimental error, to the rate constant data for the corresponding reverse equation ($k_{-1}$ step) of $Ru^{III}(edta)L$ complexes.

### 3.7. Substitution reactions with the $Ru^{II}(edta)(H_2O)^{2-}$ complex

Substitutions of $Ru^{II}(edta)(H_2O)^{2-}$ with $CH_3CN$, $SCN^-$ and isonicotinamide (isn) were also reported by Matsubara and Creutz [6]. However, this has not received much further attention. The reason may be that the substitution behaviour of Ru(II)edta does not differ much from other Ru(II) complexes. Also, there is a disadvantage in working with the Ru(II)edta system as it is very sensitive to aerial oxidation and the presence of Ru(III) in the system causes erroneous results. Notwithstanding the above facts, the rate of substitution of $Ru^{II}(edta)(H_2O)^{2-}$ with $CH^3CN$, $SCN^-$ and isn was found to be first-order with respect to both $Ru^{II}(edta)$ and entering ligand concentrations. In all cases the reaction did not exhibit any pH dependence in the pH range 3.0–5.5 which indicates that the reactivity of $Ru^{II}(edta\text{–}H)(H_2O)^-$ and $Ru^{II}(edta)(H_2O)^{2-}$ are comparable. Thus the driving force in Ru(III) which arises due to the unprotonated free carboxylate group is seem to be absent in the Ru(II)–edta system. It appears, therefore, that two labilisation mechanisms are operative. Unlike Ru(III), the Ru(II) substitutions do not proceed via a pathway requiring a free, unprotonated carboxylate group. Labilisation in this system is ascribed to the coordination of the chelating ligand edta and lowering of the effective positive charge to the metal centre which reduces the barrier to a dissociative substitution process. The values of the forward rate constant ($k_f$) of the substitution reaction (Eq. (15))

$$Ru^{II}(edta)(H_2O)^{2-} + L \underset{k_r}{\overset{k_f}{\rightleftarrows}} Ru(edta)(L)^{2-} + H_2O \qquad (15)$$

range from $2.7 \pm 0.2 M^{-1} s^{-1}$ to $30 \pm 15 M^{-1} s^{-1}$ at 25 °C. The values of reverse rate constants ($k_r$) were reported to be negligibly small.

## 4. Oxidation reactions catalysed by Ru–pac complexes

Dioxygen complexes of transition metals play an important role in a number of biological and chemical reactions. Synthetic metal complexes of dioxygen serve as models in a variety of reactions; they have potential use in electrochemical cells for air-batteries [22]. The complexes also serve as oxidising agents or reactive intermediates in catalytic oxidation of organic compounds.

### 4.1. Interaction of Ru–pac complexes with $O_2$ and $H_2O_2$

The formation of a Ru(IV)–peroxo complex species in the reaction of Ru(III)–edta complex and dioxygen ($O_2$) was first reported by Ezerskaya and Solovykh [23,24]. Taqui Khan et al. [25,26] also proposed the formation of a peroxo species $[\{Ru^{IV}(edta)\}_2O_2]^{2-}$ as a catalytic intermediate in the oxidation of various organic substrates [25,26] with molecular oxygen catalysed by the Ru(III)–edta complex. Spectral, electrochemical and kinetic evidence were presented for substantiating the formation of a Ru(IV)–peroxo complex in the catalytic processes.

However, formation of $[\{Ru^{IV}(edta)\}_2O_2]^{2-}$ in the oxidation of $Ru^{III}(edta)(H_2O)^-$ with molecular oxygen or $H_2O_2$ was questioned by Hurst et al. [27]. They reported the formation of a mixed-valent dimeric μ-oxo $Ru^{III}$–$Ru^{IV}$ species in the oxidation of $[Ru^{III}(edta)(H_2O)]^-$ with $O_2$ (in a neutral or slightly alkaline solution) or $H_2O_2$ (in a neutral or slightly acidic medium). Although this mixed-valence species was reported [28] to form spontaneously at high pH in the presence of $O_2$, Hurst et al. substantiated the formation of the μ-oxo $Ru^{III}$–$Ru^{IV}$ dimer with the help of low-temperature resonance Raman spectral data. This binuclear μ-oxo $[\{Ru(edta)\}_2O]^{3-}$ complex was, however, reported to be incapable of effecting an oxidation reaction catalytically. Shepherd et al. [29], on the other hand, observed evidence in favour of the formation of a superoxide species in the reaction of Ru(III)–pac complexes (pac = edta, hedtra, ttha) with $H_2O_2$. The formation of these superoxide species was confirmed by the characteristic seven-line EPR spectrum with coupling constants $A_N = 10.0$ G and $A_H = A_{H'} = 5.0$ G. However, an entirely different species is reportedly formed [30] when the oxidising agent is *t*-BuOOH instead of $H_2O_2$. The coupling constant values estimated from EPR studies are then $A_N = 7.5$ G and $A_H = 4.0$ G.

Since, $Ru^{III}$–pac complexes (pac = edta, hedtra, $me_2$edda) are found to be active in catalysing the epoxidation of olefins [26,31], the reviewer opines in favour of the formation of Ru–oxenoid species in the reaction of $Ru^{III}$-pac complexes with $H_2O_2$ or other oxidising agents.

### *4.2. Oxidation of organic compounds catalysed by Ru–pac complexes*

Taqui Khan's group had observed that the $Ru^{III}(edta)(H_2O)^-$ complex can catalyse the oxidation of various organic substrates (phosphines [26], amines [32], sulphide [33], etc.) with molecular oxygen. However, the rate of oxidation is too slow for its successful commercial application. This group also reported [34] a system comprising $[Ru^{III}(edta)(H_2O)]^-$/ascorbic acid/$H_2O_2$ (or $O_2$) as an analogue of the Udenfriend system [35] ($Fe^{II}$–edta/ascorbic acid/$O_2$). The system is capable of performing epoxidation of cyclohexene and hydroxylation of cyclohexane catalytically. The formation of a $Ru^{IV}{=}O$ intermediate, as proposed by them [34], is consistent with the electrochemical generation of such a species reported by Zhang et al. [36].

The formation of high-valent metal oxo species as an intermediate is the key step in the catalytic oxygenation of organic compounds with single oxygen-atom donating agents (XO) like NaOCl, $KHSO_5$, PhIO, etc. The rate of formation of the metal–oxo complexes in the reaction between the metal complexes and XO is very important as it governs the efficiency of the catalytic processes. The $Ru^{III}$–edta complex reacts with XO to yield a high-valent terminally coordinated $[Ru^{V}(edta)(O)]^-$ species which was isolated and characterised by physicochemical analysis [37]. The rate of oxo complex formation is first-order both in $Ru^{III}(edta)(H_2O)^-$ and XO concentrations. Based on the kinetic observations, a mechanism involving substitution of $Ru^{III}(edta)(H_2O)^-$ with XO in a rate-determining aquo-replacement step followed by rapid electron transfer to produce $[Ru^{V}(edta)(O)]^-$ is outlined in Eq. (16).

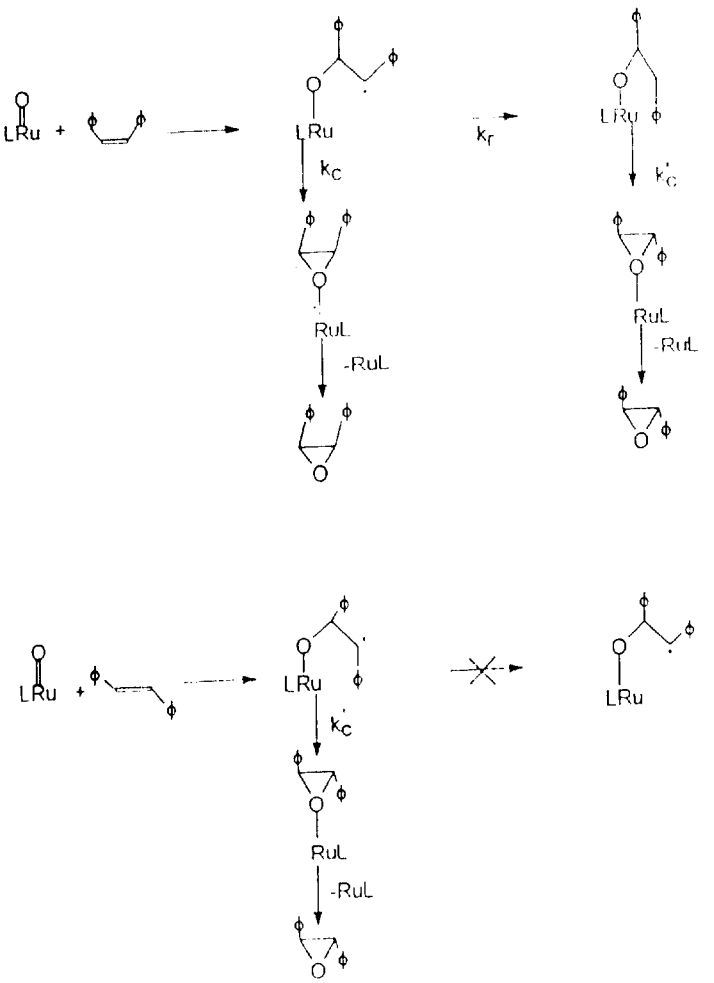
$$[Ru^{III}(edta)(H_2O)]^- + XO \xrightarrow{k_{OX}} [Ru^{III}(edta)(OX)]^- \rightarrow [Ru^{V}(edta)(O)]^- \quad (16)$$

The values of the rate constants ($k_{OX}$) for various oxidants (XO) are $0.07M^{-1}s^{-1}$ (NaOCl) [37], $0.89M^{-1}s^{-1}$ ($KHSO_5$) [38] and $75.8M^{-1}s^{-1}$ (PhIO) [39]. The kinetic results are suggestive that the rate of formation of Ru(V)–OXO species is substitution-controlled. (It is not only governed by the oxidation potentials, but also the nucleophilicity of the oxidants (XO) for replacing the aquo molecule from the $[Ru^{III}(edta)(H_2O)]^-$ complex.)

$[Ru^{V}(edta)(O)]^-$ effects O-atom transfer to [37] in a water–dioxane medium. It generally epoxidises olefins, oxidises alcohols to aldehydes or ketones and hydroxylates saturated C–H bonds for a wide range of substrates. A strict stereochemical retention (i.e. *cis*-epoxide from *cis*-stilbene and *trans*-epoxide from *trans*-stilbene) was observed in the epoxidation of stilbenes with $[Ru^{V}(edta)(O)]^-$ [37]. A four-membered metallo cyclooxetane intermediate was suggested in order to explain the stereo-selectivity observed in the reaction [37]. In contrast, the $Ru^{III}$–(pac)/*t*-BuOOH system (pac = hedtra, $me_2$edda) epoxidise stilbenes effectively with the loss of stereochemistry for *cis*-stilbene. A large amount of *trans*-epoxide versus *cis*-epoxide (5.5:1) was reportedly observed [31] to form from *cis*-stilbene, whereas *trans*-stilbene is converted to *trans*-epoxide only. This indicates a predominantly radicaloid character of the $Ru^{III}$(hedtra)/*t*-BuOOH epoxidation process. The loss of stereochemistry via the radical addition pathway can be explained in terms of competition between rotation within the radical intermediate with that of ring-closure to form the epoxide product (Scheme 1). In the lesser strained radical intermediate the rate of rotation is too low to compete with ring-closure and as a consequence only *trans*-epoxide is formed from *trans*-stilbene. The *cis*-radical intermediate may rotate in competition with ring-closure to produce a mixture of *trans* and *cis*-epoxides. The pac ligands contain harder N and O donors. Therefore, the stronger Ru–O bonds in Ru(V)–oxo complexes containing pac ligands effect the O-atom transfer via a radical pathway for epoxidation of olefins. Although the coordination environment of Ru(III)–edta and Ru(III)–hedtra and their oxo-adducts are virtually identical in ligand donors and steric effects, the steric retention of *cis*-epoxide stereochemistry [37] may be due to a solvation effect as the epoxidation was carried out in a mixed solvent (50:50 water–dioxane) system. A crowded coordination sphere of the larger dioxane molecule might have influenced the approach orientation of the stilbenes. The influence of solvent composition on the Ru(III)–pac complex catalysed epoxidation would be worthy of further investigation in order to explore the possibility of changing and controlling the epoxidation stereochemistry.

## 5. Electrocatalysis with the Ru(III/II)–edta complex

The reductive electrochemistry of $[Ru^{II}(Hedta)(NO^+)]^0$ was reported by Meyer et al. [40,41]. The nitrosyl complex was shown to be an effective electrocatalyst for



Scheme 1.

the reduction of $NO_2^-/HNO_2$ to yield $N_2O$, $N_2$, $NH_3OH^+$ or $NH_4^+$ as reaction products. Individual steps involved in a typical six-electron reduction of $NO_2^-$ to $NH_4^+$ are shown in Eqs. (17)–(19).

$$[Ru^{II}(Hedta)(H_2O)]^- + NO_2^- + 2H^+ \rightarrow [Ru^{II}(Hedta)(NO^+)]^0 + 2H_2O \quad (17)$$

$$[Ru^{II}(Hedta)(NO^+)]^0 + 6e + 5H^+ \rightarrow [Ru^{II}(Hedta)(NH_3)]^- + H_2O \quad (18)$$

$$[Ru^{II}(Hedta)(NH_3)]^- + H^+ + H_2O \rightarrow [Ru^{II}(Hedta)(H_2O)]^- + NH_4^+ \quad (19)$$

Similar reactions can be written for reduction to the intermediate oxidation states of $N_2O$, $N_2$ or $NH_3OH^+$. An element of product selectivity is available by making appropriate choices in pH and the applied potential.

Another intriguing example of reductive electrochemical properties of the Ru–edta complex is available in very recent reports [42,43], where electrocatalytic reduction of the coordinated hydrazinium ion ($N_2H_5^+$) to ammonia is described. The efficiency of the system expressed in terms of moles of ammonia per mole of catalyst per hour is 14.4 at pH 2.8 (9.5 at pH 1.9) with 100% coulombic efficiency, as calculated in constant potential electrolysis at −0.05 V (Hg) vs SCE. A working mechanism proposed for the catalytic reaction is outlined below (Eqs. (20)–(26)).

$$[Ru^{III}(edta)(H_2O)]^- + N_2H_5^+ \rightarrow [Ru^{III}(edta)(N_2H_5)] + H_2O \quad (20)$$

$$[Ru^{III}(edta)(N_2H_5)] + 2e = = = [Ru^{I}(edta)(N_2H_5)]^{2-} \quad (21)$$

$$[Ru^{I}(edta)(N_2H_5)]^{2-} = = = [Ru^{III}(edta)(NH_2)]^{2-} + NH_3 \quad (22)$$

$$[Ru^{III}(edta)(NH_2)]^{2-} + H^+ \rightarrow [Ru^{III}(edta)(NH_3)]^- \quad (23)$$

$$[Ru^{III}(edta)(NH_3)]^- + H_2O \rightarrow [Ru^{III}(edta)(H_2O)] + NH_3 \quad (24)$$

$$[Ru^{III}(edta)(NH_3)]^- + N_2H_5^+ \rightarrow [Ru^{III}(edta)(N_2H_5)] + NH_3 \quad (25)$$

$$[Ru^{III}(edta)(H_2O)]^- + N_2H_5^+ \rightarrow [Ru^{III}(edta)(N_2H_5)] + H_2O \quad (26)$$

The notable feature of this catalytic system is that the electroreduction of hydrazine catalysed by the $Ru^{III}(edta)(N_2H_5)$ complex is achieved at very low reduction potential (−0.05 V vs SCE) with 100% coulombic efficiency. This is probably the first example of a transition metal complex catalysed activation of the N–N bond in water solution.

## 6. Mixed-ligand complexes of ruthenium(II) and ruthenium(III) containing the pac ligand

In many ways, the chemistry of mixed-ligand complexes of ruthenium(II) and ruthenium(III) containing the pac ligand is of great interest in its own right. In context to the catalytic reactions, the formation of mixed-ligand complexes of $Ru^{III}$–edta takes place through rapid aquo-substitution of the catalytic process. In general, formation of mixed-ligand complexes of $Ru^{III}$–edta takes place through a

rapid aquo-substitution step (for monodentate ligand) followed by chelation (for bidentate ligand) through the removal of the one coordinated carboxylate group. Important complexes of this class are discussed below.

### 6.1. Mixed-ligand complexes of π-accepting ligands

Mixed-ligand complexes of ruthenium(II)–edta containing π-acceptor ligands X (X = $N_2$, CO, NO, RCN) were first reported by Diamantis and Dubrawski [44] in 1981. The $[Ru^{II}(H_nedta)X_n]$ ($n=1$, 2, X = $N_2$, CO, RO, RCN) complexes were prepared by reacting aqueous solutions of $[Ru^{II}(Hedta)(H_2O)]^-$ (formed by the reduction of $Ru^{III}(Hedta)(H_2O)$ with $H_2$ on platinum black) with the appropriate ligand. In the case of X = $N_2$, a terminal and a bridging complex were identified [44]. Taqui Khan et al. in subsequent papers reported the synthesis and structural information of mixed-ligand ruthenium(III) complexes of edta containing the π-accepting ligands NO [45], phosphines and arsines [46], CO [47] and $SnCl_3$ [48]. The stabilisation of ruthenium(III) species (higher oxidation state) with these π-acceptors can be explained in terms of the combined effect of the presence of the hard donor atoms (N, O) and the chelate effect of edta in [Ru(Hedta)(X)] complexes. Another set of mixed-ligand complexes of the type $[Ru^{II}(H_2edta)L]$ (L = 2, 2′-bipy, 4,4′-dimethyl, 2,2′-bipy, 1,10-phenanthroline, dimethylglyoximate) and $[Ru^{III}(H_2edta)L_2]$ (L = $(SCN)_2$, acetylacetonate, dimethylglyoximate, diethyldithiocarbamate) were reportedly prepared [49] by substitution reactions of $Ru^{II}(Hedta)(H_2O)^-$ and $Ru^{III}(Hedta)(H_2O)$, respectively. The complexes were characterised by analytical and spectroscopic methods including $^{13}C$ NMR and were shown to accommodate L in the equatorial positions, giving rise to a molecule possessing a $C_2$ axis. Resistance to the oxidation of these mixed-ligand complexes measured by cyclic voltametric studies was found to depend on the nature of the ligand L and followed the sequence NO, CO > RCN > bipy, *o*-phen > Py > $N_2$ (terminal) > SCN > $N_2$ (bridging) > acac > dmg.

### 6.2. Mixed-ligand complexes of DNA-bases and related ligands

The Ru–pac complexes are known to be potential antitumour agents [50,51] since some tumours concentrate the Ru–pac complex. In this connection, Shepherd et al. reported mixed-ligand complexes [52–59] of Ru–pac (pac = hedtra, ttha) with a series of ligands related to DNA-bases. The binding sites of these biochemically important ligands have been discussed in relation to the importance of these complexes in chemotherapy. A novel $\eta^2$-coordination mode for Ru–pac (pac = ttha, hedtra) at the C5–C6 olefinic double bonds of uridine- and cytidine-related bases was reported along with the normal binding sites N3 (or N1) in the absence of methyl or ribose blocking groups at N1 or N3 sites. The important chemical feature is that the pac environment favours π-donation by the Ru centre. However, no experimental evidence for the $\eta^2$-attachment was observed in the case of aromatic N-heterocycle (pyridine, pyrazine etc.) and thymidine base in their reaction with the Ru(II)–hedtra complex. This assumes the importance of the pyrimidine structure

for allowing $\eta^2$-coordination. The affinity of $Ru^{II}$–pac complexes for the $\eta^2$ pyrimidine site has been shown to be a balance of electronic and steric factors. The work explores a new method for altering the pyrimidine nucleobase components of DNA and appears to be of tremendous significance in the design and development of a new family of antitumour metallodrugs and reagents for molecular biochemistry. Even more remarkable than the $\eta^2$-coordination is the $\eta^4$-coordination reported very recently by Shepherd [60] in the complexation of *S,S*-[$Ru^{II}$($Me_2$edda] with potentially bidentate dienes. Two free coordination sites of the $Ru^{II}$–complex must be available to form $\eta^4$-coordination with dienes. Energetics of second olefinic attachment in the strained $Ru^{II}$–pac is achievable with modest chelate ring rearrangements.

The synthesis and characterisation of some mixed-ligand complexes of $Ru^{III}$–edta containing various purine and pyrimidine bases [61–63] along with some spectral and electrochemical data are also available in the literature. No $\eta^2$-coordination was reported. Recently [64], the reactivity of $Ru^{III}(edta)(H_2O)^-$ with nucleic bases, nucleosides and DNA (calf-thynms) was studied kinetically. Careful analysis and comparison of the stopped-flow kinetic data suggest that the binding of $Ru^{III}(edta)(H_2O)^-$ with DNA probably takes place through the adenine base unit in a kinetically preferred pathway.

## 7. Binuclear complexes of Ru–pac

Diruthenium(III) μ-oxo complexes containing edta and bridging amino-acids were reported recently by Taqui Khan's group [65]. This work stems from an interest in developing the chemistry of μ-oxo μ-acetato complexes of ruthenium [66,67] parallel to that of the diiron complexes cores in non-haeme proteins, which are known to be active centres in various metabolisms [68,69]. The $[\{Ru^{III}(edta)L\}_2O]^{6-}$ complexes (L = alanine, phenylalanine and valine) [65] were synthesised and characterised by physico-chemical methods. They are stable under inert atmosphere, but undergo an oxidative deamination reaction in the presence of oxygen to yield α-keto acid and ammonia.

The kinetics and mechanism of redox reactions involving mixed-valence complexes containing the Ru–edta moiety were first reported by Haim et al. [70]. Oxidation of the mixed-valence compound $[Ru^{II}(NH_3)_5\ pzRu^{III}(edta)]^+$ by peroxydisulphate ($S_2O_8^{2-}$) proceeds through a combined $S_2O_8^{2-}$-independent and $S_2O_8^{2-}$-dependent pathway. The $S_2O_8^{2-}$-independent step concerns the slow decomposition of mixed-valence dinuclear species to $[Ru^{II}(NH_3)_5pz]^{2+}$ and $[Ru^{III}(edta)(H_2O)]^-$, followed by the rapid oxidation of $[Ru^{II}(NH_3)_5pz]^{2-}$ to $[Ru^{III}(NH_3)_5pz]^{3-}$. Whereas in the $S_2O_8^{2-}$-dependent pathway the reaction between the dinuclear complex $[Ru^{II}(NH_3)_5pzRu^{III}(edta)]^+$ and $S_2O_8^{2-}$ resulted in the formation of $Ru^{III}$–$Ru^{III}$ species. Further kinetic observation on the oxidation of the reduced form ($Ru^{II}$–$Ru^{II}$) of the mixed-valent dinuclear species ($Ru^{II}$–$Ru^{III}$) shows that it reacts with $S_2O_8^{2-}$ in a biphasic manner. The first phase corresponds to the formation of a mixed-valence $[Ru^{III}(NH_3)_5pzRu^{II}(edta)]^+$ compound which is an electronic isomer

of the $[Ru^{II}(NH_3)_5pzRu^{III}(edta)]^+$ compound. The $[Ru^{III}(NH_3)_5pzRu^{II}(edta)]^+$ species undergoes rapid intramolecular electron transfer to produce a stable $[Ru^{II}(NH_3)_5pzRu^{III}(edta)]^-$ isomer. The second phase of this reaction involves the oxidation of $Ru^{II}$–$Ru^{III}$ compounds as described above. Another recent paper [71] by Haim et al. reports the intramolecular electron transfer from $[Ru^{II}(edta)]^{2-}$ to $[Co^{III}(NH_3)_5]^{3+}$ through N-heterocyclic bridging ligands (L) in binuclear complexes of the type $[Ru^{II}(edta)LCo^{III}(NH_3)_5]^{2+}$ (L = pyrazine, 4,4′-bipyridine, 3,3′-dimethyl-4,4′-bipyridine, *trans*-1,2-bis(4-pyridyl)ethylene, 1,4-bis(4-pyridyl)-butadyne). The decrease in electron transfer-rate constant with increasing the bridging distance between two metal centres is ascribed to the increase in solvent reorganisation energy with increasing metal–metal distance.

Another important class of dinuclear complexes are cyano-bridged mixed-valence heterobinuclear complexes of the type $[Ru^{III}(pac)NcFe^{II}(CN)_5]^{n-}$ ($n=5$ for pac = $edta^{4-}$; $n=4$ for pac = $hedtra^{3-}$) [72,73]. These mixed-valence complexes are easy to synthesise by facile and straightforward aquo-substitution by $[Fe(CN)_6]^{4-}$ in aqueous solution. These complexes exhibit intervalence charge transfer (ICVT) in the near-IR region (940–950 nm). An observed thermochromic effect has been explained in terms of a modified Hush theory [74]. These compounds seem to be very promising materials for developing materials for non-linear optics with reference to a dinuclear pentammine ruthenium complex which has already secured its place in this context [75]. The synthesis and physico-chemical studies of some other novel binuclear complexes of the types $[\{Ru^{III}(edta)\}_2L]^{2-}$ and $[Ru^{III}(edta)LFe^{II}(CN)_5]^{4-}$ (where L = pyrazine, 4,4′-bipyridine, 3,3′-dimethyl-4,4′-bipyridine, *trans* 1,2-bis(4-pyridyl)ethylene) [76,77] have been reported very recently from this group. All these binuclear complexes show weak metal–metal interaction depending on the nature of the bridging ligands.

A different type of binuclear ruthenium complex containing a pac ligand other than edta was reported by Shepherd et al. [78,79]. The pyrimidine- and bipyridyl-bridged $[Ru^{II}_2(ttha)L]$ (L = pyrimidine, 4,4′-bipyridyl) complexes were prepared and characterised in solution by spectral methods. The stability of these complexes in the mixed oxidation state is discussed with reference to the role of carboxylate anionic donors which stabilise the Ru(III)-state, thus giving isolated valence properties.

## 8. Miscellaneous reactions

The interaction of sulphur(IV) oxides with $[Ru^{III}(edta)(H_2O)]^-$ in aqueous solution resulted in the formation of a stable product as indicated by EPR and electrochemical results [80]. The experimental results further suggest the formation of a μ-oxo $[\{Ru^{III}(edta)\}_2O]^{4-}$ intermediate in a rapid sulphite independent step. Another recent publication [81] reports the pyridyl to amido and amido to pyridyl isomerisation in an isonicotinamide complex of ruthenium(III) containing an edta ligand. Although the substitution kinetics of $[Ru^{III}(edta)(H_2O)]^-$ with isonicotinamide were reported a long time ago [6], where coordination of the isonicotinamide ligand

proposedly takes place through the pyridine-N atom, experimental evidence in favour of pyridyl-N to amido-N isomerisation along with the detailed kinetic results are provided in this report [81]. An electron transfer reaction involving the mononuclear Ru(III)–edta system has been reported very recently [82]. Kinetic and mechanistic investigation of the reduction of $[Ru^{III}(edta)(pz)]^-$ with ascorbic acid and catechol shows that the reduction process occurs through an outersphere electron transfer pathway [82].

The possibility of using Ru–pac complexes (pac = edta, ttha) as nitric oxide (NO) scavenger was explored recently [83,84]. Overproduction of NO is implicated in a number of disease states such as epilepsy, arthritis, hypertension and septic shock [85,86]. The scavenging and removal of NO is a therapeutic approach for the treatment of NO overload diseases. The $Ru^{III}(edta)(H_2O)^-$ complex by virtue of its remarkable lability is reported to reduce [83] the level of NO (measured as nitrite) in the cell culture medium of NO producing RAW 264 macrophages [83]. The other pac complex, $[Ru_2^{III}(ttha)(H_2O)_2]^{2-}$, also reacts directly [84] with NO to form the corresponding nitrosyl complex.

## 9. Conclusion

The purpose of this review article is to focus various intriguing aspects of the chemistry of Ru–pac complexes. The majority of the work described has only appeared in the recent past. The catalytic ability of Ru–pac complexes in various organic transformation reactions appears to be encouraging and further development in this area is awaited. It would be of great interest to see Ru–pac complexes anchored in some solid support (for example polymeric matrices, zeolite cavity or clay interlayer) performing catalysis with a better degree of preference than that observed in homogeneous reaction. On the other hand, Ru(III)–pac complexes by virtue of their remarkable lability provide a facile route for preparing various mixed-ligand complexes. Some of these are of bio-chemical importance [55–64], and some [72,73] may find a place in developing molecular devices. In coming years the chemistry of these Ru–pac complexes is surely going to be exciting!

## References

[1] M. Mukaida, H. Okuno, T. Ishimori, Nippon Kagaku Zasshi 86 (1965) 589.
[2] N.A. Ezorskaya, T.P. Solovykh, Russ. J. Inorg. Chem. (Engl. Transl.) 11 (1966) 991.
[3] J. Scherzer, L.B. Clapp, J. Inorg. Nucl. Chem. 30 (1968) 1107.
[4] T. Matsubara, C. Creutz, J. Am. Chem. Soc. 100 (1978) 6255.
[5] Y. Yoshino, T. Uehiro, M. Saito, Bull. Chem. Soc. Jpn. 52 (1979) 1060.
[6] T. Matsubara, C. Creutz, Inorg. Chem. 18 (1979) 1956.
[7] K. Shimizu, T. Matsubara, G.P. Sato, Bull. Chem. Soc. Jpn. 47 (1974) 1651.
[8] K. Shimizu, Bull. Chem. Soc. Jpn. 50 (1977) 2921.
[9] N. Oyama, F.C. Anson, J. Electroanal. Interfacial. Electrochem. 88 (1978) 289.
[10] M.M. Taqui Khan, H.C. Bajaj, Z. Shirin, K. Venkatasubramanian, Ind. J. Chem. (A) 31 (1992) 303.

[11] M.M. Taqui Khan, H.C. Bajaj, Z. Shirin, K. Venkatasubramanian, Polyhedron 11 (1992) 1059.
[12] P.C. Ford, Coord. Chem. Rev. 5 (1970) 75.
[13] J.N. Armor, H.A. Scheidegger, H. Taube, J. Am. Chem. Soc. 90 (1968) 5928.
[14] H. Ogino, M. Shimura, Adv. Inorg. Chem. Bio-inorg. Mech. 4 (1985) 107.
[15] H. Ogino, T. Katsuyama, S. Ito, Bull. Chem. Soc. Jpn. 63 (1990) 1370.
[16] H.C. Bajaj, R. Van Eldik, Inorg. Chem. 27 (1988) 4052.
[17] H.C. Bajaj, R. Van Eldik, Inorg. Chem. 28 (1989) 1980.
[18] H.C. Bajaj, R. Van Eldik, Inorg. Chem. 29 (1990) 2855.
[19] D. Chatterjee, H.C. Bajaj, J. Chem. Soc. Dalton Trans. (1993) 1065.
[20] H.E. Tomna, P.S. Santos, M.P.D. Mattioli, L.A.A. Oliveira, Polyhedron 6 (1987) 603.
[21] M.M. Taqui Khan, D. Chatterjee, A. Hussain, M.A. Moiz, Polyhedron 9 (1990) 2681.
[22] D.T. Sawyer, E.T. Seo, Inorg. Chem. 16 (1977) 499.
[23] N.A. Ezerskaya, T.P. Solovykh, Zh. Neorg. Chim. 12 (1967) 2922.
[24] N.A. Ezerskaya, T.P. Solovykh, Zh. Neorg. Chim. 13 (1968) 186.
[25] M.M. Taqui Khan, A. Hussain, G. Ramachandraiah, M.A. Moiz, Inorg. Chem. 25 (1986) 3023.
[26] M.M. Taqui Khan, M.R.H. Siddiqui, A. Hussain, M.A. Moiz, Inorg. Chem. 25 (1986) 2765.
[27] J. Zhou, W. Xi, J.K. Hurst, Inorg. Chem. 29 (1990) 160.
[28] K. Shimizu, T. Matsubara, G.P. Sato, Bull. Chem. Soc. Jpn. 47 (1974) 1651.
[29] S. Zhang, R.E. Shepherd, Inorg. Chem. 27 (1988) 4712.
[30] S. Zhang, R.E. Shepherd, Inorg. Chim. Acta 193 (1992) 217.
[31] R.E. Shepherd, Inorg. Chim. Acta 209 (1993) 201.
[32] M.M. Taqui Khan, S.A. Mirza, H.C. Bajaj, J. Mol. Catal. 33 (1987) 67.
[33] M.M. Taqui Khan, H.C. Bajaj, D. Chatterjee, J. Mol. Catal. 71 (1992) 177.
[34] M.M. Taqui Khan, R.S. Shukla, A. Prakash Rao, Inorg. Chem. 28 (1989) 452.
[35] S. Udenfriend, C.T. Clark, J. Axelrod, B.B. Brodie, J. Biol. Chem. 208 (1954) 731.
[36] S. Zhang, L.A. Holl, R.E. Shepherd, Trans. Met. Chem. 17 (1992) 390.
[37] M.M. Taqui Khan, D. Chatterjee, R.R. Merchant, P. Paul, S.H.R. Abdi, M.R.H. Siddiqui, D. Srinivas, M.A. Moiz, M.M. Bhadbhade, K. Venkatasubramaniun, Inorg. Chem. 31 (1992) 2711.
[38] M.M. Taqui Khan, D. Chatterjee, R.R. Merchant, A. Bhatt, J. Mol. Catal. 63 (1990) 147.
[39] M.M. Taqui Khan, M.A. Moiz, S.D. Bhatt, R.R. Merchant, D. Chatterjee, J. Mol. Catal. 67 (1991) 1.
[40] M.R. Rhodes, T.J. Meyer, Inorg. Chem. 27 (1988) 4772.
[41] M.R. Rhodes, M.H. Barley, T.J. Meyer, Inorg. Chem. 30 (1991) 629.
[42] G. Ramchandraiah, J. Am. Chem. Soc. 116 (1994) 6733.
[43] R. Prakash, B. Tyagi, D. Chatterjee, G. Ramachandraiah, Polyhedron 16 (1997) 1235.
[44] A.A. Diamantis, A.V. Dubrawski, Inorg. Chem. 20 (1981) 1142.
[45] M.M. Taqui Khan, K. Venkatasubramanian, Z. Shirin, M.M. Bhadbhade, J. Chem. Soc. Dalton Trans. (1992) 885.
[46] M.M. Taqui Khan, D. Chatterjee, M.R.H. Siddiqui, H.C. Bajaj, K. Venkatasubramanian, M.A. Moiz, Polyhedron 12 (1993) 1443.
[47] M.M. Taqui Khan, A. Hussain, M.M. Moiz, Polyhedron 11 (1992) 687.
[48] M.M. Taqui Khan, Ind. J. Chem. (A) 32 (1993) 96.
[49] A.A. Diamantis, J.V. Dubrawski, Inorg. Chem. 22 (1983) 1934.
[50] R.P. Dwyer, E. Mayhew, E.M.F. Roe, A. Shulman, Brit. J. Cancer 19 (1965) 195.
[51] M.J. Clarke, Metal Ions in Biological Systems, vol. 11, Wiley Interscience, New York, 1980, p. 231.
[52] S. Zhang, L.A. Hall, R.E. Shepherd, Inorg. Chem. 29 (1990) 1012.
[53] R.E. Shepherd, S. Zhang, F.-T. Lin, R.A. Korlets, Inorg. Chem. 31 (1992) 1457.
[54] R.E. Shepherd, S. Zhang, Inorg. Chim. Acta 191 (1992) 271.
[55] R.E. Shepherd, S. Zhang, Trans. Met. Chem. 19 (1994) 146.
[56] R.E. Shepherd, Y. Chen, S. Zhang, R.A. Kortes, Ru(II) pac complexes for improved DNA probes, in: S. Isied (Ed.), Taube Insight, ACS Symposium Series, American Chemical Society, Washington, DC, 1996, accepted for publication.
[57] R.E. Shepherd, S. Zhang, Ya Chen, Inorg. Chim. Acta (in press).
[58] Ya Chen, R.E. Shepherd, Inorg. Chim. Acta (submitted).
[59] Ya Chen, F.-T. Lin, R.E. Shepherd, Inorg. Chem. (submitted).

[60] S. Zhang, Ya Chen, R.E. Shepherd, Inorg. Chim. Acta 230 (1995) 77.
[61] B. Taqui Khan, K. Annapoorna, Inorg. Chim. Acta 171 (1990) 157.
[62] B. Taqui Khan, K. Annapoorna, Inorg. Chim. Acta 176 (1990) 241.
[63] B. Taqui Khan, K. Annapoorna, Polyhedron 10 (1991) 2565.
[64] D. Chatterjee, H.C. Bajaj, A. Das, J. Chem. Soc. Dalton Trans. (1995) 2497.
[65] M.M. Taqui Khan, A. Hussain, M.A. Moiz, D. Chatterjee, R.B. Thorat, Polyhedron 12 (1993) 1437.
[66] Y. Sasaki, M. Suzuki, A. Tokiwa, M. Ebihara, T. Yamagudi, C. Kabuto, T. Ito, J. Am. Chem. Soc. 110 (1988) 625.
[67] A. Syamala, A.R. Chakravarti, Inorg. Chem. 30 (1991) 4699.
[68] I.J. Higgins, D.J. Best, R.C. Hammod, Nature (London) 286 (1980) 581.
[69] R.E. Stenkamp, L.A. Seiker, L.H. Jensen, J. Sanders-Lochr, Nature (London) 291 (1981) 263.
[70] H.S. Ram, A. Haim, Inorg. Chem. 30 (1991) 1319.
[71] L.A. De Oliveira, L.D. Ciana, A. Haim, Inorg. Chim. Acta 225 (1994) 129.
[72] D. Chatterjee, H.C. Bajaj, A. Das, Inorg. Chem. 32 (1993) 4049.
[73] D. Chatterjee, H.C. Bajaj, A. Das, Inorg. Chim. Acta 224 (1994) 189.
[74] N.S. Hush, Prog. Inorg. Chem. 8 (1967) 391.
[75] W.M. Laidlaw, R.G. Denning, T. Verbiest, E. Chanchard, A. Persoons, Nature (London) 363 (1993) 58.
[76] A. Das, H.C. Bajaj, D. Chatterjee, Polyhedron 14 (1995) 3585.
[77] A. Das, H.C. Bajaj, Polyhedron 16 (1997) (in press).
[78] S. Zhang, R.E. Shepherd, Trans. Met. Chem. 17 (1992) 97.
[79] S. Zhang, R.E. Shepherd, Trans. Met. Chem. 17 (1992) 199.
[80] D. Chatterjee, H.C. Bajaj, A. Hussain, J. Coord. Chem. (A) 31 (1994) 329.
[81] D. Chatterjee, H.C. Bajaj, J. Chem. Soc. Dalton Trans. (1995) 3145.
[82] D. Chatterjee, J. Chem. Soc. Dalton Trans. (1996) 4389.
[83] E. Slade, S.P. Fricker, N.A. Powell, B.A. Murrer, M.T. Wilson, N. Davies, Proceedings of 6th International Symposium on Platinum Group Metal Chemistry, 1996, p. 44.
[84] Ya Chen, R.E. Shepherd, J. Inorg. Biochem. (submitted in October 1996).
[85] H.E. Toma, K. Araki, J. Coord. Chem. 24 (1991) 1.
[86] M.M. Taqui Khan, D. Chatterjee, H.C. Bajaj, Ind. J. Chem. (A) 31 (1992) 152.
[87] M.M. Taqui Khan, D. Chatterjee, H.C. Bajaj, K.N. Bhatt, S. Sanalkumar, Ind. J. Chem. (A) 31 (1992) 714.
[88] D. Chatterjee, A. Das, H.C. Bajaj, Trans. Met. Chem. 19 (1994) 111.
[89] D. Chatterjee, H.C. Bajaj, Ind. J. Chem. (A) 32 (1993) 772.