

Relative reactivity of N- and S-donor ligands in substitution reactions of aquaethylenedinitrilotetraacetatoruthenium(III) in aqueous solution *

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4-Sulfanylpyridine, a potential bridging ligand, reacted with $[\text{Ru}(\text{edta})(\text{H}_2\text{O})]^-$ following a facile aqua substitution path through S-co-ordination of the pendant thione group or through N-co-ordination. The substitution reaction was studied as a function of pH (0.4–5.0), temperature (25–45 °C), pressure (0.1 to 100 MPa) and concentration. Second-order rate constants for the N- and S-donor complex-formation reactions are 4950 ± 60 and $1560 \pm 50 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C respectively. The N-co-ordinated ruthenium(III) complex reacts to give the S-co-ordinated product with a rate constant of $0.07 \pm 0.02 \text{ s}^{-1}$ at 25 °C. Detailed kinetic studies, including the determination of all activation parameters (ΔH^\ddagger , ΔS^\ddagger and ΔV^\ddagger), revealed unambiguously that formation of the S-substituted product is favored thermodynamically, whereas that of the N-substituted product is favored kinetically. The N-co-ordinated complex reacts to give the S-co-ordinated complex *via* a dissociative process. Depending on the reaction conditions, mono- and weakly interacting asymmetric bi-nuclear complexes have been synthesized and characterized.

The extreme lability of the aqua molecule in the $[\text{Ru}(\text{edta})(\text{H}_2\text{O})]^-$ complex (edta = ethylenedinitrilotetraacetate) has attracted significant attention from kineticists in the past 20 years.^{1–13} Although edta is a hexadentate ligand, it is five-co-ordinated in this complex with a free carboxylate arm, and the sixth co-ordination position is occupied by a water molecule.

The chemistry of aminopolycarboxylate complexes of Ru^{II} , Ru^{III} is also of continued interest due to their biochemical importance^{14–17} and catalytic activity in oxidation reactions.^{18–20} On dissolution of $\text{K}[\text{Ru}(\text{Hedta})\text{Cl}] \cdot 2\text{H}_2\text{O}$ the complex undergoes rapid aquation to produce $[\text{Ru}(\text{edta})(\text{H}_2\text{O})]^-$.^{1–6} N-Donor heterocycles and their derivatives react with $[\text{Ru}(\text{edta})(\text{H}_2\text{O})]^-$ through a facile aqua substitution reaction on a stopped-flow timescale.^{6–9} A few reports are known where S-donors react following a similar mechanistic path.^{10–12} High lability of the aqua ligand in $[\text{Ru}(\text{edta})(\text{H}_2\text{O})]^-$ has been attributed to intramolecular hydrogen bonding involving the free carboxylate group and the co-ordinated water molecule.^{1–8} We have now studied the aqua substitution reaction in $[\text{Ru}(\text{edta})(\text{H}_2\text{O})]^-$ with 4-sulfanylpyridine (L) to resolve the relative reactivity of N- and S-donor sites and further to probe the extraordinary lability of the aqua ligand in $[\text{Ru}(\text{edta})(\text{H}_2\text{O})]^-$. We also report the synthesis and characterization of a new mono- and an asymmetric bi-nuclear complex.

Experimental

The complex $\text{K}[\text{Ru}(\text{Hedta})\text{Cl}] \cdot 2\text{H}_2\text{O}$ was prepared following the published procedure.¹³ 4-Sulfanylpyridine, $[\text{NBu}_4][\text{ClO}_4]$ (Aldrich) and methanol (AR; Ranbaxy, India) were used as received. Microanalytical studies (C, H, N) were carried out using a Carlo Erba elemental analyser. Electronic spectra were recorded on Shimadzu UV-3101 PC and Cary 5 spectrophotometers,

IR spectra on a Carl-Zeiss Specord M80 spectrometer using KBr pellets. Electrochemical experiments were performed on a PAR 273A instrument using a conventional three-electrode cell assembly and $[\text{NBu}_4][\text{ClO}_4]$ as electrolyte. A saturated calomel reference electrode and a platinum working electrode were used. All potentials are reported with respect to the SCE. pH Measurements were carried out with a Digisun pH meter. Kinetic studies were performed on a High-Tech SF 51 stopped-flow spectrometer by monitoring the change in absorbance either at 350 nm (λ_{max} for $[\text{Ru}(\text{edta})(\text{pyridine})]^-$ derivatives; see below) or at 540 nm (λ_{max} for $[\text{Ru}(\text{edta})(\text{S-donor})]^-$ complex; see below). Kinetic measurements at elevated pressure were performed on a laboratory made high-pressure stopped-flow unit.²¹ In all kinetic studies pseudo-first-order conditions were maintained by using an excess of 4-sulfanylpyridine, and the corresponding first-order plots were linear for at least three half-lives of the reactions. Rate constant data are reported as an average of three triggerings and are reproducible within $\pm 5\%$. The pH and ionic strength of the kinetic solutions were maintained using either hydrochloric acid or acetic acid–acetate buffer, and KCl solutions, respectively. Doubly distilled water was used throughout.

Synthesis

$[\text{Ru}(\text{Hedta})\text{L}] \cdot 2\text{H}_2\text{O}$ 1. The salt $\text{K}[\text{Ru}(\text{Hedta})\text{Cl}] \cdot 2\text{H}_2\text{O}$ (200 mg, 0.4 mmol) was dissolved in warm water (5 cm³) to which 4-sulfanylpyridine (66 mg, 0.6 mmol) dissolved in methanol (10 cm³) was added. The solution immediately changed to deep red and was stirred at room temperature for 10 min. Then the volume was reduced to ca. 5 cm³, to which an excess of cold acetone was added. The desired red complex was precipitated, filtered off and washed thoroughly with acetone. The red solid was redissolved in methanol and filtered. The red filtrate was dried *in vacuo* and recrystallized from a methanol–acetone mixture to obtain the pure desired mononuclear complex [yield: 170 mg, 80%; C, H, N calc. (exptl.): 32.1, 4.0, 8.0 (31.9, 4.1, 7.9%)]. $E_1(\text{Ru}^{\text{III}}) = -0.40 \text{ V}$ with reference to SCE [$(E_{\text{pa}} - E_{\text{pc}}) \geq 200 \text{ mV}$ and $I_{\text{pa}}/I_{\text{pc}} = 0.4$].

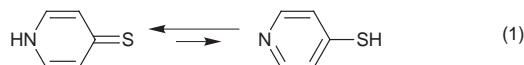
* Supplementary data available: first-order rate constants. For direct electronic access see <http://www.rsc.org/suppdata/dt/1998/1563/>, otherwise available from BLDSC (No. SUP 57359, 3 pp.) or the RSC Library. See Instructions for Authors, 1998, Issue 1 (<http://www.rsc.org/dalton>).

[{Ru(Hedta)}₂L]·2H₂O **2.** A similar method to that described above was adopted for the synthesis of the binuclear complex using K[Ru(Hedta)Cl]·2H₂O (200 mg, 0.4 mm) and 4-sulfanylpyridine (22 mg, 0.2 mm) in a 2:1 molar ratio [yield: 140 mg, 75%; C, H, N calc. (exptl.): 31.4, 3.7, 7.6 (31.1, 3.9, 7.4%)]. Cyclic voltammetry at low pH (<3) gave two peaks with reference to SCE at 0.09 V [$E_1(\text{Ru}^{\text{III}}-\text{N}) = 0.09 \text{ V}$, $E_{\text{pa}} - E_{\text{pc}} = 90 \text{ mV}$ and $I_{\text{pa}}/I_{\text{pc}} = 0.9$] and at -0.34 V [$E_2(\text{Ru}^{\text{III}}-\text{S}) = -0.34 \text{ V}$, $E_{\text{pa}} - E_{\text{pc}} \approx 150 \text{ mV}$ and $I_{\text{pa}}/I_{\text{pc}} < 0.4$]. However, for the blue species (pH ≈ 8) two respective E values were obtained for $\text{Ru}^{\text{III}}-\text{Ru}^{\text{II}}$ couples, -0.07 and -0.62 V (see Discussion). Thus, for the blue species the E value for the $\text{Ru}^{\text{III}}-\text{Ru}^{\text{II}}$ couple of the $\text{Ru}(\text{edta})(\text{N-donor})$ center remains practically unaffected while there is an appreciable cathodic shift of 280 mV for that of the S-co-ordinated center. Presumably an increase in electron density in the $\text{Ru}(\text{edta})-\text{S-donor}$ unit, due to removal of the proton on NH of complex **2**, accounts for this cathodic shift.

Significant absorption bands in the IR spectra of complexes **1** and **2** are: ≈ 2400 (N-H), ≈ 1720 (unco-ordinated CO_2H), ≈ 1635 (co-ordinated CO_2^-), $\approx 3300 \text{ cm}^{-1}$ (H_2O). The characteristic band for 4-sulfanylpyridine at $\approx 1150 \text{ cm}^{-1}$ due to C=S stretching is less intense for complex **1** and insignificant for **2**.

Results and Discussion

The salt $\text{K}[\text{Ru}(\text{Hedta})\text{Cl}] \cdot 2\text{H}_2\text{O}$ when dissolved in water hydrolyses rapidly and exists as $[\text{Ru}(\text{edta})(\text{H}_2\text{O})]^-$ between pH 5.0 and 6.0, which reacts with N-donor heterocycles and S-donors through an aqua substitution pathway to yield mono- and bi-nuclear complexes depending on the conditions. 4-Sulfanylpyridine exists in aqueous solution in two tautomeric forms,²² viz. the thione and thiol forms (1).



During the synthesis of either the mono- or bi-nuclear complexes the pH of the solution containing $[\text{Ru}(\text{Hedta})(\text{H}_2\text{O})]$ remained around 2.75, and at this pH the ligand L exists as the thione, the predominant species²² [equations (1), (6) and (7), see below]. Thus L has a pendant thione group capable of co-ordinating to the ruthenium(III) centre. Co-ordination of the thione group in complex **1** is confirmed by the intense red color which is characteristic for S-bonded ruthenium(III) complexes.¹⁰⁻¹² Moreover, $[\text{Ru}(\text{edta})(\text{py})]^-$ complexes do not have any characteristic absorbance beyond 350 nm.^{6,9,23} Complex **1** does not show any change in color with change in pH, whereas **2** changes reversibly from wine red to blue on changing the pH of the aqueous solution from 3.5 to 8.0 (Fig. 1). This acid-base behavior can be explained on the basis of deprotonation of the N-H group (Scheme 1), as deprotonation of the pendant CO_2H group in the $\text{Ru}(\text{Hedta})$ moiety is not expected to have any pronounced effect on the energy gap between the HOMO and LUMO for complex **2**.

This is further underlined by the fact that a similar change in the pH has no such effect on the UV/VIS spectra for complex **1**. Presumably removal of the N-H proton increases the electron density in the bridging ligand and thereby permits more effective mixing of the ligand orbitals with the metal orbitals and accounts for the stronger interaction between the two ruthenium(III) centers as well as for the blue shift of the spectra. The protonation constant for this acid-base equilibrium was determined by spectrophotometric titration at 566 nm and it was obtained from the intercept of a plot of $\log[(A - A_a)/(A_b - A)]$ vs. pH²⁴ (A_a is the absorbance at pH 3.5, A_b that at pH 8.0 and A is the absorbance at different experimental pH). The $\text{p}K$ was found to be 5.0 ± 0.2 at 25 °C. As expected, it is much lower than $\text{p}K_2$ for the unco-ordinated pyridine (8.65).²²

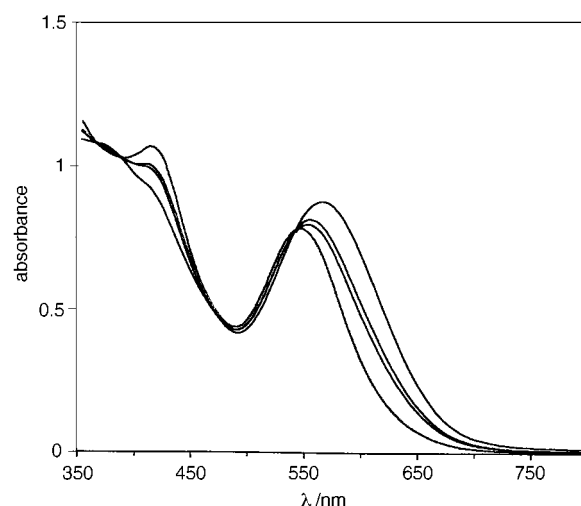
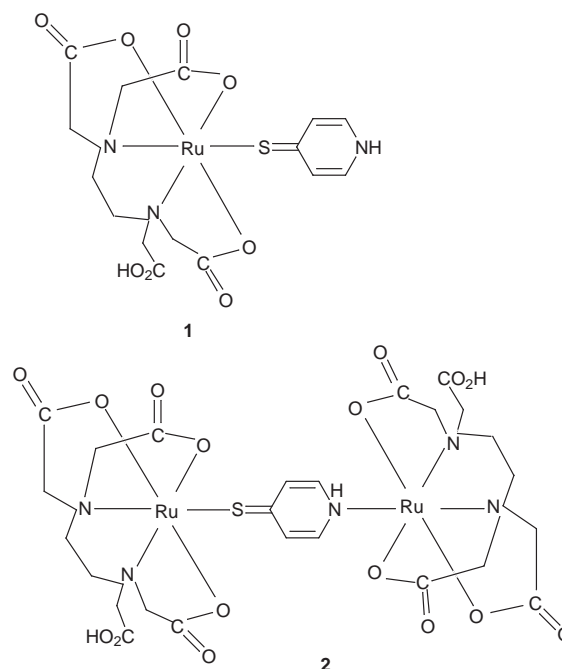
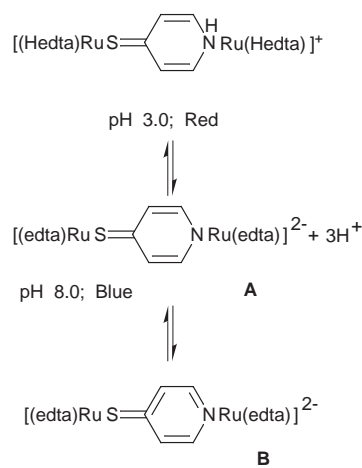


Fig. 1 The UV/VIS spectra of $[\{\text{Ru}(\text{edta})\}_2\text{L}]$ ($\text{L} = 4\text{-sulfanylpyridine}$) at different pH in aqueous solution, $[\{\text{Ru}(\text{edta})\}_2\text{L}] = 1.55 \times 10^{-4} \text{ M}$, at 25 °C. pH 4.6, 4.93, 5.12 and 5.87 (bottom to top at 566 nm)

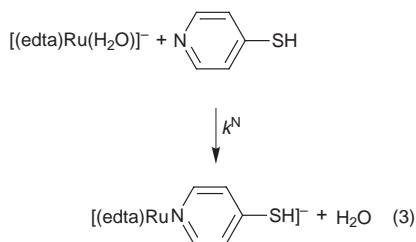
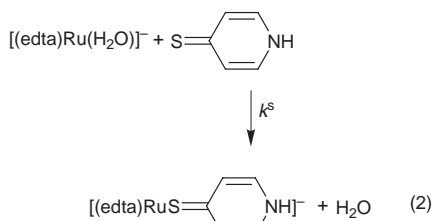


Scheme 1

However it is difficult to speculate whether complex **2** exists either as **A** or as **B**, or as an equilibrium mixture of both (Scheme 1).

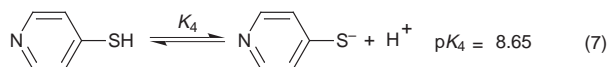
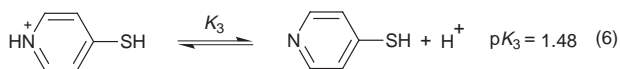
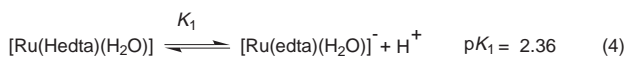
Kinetics

The ligand 4-sulfanylpiperidine can co-ordinate to the ruthenium(III) center in $[\text{Ru}(\text{edta})(\text{H}_2\text{O})]^-$ either through the S- or through the N-donor group [equations (2) and (3)], where k^{S}

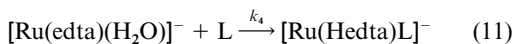
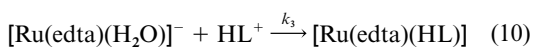
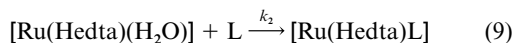
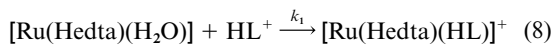


and k^{N} are the rate constants for the formation of the S- and N-co-ordinated complexes, respectively. Kinetics of thione/thiol co-ordination of the heterocyclic ligand to the ruthenium(III) center can be monitored at 540 nm, whereas co-ordination at N can be studied⁶⁻⁹ at 350 nm. A series of preliminary experiments showed that addition of buffer components had no effect on the behavior of the system when it is added to a solution containing the entering nucleophile L prior to mixing within the stopped-flow instrument.

Both the reactants $[\text{Ru}(\text{edta})(\text{H}_2\text{O})]^-$ and 4-sulfanylpiperidine are protic and may be involved in acid-base equilibria, (4)–(7).



Since we have restricted our kinetic studies to the pH range of 0.4 to 5.0, equilibrium (5) and (7) can be neglected. Thus in principle four reactions [equations (8)–(11)] are possible, which leads to expression (12)^{25,26} for the observed pseudo-first-order



$$k_{\text{obs}} = \frac{k_1[\text{H}^+]^2 + k_2K_3[\text{H}^+] + k_3K_1[\text{H}^+] + k_4K_1K_3}{([\text{H}^+] + K_1)([\text{H}^+] + K_3)} \times [\text{L}]_{\text{T}} \quad (12)$$

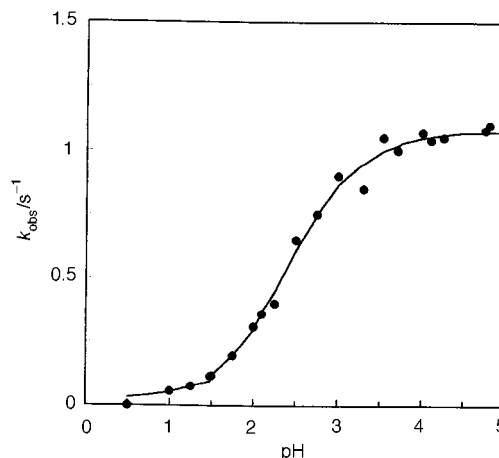


Fig. 2 Variation of k_{obs} with pH for the reaction of $[\text{Ru}(\text{edta})(\text{H}_2\text{O})]^-$ with 4-sulfanylpiperidine studied at $\lambda = 540$ nm, $[\text{Ru}(\text{edta})(\text{H}_2\text{O})]^- = 1.2 \times 10^{-5}$ M, $[4\text{-sulfanylpiperidine}] = 6.9 \times 10^{-4}$, 303 K and $I = 0.2$ M KCl. The solid curve is calculated from the resolved rate constants

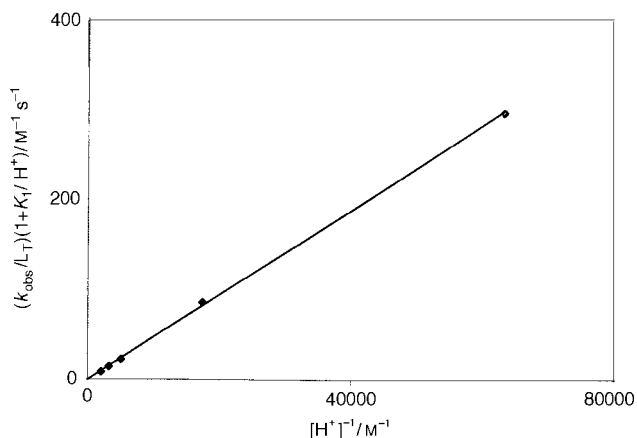


Fig. 3 Plot of $(k_{\text{obs}}/[\text{L}]_{\text{T}})(1 + K_1/[\text{H}^+])$ vs. $[\text{H}^+]^{-1}$

rate constant. Observed pseudo-first-order rate constants as a function of pH (SUP 57359), for reactions monitored at 540 nm, are shown in Fig. 2. The observed pH dependence of the process can be associated with equilibria (2) and (4) and reactions (8)–(11). For the monitoring wavelength of 540 nm, k_1 , k_2 , k_3 and k_4 represent second-order forward rate constants for thione co-ordination to the edta complex of Ru^{III} .

However at $\text{pH} > 3$, equation (12) can be rewritten as (13),²⁶

$$(k_{\text{obs}}/[\text{L}]_{\text{T}})(1 + K_1/[\text{H}^+]) = k_2 + k_4K_1[\text{H}^+]^{-1} \quad (13)$$

since above pH 3 the contributions from reactions (8) and (10) are presumably negligible. Thus it is possible to evaluate k_2 and k_4 from a plot of $(k_{\text{obs}}/[\text{L}]_{\text{T}})(1 + K_1/[\text{H}^+])$ vs. $[\text{H}^+]^{-1}$ (Fig. 3). Values for k_2 and k_4 obtained from this plot are 110 ± 15 and $1560 \pm 50 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C, respectively. Furthermore, for studies at $\text{pH} < 3$ equation (12) can be rearranged²⁶ by correcting for the contribution of k_2 and k_4 to (14). Thus it is possible to

$$\{(k_{\text{obs}}/[\text{L}]_{\text{T}})([\text{H}^+] + K_1)([\text{H}^+] + K_3) - (k_2K_3[\text{H}^+] + k_4K_1K_3)\}[\text{H}^+]^{-1} = k_1[\text{H}^+] + k_3K_1 \quad (14)$$

evaluate k_1 (from the slope) and k_3 (from the intercept) from a plot of the left-hand side of equation (14) vs. $[\text{H}^+]$ (Fig. 4) and these were found to be 28 ± 2 and $223 \pm 10 \text{ M}^{-1} \text{ s}^{-1}$, respectively, at 25 °C. As expected the values for k_1 and k_3 are lower than k_2

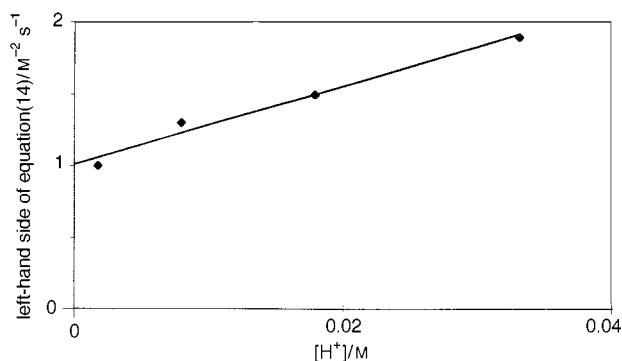


Fig. 4 Plot of $\{(k_{\text{obs}}/[L]_{\text{T}})([H^+] + K_1)([H^+] + K_3) - (k_2K_3[H^+] + k_4K_1K_3)\}[H^+]^{-1}$ vs. $[H^+]$

and k_4 , respectively. The calculated pH profile (Fig. 2) correlated well with that of the experimentally obtained k_{obs} , which substantiates the validity of the assumptions made in order to resolve k_1 , k_2 , k_3 and k_4 using equations (12)–(14).

Reaction at pH 0.4

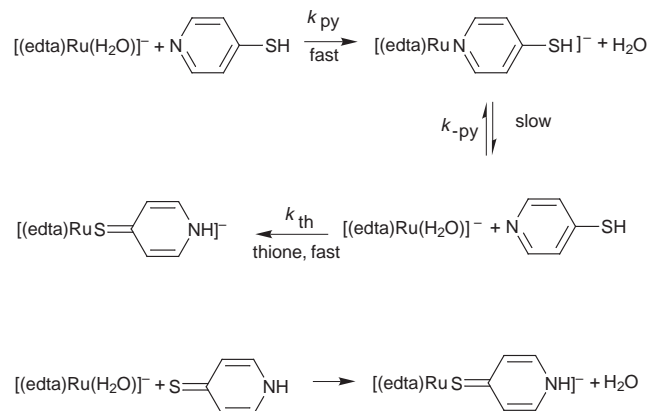
At this pH the ligand exists predominantly (>97%) as HL and the Ru(edta) complex is present exclusively in its protonated form, $[\text{Ru}(\text{Hedta})(\text{H}_2\text{O})]$, such that only equation (8) is important. Reactions were studied at two different wavelengths, 350 and 540 nm. Under the specified condition no change was observed at 350 nm while growth was registered at 540 nm, which signifies the formation of the Ru(Hedta)(S-donor) complex. The electronic spectrum for the reaction solution matches the spectrum for the authentic $[\text{Ru}(\text{Hedta})(\text{S-donor})]^-$ complex **1** in the visible region. Presumably the positive charge on the protonated N atom in the pyridine unit [equation (6)] restricts its possibility for ligation to the ruthenium(III) center. A plot of the pseudo-first-order rate constants (k_{obs}) (SUP 57359) vs. $[L]$ is linear with a small intercept; k_{obs} is independent of ionic strength and remains unchanged over a concentration range of 0.1 to 0.5 M KCl. Since at this pH only reaction (8) has any significance, this second-order rate constant can be presented as k_1 . Thus these observations agree well with the proposed rate equation (15).

$$k_{\text{obs}} = k_1[L]_{\text{T}} + k_r^{\text{s}} \quad (15)$$

The values of k_1 and k_r^{s} obtained from a plot of k_{obs} vs. $[L]_{\text{T}}$ are $26.3 \pm 1.5 \text{ M}^{-1} \text{ s}^{-1}$ and $0.005 \pm 0.003 \text{ s}^{-1}$, respectively, at 25 °C. However the value obtained for the reverse aquation reaction (k_r^{s}) is not of much significance due to the high error. Moreover, the k_1 value at 25 °C is in good agreement with that obtained from the pH-variation experiments, described above.

Reactions at pH 5.0

At pH 5.0 the edta complex of ruthenium and ligand exist exclusively in the form of $[\text{Ru}(\text{edta})(\text{H}_2\text{O})]^{-1-3,6-12}$ and L^{22} [equations (4) and (6)]. As mentioned before, the substitution reaction was studied at both 350 and 540 nm. Two consecutive reactions were recorded when the reaction was monitored at 540 nm and were studied on two different timescales. The absorbance change due to the initial step was more than 90% of the total change. The first reaction, which is almost complete (at least 3 half-lives) within 20 s, is followed by a slow reaction which goes to completion within 300 s. Detailed analysis showed that for the first reaction, the thione co-ordination to the ruthenium(III) center, a plot of the pseudo-first-order rate constants vs. $[L]_{\text{T}}$ (SUP 57359) is linear with a small intercept, whereas k_{obs} remains unchanged with change in ionic strength. Thus the reaction monitored at 540 nm on



Scheme 2

Table 1 Summary of k_{obs} as a function of temperature and pressure for the reaction

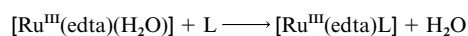
$[\text{Ru}^{\text{III}}(\text{edta})(\text{H}_2\text{O})] + L \longrightarrow [\text{Ru}^{\text{III}}(\text{edta})L] + \text{H}_2\text{O}$				
Ligand concentration/M	pH	$T/^\circ\text{C}$	P/MPa	$10 k_{\text{obs}}/\text{s}^{-1}$
0.002	0.4 ^a	25	0.1	0.570
			5	0.575
			25	0.613
			50	0.752
			75	0.893
			100	0.995
			30	0.632
			34.5	0.688
			41.2	0.842
			45	0.984
0.000 15	5.0 ^b	25	0.1	2.05
			5	2.13
			25	2.24
			50	2.35
			75	2.48
			100	2.56
			30	2.36
			34	3.10
			40	4.56
			48	5.98
0.000 15	5.0 ^{b,c}	25	5	0.72
			25	0.70
			50	0.63
			75	0.51
			100	0.43
			29	0.96
			35	1.34
			41.5	1.77
45	2.49			

^a $I = 0.4 \text{ M}$ (HCl). ^b 0.1 M acetic acid–acetate buffer, $I = 0.2 \text{ M}$ (KCl). ^c For the slow step, *i.e.* dissociation of the ligand. First-order rate constant, s^{-1} .

the faster timescale can be represented by equation (10) and the proposed rate equation is (16) where k_r^{s} , the rate constant for the reverse aquation reaction, is $0.01 \pm 0.006 \text{ s}^{-1}$.

$$k_{\text{obs}} = k_4[L] + k_r^{\text{s}} \quad (16)$$

For the second and slower growth in absorbance at 540 nm the observed pseudo-first-order rate constant (SUP 57359) was found to be independent of $[L]$ and equal to $0.07 \pm 0.02 \text{ s}^{-1}$ at 25 °C. This value is very close to the rate constant reported⁶ for the reverse aquation reaction of $[\text{Ru}(\text{edta})(\text{py})]^-$, which implies that the second and slower growth is the formation of the thione co-ordinated complex *via* dissociation of the N-co-ordinated ruthenium(III) complex (Scheme 2). Moreover, a possible contribution to this second step due to the reaction of $[\text{Ru}(\text{edta})(\text{OH})]^{2-}$ with 4-sulfanylpicridine can be neglected

Table 2 Summary of rate constants and activation parameters for the reaction

Ligand	$k/\text{M}^{-1} \text{s}^{-1}$	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J K}^{-1} \text{mol}^{-1}$	$\Delta V^\ddagger/\text{cm}^3 \text{mol}^{-1}$	Ref.
4-Sulfanylpiperidine ^a	26 ± 2.0	21.3 ± 1.5	-146 ± 6	-15.2 ± 1.0	This work
<i>b</i>	1460 ± 50	37 ± 3	-60 ± 9	-6.6 ± 0.5	This work
<i>b,c</i>	0.07 ± 0.02	97 ± 2	-54 ± 6	15.4 ± 1.5	This work
<i>b,d</i>	0.032 ± 0.02	83 ± 1	4 ± 2	14.5 ± 1.5	This work
Thiourea ^b	2970 ± 50	22.3 ± 1.4	-105 ± 5	-6.8 ± 0.6	1
Dimethylthiourea ^b	1450 ± 25	25.3 ± 1.3	-107 ± 4	-8.8 ± 0.2	1
Tetramethylthiourea ^b	154 ± 5	28.9 ± 3.3	-107 ± 11	-12.2 ± 0.5	1
Thiocyanate ^b	270 ± 27	37.2 ± 2.1	-75 ± 5.5	-9.6 ± 0.3	1
Azide ^b	1885 ± 80	24.8 ± 1.4	-99 ± 5	-9.0 ± 0.6	1
	2070 ± 97^c	26.4 ± 3.0^c	-94 ± 10^c	-9.9 ± 0.5^c	

^a 25 °C, pH 0.4 (HCl) and $I = 0.2 \text{ M}$ (HCl). ^b 25 °C, pH 5.0 (acetic acid–acetate buffer, 0.1 M), $I = 0.2 \text{ M}$ (KCl). ^c For the slow step, *i.e.* dissociation of ligand. First-order rate constant, s^{-1} . ^d Reaction of $[\text{Ru}(\text{edta})(\text{py})]^-$ with 4-sulfanylpiperidine, first-order rate constant in s^{-1} . ^e 25 °C, pH 6.0 (acetic acid–acetate buffer, 0.1 M) and $I = 0.2 \text{ M}$ (KCl).

mainly for two reasons; first at this pH $[\text{Ru}(\text{edta})(\text{OH})_2]^-$ is <0.3% and secondly the observed pseudo-first-order rate constant would have been expected to show a dependence on $[4\text{-HSC}_5\text{H}_4\text{N}]$.

This proposition was confirmed by studying the pyridine substitution in $[\text{Ru}(\text{edta})(\text{py})]^-$ by L. This reaction is slow but is complete within the stopped-flow timescale and was studied at 540 nm. Pseudo-first-order rate constants (SUP 57359) for it were found to be independent of $[\text{L}]$. Furthermore, the rate constant for the pyridine dissociation, which is the slow step, is close to that reported earlier by Matsubara and Creutz⁶ (0.06 s^{-1} at 25 °C). Thus, the above observation clearly demonstrates that the slow step in the reaction of sulfanylpiperidine with $[\text{Ru}(\text{edta})(\text{H}_2\text{O})]^-$ (at 540 nm) is the formation of the S-co-ordinated $[\text{Ru}(\text{edta})(\text{S-donor})]^-$ complex *via* dissociation of the N-co-ordinated species.

The temperature and pressure dependences were investigated under conditions where the reactions are independent of pH, *i.e.* at pH <0.5 and >4.0. The observed rate constants are summarized in Table 1 and the corresponding activation parameters in Table 2. The small value of ΔH^\ddagger and large negative value of ΔS^\ddagger for the substitution by 4-sulfanylpiperidine are in close agreement with those reported for the anation reaction of $[\text{Ru}(\text{edta})(\text{H}_2\text{O})]^-$ by pyridine, thiocyanate, azide, thiourea and substituted thiourea.^{1–10} The significant negative volume of activation for these reactions is also in close agreement with those reported earlier for SCN^- , N_3^- , thiourea and substituted thiourea (Table 2).¹ For these series of ligands ΔV^\ddagger lies between -6 and $-13 \text{ cm}^3 \text{ mol}^{-1}$. The difference between the ΔV^\ddagger values at pH 5.0 ($\Delta V^\ddagger = -6.6 \text{ cm}^3 \text{ mol}^{-1}$) and at 0.4 ($-15.2 \text{ cm}^3 \text{ mol}^{-1}$) can at best be explained by a changeover in mechanism from an interchange associative process to an associative one on the basis of an early transition state at pH 5, where bond formation and breakage are both important, and a late transition state at pH 0.4, where bond formation is more pronounced than breakage. For the slow step, which is independent of ligand concentration, the large positive ΔV^\ddagger clearly signifies the operation of a process where the N-bonded ligand dissociates. The large ΔH^\ddagger value also signifies this. Thus we are not dealing with a simple intramolecular isomerization from the N- to the S-co-ordinated complex. Instead, the N-co-ordinated complex {formed by the reaction of $[\text{Ru}(\text{edta})(\text{H}_2\text{O})]^-$ with L, $k = 4950 \text{ M}^{-1} \text{ s}^{-1}$, see below} dissociated to $[\text{Ru}(\text{edta})(\text{H}_2\text{O})]^-$ with $k_r^{\text{N}} = 0.07 \text{ s}^{-1}$ followed by its reaction with excess of L present in solution to give the S-co-ordinated complex.

When the reaction was monitored at 350 nm an initial growth and then a decay in absorbance was observed. Two different reactions were studied separately on two different timescales 5 and 50 s. An increase in absorbance at 350 nm can only be explained on the basis of aqua substitution by the N-donor heterocyclic ligand.^{6–9} The rate expression (17) is consistent

$$k_{\text{obs}} = k_r^{\text{N}}[\text{L}]_{\text{T}} + k_r^{\text{N}} \quad (17)$$

with the kinetic observations (SUP 57359) under these conditions. The second-order forward rate constant, k_r^{N} , obtained from the slope of a plot of k_{obs} vs. $[\text{L}]_{\text{T}}$, is $4950 \pm 60 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C, comparable to the value reported for the aqua substitution reaction of $[\text{Ru}(\text{edta})(\text{H}_2\text{O})]^-$ by pyridine.⁶ The rate constant for the reverse aquation of the N-donor ruthenium(III) complex, k_r^{N} , is $0.10 \pm 0.05 \text{ s}^{-1}$ in fair agreement with those reported for the dissociation of pyridine from $[\text{Ru}(\text{edta})(\text{py})]^-$.⁶

Analysis of the decay in absorbance at 350 nm reveals that plots of $\log(\Delta A)$ vs. time are linear and the observed pseudo-first-order rate constants, k_{obs} (SUP 57359), depend linearly on $[\text{L}]$ but are independent of ionic strength. The second-order rate constant at 25 °C is $1430 \pm 45 \text{ M}^{-1} \text{ s}^{-1}$, which is close (within the experimental error) to the value observed ($1460 \pm 45 \text{ M}^{-1} \text{ s}^{-1}$) for the sulfur co-ordination step (10) monitored at 540 nm. Thus the decrease in absorbance at 350 nm is due to the aqua substitution in $[\text{Ru}(\text{edta})(\text{H}_2\text{O})]^-$ by the S-donor ligand. This signifies that there are two parallel reactions (Scheme 2), which can be resolved by monitoring the reaction at 350 nm. However, we did not observe any appreciable change in absorbance on the longer timescale, which can be correlated to the dissociation of the N-donor complex (Scheme 2). Moreover, the electronic spectrum of the reaction mixture which was allowed to stand at room temperature for a few minutes matches well that for complex **1** in the visible region. Thus formation of the S-co-ordinated product *via* the N-co-ordinated one is not a simple intramolecular isomerization reaction, but rather a clear example of relative reactivity and stability of the N- and S-donor ligand towards the aqua substitution reaction in $[\text{Ru}(\text{edta})(\text{H}_2\text{O})]^-$, which is the first of its kind in $\text{Ru}^{\text{III}}(\text{edta})$ chemistry.

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† The $[\text{Ru}(\text{edta})(\text{py})]^-$ complex was prepared *in situ* by mixing equal volumes of $1.2 \times 10^{-4} \text{ M}$ $[\text{Ru}(\text{edta})(\text{H}_2\text{O})]^-$ and $6.0 \times 10^{-4} \text{ M}$ pyridine in acetate–acetic acid buffer. To this resulting solution $1.2 \times 10^{-2} \text{ M}$ of L was mixed in the stopped-flow chamber.

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