Kinetics and Mechanism of the Substitution of $[(NH_3)_5Ru^{III}(edta)Ru^{III}(H_2O)]^{2+}$ (edta = ethylenediaminetetraacetate) by Thiourea in Aqueous Solution

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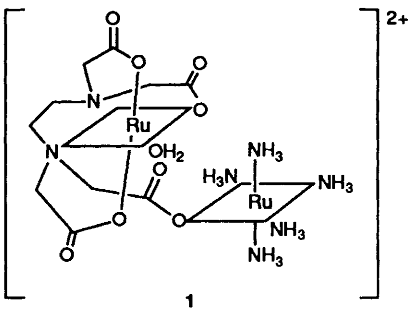
The substitution of the H_2O ligand of the complex $[(NH_3)_5Ru^{III}(edta)Ru^{III}(H_2O)]^{2+}$ (edta = ethylenediaminetetraacetate) by thiourea was studied spectrophotometrically. Rate and activation parameters are found to be consistent with an associative interchange mechanism. Experimental results are discussed with reference to literature data for the corresponding substitution of mononuclear $[Ru^{III}(edta)(H_2O)]^-$.

The substitution reactions of edta (ethylenediaminetetraacetate) and other related polyaminopolycarboxylate complexes of Ru^{III} continues to be of interest.[1–7] These edta-type ligands have also been shown to labilise the substitution reactions of complexes of Co^{III},[8] Ti^{III},[9] Os^{III},[10] Fe^{III}[10] and Cr^{III}.[11] The controversy regarding mechanism still persists. Ogino *et al.*[7] proposed transient co-ordination of a pendant group. On the other hand, the interaction of a pendant group with a co-ordinated water molecule through hydrogen bonding and *syn* interaction between the lone pairs of electrons were introduced by Bajaj and Eldik.[4–6] However, irrespective of these postulations it has been documented that the nature of the pendant group is the key factor which controls the lability of ruthenium(III) centres through its nucleophilicity and bulk. In order to know the lability of a ruthenium(III) centre when the pendant group is a complex moiety we undertook thiourea substitution of the aqua ligand in $[(NH_3)_5Ru^{III}(edta)Ru^{III}(H_2O)]^{2+}$ where the unco-ordinated carboxylate group of $[Ru^{III}(edta)(H_2O)]^-$ is incorporated into the $[Ru^{III}(NH_3)_5]^{3+}$ moiety.

Experimental

Materials.—All chemicals used were of A.R. grade. Double distilled water was used throughout the experiments. The complex $[(NH_3)_5Ru^{III}(edta)Ru^{III}(H_2O)]Cl_2{\cdot}2H_2O$ **1** was prepared by mixing $[Ru^{III}(Hedta)(H_2O)]$[12] and $[Ru(NH_3)_5Cl]Cl_2$[13] stoichiometrically in the minimum volume of water. The mixture was stirred for 5 h at room temperature and a yellowish brown precipitate was obtained by addition of ethanol. It was filtered off, washed with 80% ethanol–water and dried under vacuum. Elemental analyses were in accord with the formula given. The UV/VIS spectrum in water exhibited a strong peak at 270 (ε = 1148) and a weak shoulder at 330 nm (ε = 250 dm^3 mol^{-1} cm^{-1}). The IR spectrum of the solid did not show any band at 1740 cm^{-1} corresponding to free carboxylate stretching, which is consistent with the co-ordination of pendant carboxylate group. The cyclic voltammogram in water (0.1 mol dm^{-3} $NaClO_4$) exhibited two quasi-reversible peaks at +0.09 and −0.17 V (*vs.* saturated calomel electrode, SCE) assigned to $Ru^{III}Ru^{III}$–$Ru^{III}Ru^{II}$ and $Ru^{III}Ru^{II}$–$Ru^{II}Ru^{II}$ redox couples respectively.

Physical Measurements.—Electronic spectra were recorded on a Shimadzu UV/VIS spectrophotometer, IR spectra as KBr pellets on a Carl Zeiss Specord M80 spectrometer. Electrochemical studies were performed with PAR 174A electrochemical instruments using glassy carbon as working electrode and a SCE as reference.



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Kinetics.—The substitution reaction was followed spectrophotometrically at 470 nm[2],† by using a HI-TECH stopped-flow (SF 51) spectrophotometer coupled with an Apple IIe data analyser. pH Measurement was carried out with a Digisun pH meter. Acetate, phosphate and borate buffers were used to control the pH and $NaClO_4$ for adjusting the ionic strength. The rate constants are reproducible within ±4%.

Results and Discussion

Preliminary experiments showed that under the reaction conditions the buffer components and ClO_4^- (used to control the ionic strength) had no effect on the kinetic behaviour of the system when these were added to ligand solution prior to mixing with complex **1** in the stopped-flow chamber.

The rate of reaction was found to be first order with respect to the concentration of complex **1**. The observed rate constant (k_{obs}) increased linearly with increasing ligand concentration in the range studied. The pH dependence of the observed rate constant is depicted in Fig. 1. As seen, the rate of reaction is independent of pH in the region 1.1–3.0 and decreases

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† The characteristic peak of thioligand complexes of edta-bound Ru^{III} appears in the region 460–500 nm.

Table 1 Rate and activation parameters of ligand substitution reactions with thiourea

System	T/°C	k/dm^3 mol^{-1} s^{-1}	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}
$[(NH_3)_5Ru(edta)Ru(H_2O)]^{2+}$-tu[a]	25	48.8	48.4 ± 4	−50.4 ± 13
	35	87.2		
	45	178		
$[(NH_3)_5Ru(edta)Ru(OH)]^{+}$-tu[b]	25	3.9	51 ± 0.4	−63 ± 1.1
	35	7.9		
	45	15.1		
$[Ru(edta)(H_2O)]^{-}$-tu[c]	25	2970	22.3 ± 1	−105 ± 5

[a] pH 2.0. [b] pH 8.0. [c] Ref. 6.

sharply with increasing pH in the range 3.0–6.0. Further increase from pH 6.0 to 8.0 does not change the observed rate constant values (Fig. 1). On the basis of the above kinetic observations the mechanism of substitution of complex **1** by thiourea (tu) is proposed to be as in Scheme 1. The corresponding rate expression is given in equation (4). At low pH (< 3),

$$[(NH_3)_5Ru(edta)Ru(H_2O)]^{2+} \overset{K_a}{\rightleftharpoons} [(NH_3)_5Ru(edta)Ru(OH)]^{+} + H^{+} \quad (1)$$

$$[(NH_3)_5Ru(edta)Ru(H_2O)]^{2+} + tu \xrightarrow{k_1} [(NH_3)_5Ru(edta)Ru(tu)]^{2+} + H_2O \quad (2)$$

$$[(NH_3)_5Ru(edta)Ru(OH)]^{+} + tu \xrightarrow{k_2} [(NH_3)_5Ru(edta)Ru(tu)]^{2+} + OH^{-} \quad (3)$$

Scheme 1

$$k_{obs} = \frac{k_1[H^+] + k_2K_a}{[H^+] + K_a}[tu] \quad (4)$$

$[H^+] \gg k_2K_a$, equation (4) can be reduced to $k_{obs} = k_1[tu]$, from which k_1 was calculated as 48.8 dm^3 mol^{-1} s^{-1}. Similarly, at high pH (> 8), equation (4) can be reduced to $k_{obs} = k_2[tu]$ and the value of k_2 thus obtained is 3.9 dm^3 mol^{-1} s^{-1}. The sigmoidal curve shown in Fig. 1 underlines the validity of equation (4) with k_1 and k_2 as above and pK_a = 4.6. The pK_a value obtained kinetically is in fair agreement with that (5.1) determined by one independent potentiometric titration method.* A similar decrease in pK_a from 7.4 for $[Cr^{III}(edta)(H_2O)]^-$ to 5.8 for $[(NH_3)_5Co^{III}(edta)Cr(H_2O)]^{2+}$ was reported by Ogino *et al.*[14] The pK_a value of 5.1 for complex **1** is significantly lower than that of 7.6 for the $[Ru^{III}(edta)(H_2O)]^-$ complex. This may be ascribed due to the presence of the positively charged $Ru(NH_3)_5{}^{3+}$ species in complex **1** which will facilitate deprotonation. The significant difference in k_1 and k_2 once again demonstrates the higher lability of the aqua- as compared to the hydroxo-species.

The substitution reaction was studied at three different temperatures. The rate and activation parameters are summarised in Table 1 along with data reported[6] for the thiourea substitution of $[Ru^{III}(edta)(H_2O)]^-$. The effect of temperature was studied in the limiting pH region (2.0 and 8.5) where a change in pH due to a change in temperature could not affect the observed rate. The activation parameters determined at pH 2.0 and 8.5 do not exhibit markedly different values, which suggests a similar type of mechanism is operative for substitution of the aqua- and hydroxo-species. The significant difference in rate constants for thiourea substitution of $[Ru(edta)(H_2O)]^-$ and for complex **1** may be attributed due to the larger size of the pendant group *i.e.* $Ru(NH_3)_5{}^{3+}$ which strictly prevents the entering ligand from approaching the ruthenium(III) centre. However, the rate constants for substitution of the H_2O ligands of $[Ru^{III}(hedtra)(H_2O)]$ [hedtra = *N*-(hydroxyethyl)ethylenediaminetriacetate] (k = 22.6 dm^3 mol^{-1} s^{-1}) and $[Ru^{III}(medtra)(H_2O)]$ (medtra = *N*-methylethylenediaminetriacetate) (k = 2.3 dm^3 mol^{-1} s^{-1}) are smaller than that for complex **1** (k = 48.8 dm^3 mol^{-1} s^{-1}), which once again demonstrates the role of the carbonyl oxygen atom, rather than transient co-ordination[7] of the pendant group (which is not feasible in complex **1**), in the labilisation process through its *syn* lone pair of electrons.[6]

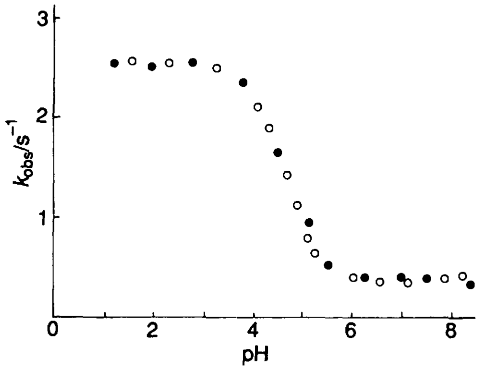

Fig. 1 Effect of pH on the observed rate constant (k_{obs}) at 25 °C, $[Ru^{III}]_T = 5 \times 10^{-4}$, [tu] = 5×10^{-2}, I = 0.1 mol dm^{-3} ($NaClO_4$); ○, experimentally obtained; ●, calculated using values k_1 = 48.8 dm^3 mol^{-1} s^{-1}, k_2 = 3.9 dm^3 mol^{-1} s^{-1} and pK_a = 4.6

In conclusion, the thiourea substitution of complex **1** has shown that the steric contribution of the bulky pendant group is large, however the carbonyl oxygen atoms plays an important role in the remarkable lability of the aqua molecule.

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* pH-Metric titration of a 1 × 10^{-3} mol dm^{-3} solution (25 cm^3) of complex **1** with 1 × 10^{-2} mol dm^{-3} NaOH was carried out in 0.1 mol dm^{-3} $NaClO_4$ at 25 °C using a Metrohm 682 titrator. Only one inflection with pK_a = 5.1 was obtained in the range pH 1.5–9.0.

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