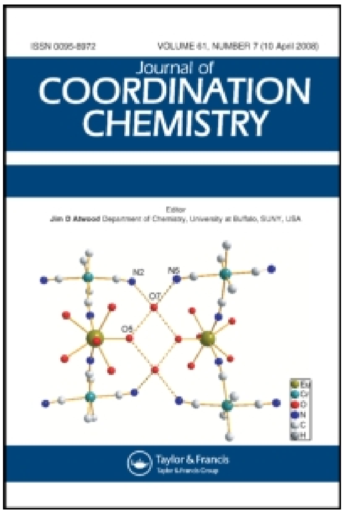

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Electrochemical Studies of Dimethyl Sulphoxide Complexes of Ruthenium(II/III) with EDTA

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ELECTROCHEMICAL STUDIES OF DIMETHYL SULPHOXIDE COMPLEXES OF RUTHENIUM(II/III) WITH EDTA

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A weak, labile, *S*-bound isomer of the $[Ru(III)(EDTA)(dmso)]^-$ complex is formed ($K_f = 1.8\,M^{-1}$) in the reaction of $[Ru(III)(EDTA)(H_2O)]^-$ with a large excess of dimethyl sulphoxide (dmso). The corresponding *S*-bound Ru^{II}–dmso complex is extraordinarily stable ($K_f = 7.7 \times 10^9\,M^{-1}$). These contrasting species can be interconverted within the time scale of cyclic voltammetry, according to a redox cycle with $E^\circ = 0.56$ V *vs* SHE, allowing a study of the kinetics of substitution reactions.

Keywords: Ruthenium–EDTA, sulphoxide complexes, electrochemistry, cyclic voltammetry

INTRODUCTION

Ruthenium–EDTA complexes have been employed in polymer-bound modified electrodes,[1-3] and their unusual chemistry has been a subject of great interest.[4-14] In this work we report the properties and reactivity of dimethyl sulphoxide complexes of ruthenium–EDTA. This system exhibits an intriguing dynamic electrochemical behaviour in aqueous solution, providing an interesting comparison with the chemistry of $[Ru(NH_3)_5(dmso)]^{2+/3+}$ complexes.[15]

EXPERIMENTAL

The $[Ru(HEDTA)(H_2O)].3H_2O$ complex was prepared by the method of Mukaida *et al.*[16] Anal.; Calcd for $RuC_{10}H_{21}N_2O_{12}$: C, 26.0; N, 6.0; H, 4.6%. Found: C, 26.0; N, 6.0; N, 3.8%. Sodium trifluoroacetate (NaTFA) and dimethyl sulphoxide (dmso), HPLC grade, were used as supplied from Aldrich.

The electronic spectra of the complexes were recorded on an HP 8451-A diode-array spectrophotometer. Cyclic voltammetry was carried out with a Princeton Applied Research instrument, consisting of a model 173 potentiostat and a model 175 universal programmer. A glassy carbon disc electrode ($A = 0.23\,cm^2$) was employed for the measurements, using a conventional Luggin capillary arrangement with an Ag/AgCl reference electrode. The measurements were carried out at 25°C, with $[NaTFA] = 0.25$ M and at pH = 4.5 (acetate buffer, 0.05 M).

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RESULTS AND DISCUSSION

The [Ru(III)(HEDTA)(H_2O)] complex undergoes two successive acid-base equilibria in aqueous solution,[4] corresponding to the deprotonation of the uncoordinated carboxylic group ($pK_a = 2.37$) and to the deprotonation of the coordinated water molecule ($pK_a = 7.63$). In the presence of acetate buffer, $4 < pH < 6$, the $[Ru(III)(EDTA)(H_2O)]^{-1}$ complex, here denoted $Ru^{III}A$, is the major species. This ion exhibits unusual fast kinetic behaviour with respect to substitution. Second-order rate constants of 30, 1860, 6300 and 20,000 $M^{-1}\,s^{-1}$ have been obtained in the presence of ligands such as acetonitrile, imidazole, pyridine and pyrazine, respectively.[4]

Solutions of $Ru^{III}A$ and of the corresponding $Ru^{II}A$ species are pale yellow, exhibiting absorption bands at 284 nm ($\varepsilon = 2800\ M^{-1}\,cm^{-1}$), 350 (680); and 282 (2900), 427 nm (260), respectively.[4] In the presence of a high concentration of dmso, *e.g.* 4 M, the $Ru^{III}A$ complex gives rise to a yellow product, displaying absorption bands at 300 nm (~3000) and 390 nm (~500). This complex can be reversibly reduced to a colourless product, exhibiting an absorption shoulder in the ultraviolet, around 300 nm.

The formation of the $[Ru(EDTA)(dmso)]^{-/2-}$ complexes can be monitored by cyclic voltammetry, as shown in Figure 1. The starting $Ru^{III}A$ complex exhibits a pair of reversible cathodic and anodic waves, indicated by (1) and (2) in Figure 1, associated with the Ru^{III}/Ru^{II} redox couple, with $E_{1/2} = -0.1$ V *vs* SHE. In the presence of a large excess of dmso a new pair of waves, (3) and (4), appears in the cyclic voltammograms, at $E^\circ = 0.56$ V (Figure 1). The anodic and cathodic waves are separated by 60–80 mV, and the ratio of the corresponding peak currents are very close to unity. The peak currents are linearly dependent on $v^{1/2}$ (v = potential scan rate), as expected theoretically for a monoelectronic reversible process.

Dimethyl sulphoxide is known to form linkage isomers by coordinating *via* O and S atoms. The *O*-bound complexes, here denoted $Ru^{II}O$ and $Ru^{III}O$, are expected to exhibit properties very similar to those of the $Ru^{II}A$ and $Ru^{III}A$ species, respectively, with E° around 0 V. In contrast, the *S*-bound complexes, $Ru^{II}S$ and $Ru^{III}S$, are expected to exhibit much higher E° because of the preferential stabilization of the Ru(II) ion arising from backbonding interactions with the sulphoxide ligand. For instance, in the case of $[Ru(NH_3)_5(dmso)]^{2+/3+}$ complexes,[15] the E° values of the $Ru^{III}S$ and $Ru^{III}O$ isomers are 1.0 and 0.01 V, respectively. The latter value is very close to the E° of the $[Ru(NH_3)_5(H_2O)]^{3+}$ complex, 0.066 V.[16]

Therefore, the waves at $E^\circ = 0.56$ V in Figure 1 can be ascribed to the *S*-bound isomer of the $[Ru(EDTA)(dmso)]^{-/2-}$ complexes. The $Ru^{III}S$ species, responsible for the cathodic peak (3) is only observed in the presence of high concentrations of dmso, *e.g.* above 0.05 M, as shown in Figure 1. Under such conditions, peak (2) due to the $Ru^{II}A$ complex practically disappears and peak (4) approaches saturation. This means that the $Ru^{III}S$ complex is a very weak complex, existing in equilibrium with the $Ru^{III}A$ species, even in 1 M dmso. In contrast, the $Ru^{II}S$ isomer seems to be extraordinarily stable.

Neglecting, to a first approximation, a possible influence from kinetic effects in the cyclic voltammograms, the equilibrium constant for the $Ru^{III}S$ complex can be estimated from the dependence of the cathodic peak currents (3), $ip_c(3)$, on the concentration of dmso, according to the following equations,

$$Ru^{III}A + dmso \overset{K}{\rightleftharpoons} (Ru^{III}S + Ru^{III}O) \qquad (1)$$

$$K = \frac{[Ru^{III}S] + [Ru^{III}O]}{[Ru^{III}A][dmso]} = \frac{(1 + K_i^{III})[Ru^{III}S]}{\{[Ru_T]-(1 + K_i^{III})[Ru^{III}S]\}[dmso]} \qquad (2)$$

where $K_i = [Ru^{III}O]/[Ru^{III}S]$ and $[Ru_T]$ is the total concentration of the $[Ru(III)(EDTA)]^-$ species.

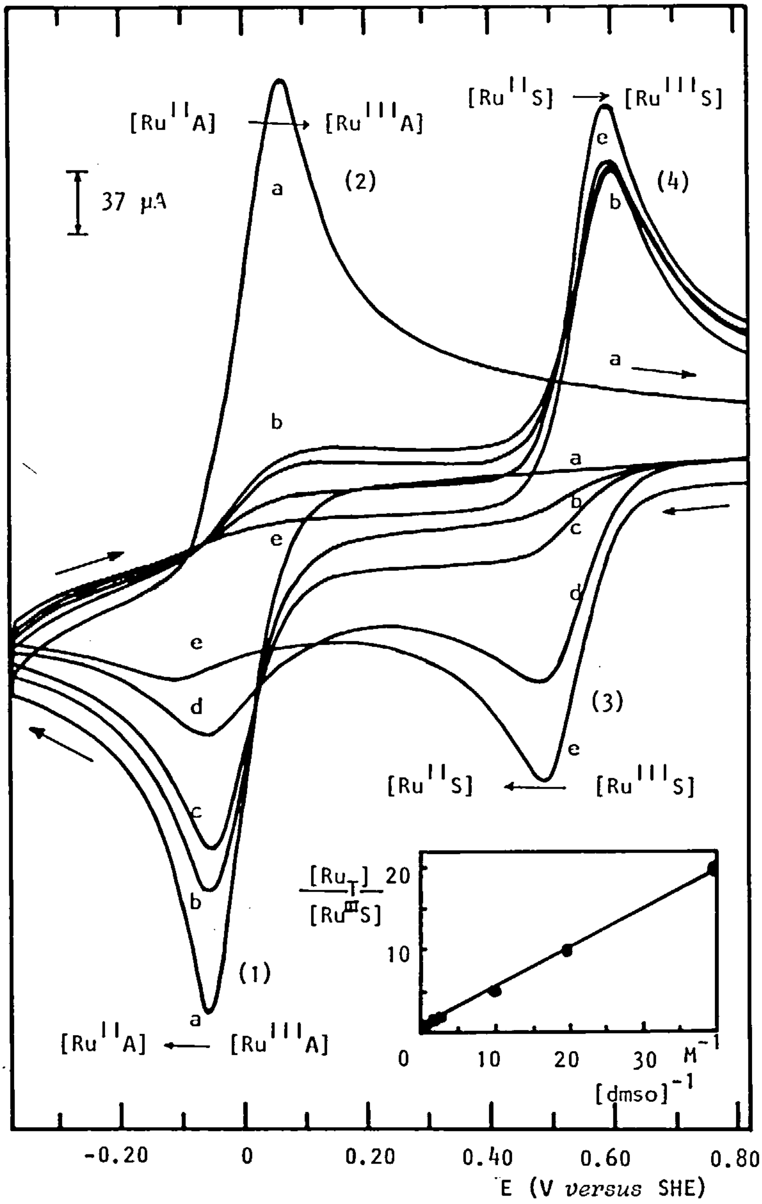

FIGURE 1 Cyclic voltammograms of the $[Ru(III)(EDTA)(H_2O)]^-$ and $[Ru(III)(EDTA)(dmso)]^-$ complexes (5 mM) in the presence of [dmso] = 0 (a), 0.050 (b), 0.10 (c), 0.50 (d) and 2.0 M (e); [NaTFA] = 0.25 M; pH 4.5 (acetate buffer 0.05 M); scan rate = 200 mV s^{-1}; T = 25°C. Inset: linear plot of $[Ru_T]/[Ru^{III}S]$ *versus* $[dmso]^{-1}$, as expressed by equation (*3*).

Equation (*2*) can also be written as in (*3*).

$$\frac{[Ru_T]}{[Ru^{III}S]} = (1 + K_i^{III}) + \frac{(1 + K_i^{III})}{K\,[dmso]} \qquad (3)$$

The ratios of $[Ru_T]/[Ru^{III}S]$ can be estimated from the quotients of the anodic peak current, $ip_a(4)$, at the saturation point, where $[Ru_T] = [Ru^{II}S]$, and the cathodic peak currents, $ip_c(3)$, measured as a function of [dmso]. The diffusion coefficients for the $Ru^{II}S$, and the cathodic peak currents, $ip_c(3)$, measured as a function of [dmso]. The diffusion coefficients for the $Ru^{II}S$ and $Ru^{III}S$ species are expected to cancel, because of their similarity. Plots of $[Ru_T]/[Ru^{III}S]$ against $[dmso]^{-1}$ were linear, as shown in the inset in Figure 1, with an intercept of 1.02 ± 0.24, and a slope of 0.538 ± 0.013. The isomerization constant, $K_i = 0.03$, calculated from the intercept, is smaller than the experimental error. For this reason, the formation of the $Ru^{III}O$ isomer can be neglected, and the association constant $K^{III} = 1.8$, calculated from the slope, can be ascribed to the $Ru^{III}S$ isomer. As a matter of fact, no evidence for the $Ru^{III}O$ isomer has been observed, even with $[dmso] > 8$ M, where $[Ru^{III}A]$ is negligible.

The association constant of the $Ru^{III}S$ complex was also estimated from spectrophotometric measurements, using the method of Morton and Lunn,[17] as $1.7 + 0.3\,M^{-1}$, at 25°C, 0.05 M, sodium acetate buffer, pH 4.5, in agreement with the electrochemical data.

Starting from the $Ru^{III}A$ complex at very negative potentials and titrating with dmso, one can see in Figure 2 that peak (2) associated with $Ru^{II}A$ decays with a proportional rise of peak (4), ascribed to $Ru^{II}S$. The plots of $ip_a(2)$ and $ip_a(4)$, or $[Ru^{II}A]$ and $[Ru^{II}S]$, *versus* [dmso] are shown in the inset of Figure 2, indicating quantitative formation of the $[Ru(EDTA)(dmso)]^{2-}$ complex.

According to the electrochemical behaviour shown in Figures 1 and 2, the $Ru^{II}S$ and $Ru^{III}S$ species can be generated in non-equilibrium conditions in the time scale of cyclic voltammetry. In this way, it is possible to investigate the dissociation of the $Ru^{III}S$ complex (case 1) and the formation of the $Ru^{II}S$ species (case 2) directly from the cyclic voltammograms.

In the first case, one can start from the $Ru^{II}S$ complex, at an applied potential of −0.2 v, with [dmso] = 0.5 M. The $Ru^{II}S$ product, which is quantitatively formed, leads to a single anodic peak (4), as shown in Figure 3.A. Under these conditions the oxidized product, $Ru^{III}S$, undergoes partial dissociation and the system can be described in terms of a reversible electrochemical step followed by a reversible chemical reaction.

$$Ru^{II}S - e^- \rightleftharpoons Ru^{III}S$$

$$Ru^{III}S + A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Ru^{III}A + S$$

In this case, from the measured ratios $ip_c(3)/ip_a(4)$ and using the appropriate working curves calculated by Shain and Nicholson,[18] it is possible to evaluate the quotient $K/(k_f + k_r)^{1/2}$, where $K = k_f/k_r$. Since K is already known, k_f and k_r can be calculated as $6 \pm 2\,s^{-1}$ and $11 \pm 3\,M^{-1}\,s^{-1}$, respectively.

According to these results the influence of kinetic effects in the cyclic voltammograms of Figure 1 should be small. As a matter of fact, starting from $Ru^{III}S$ in

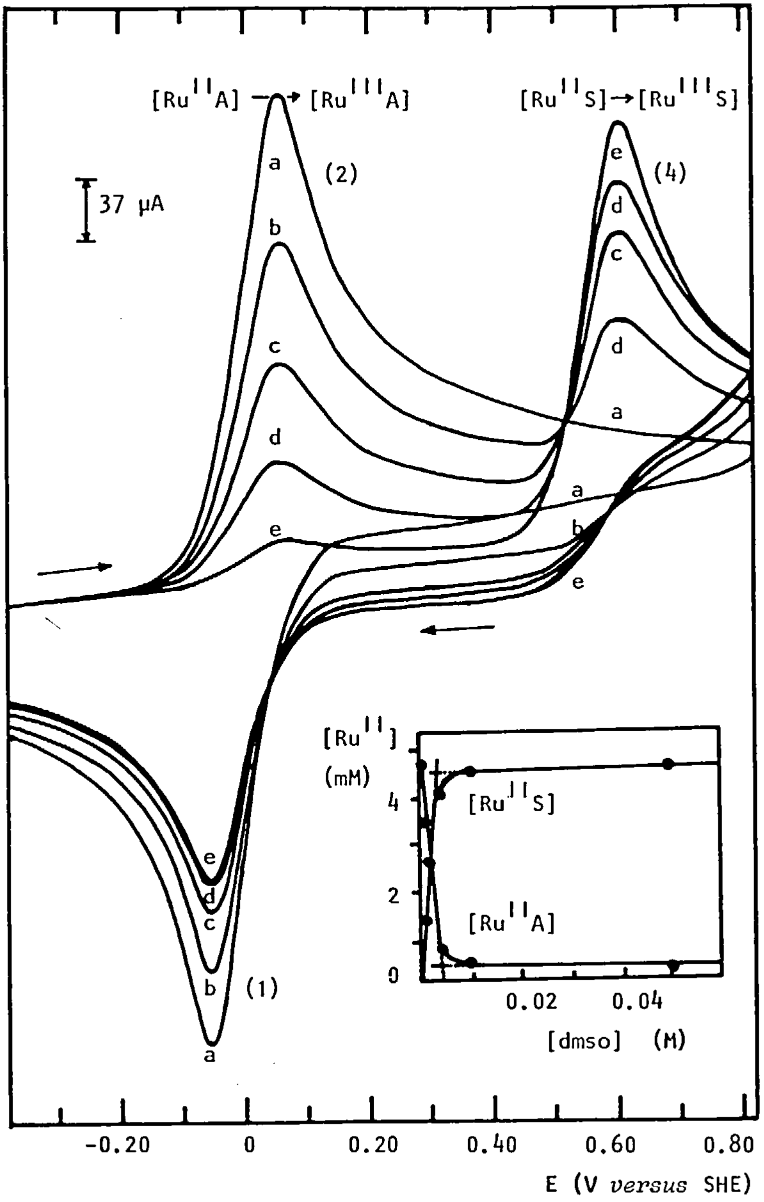

FIGURE 2 Cyclic voltammograms of the [Ru(EDTA)(H_2O)]$^{2-}$ and [Ru(EDTA)(dmso)]$^{2-}$ complexes (5 mM), in the presence of [dmso] = (a) 0, (b) 1.0, (c) 2.0, (d) 3.0, and (e) 10 mM; [NaTFA] = 0.25 M; pH 4.5 (acetate buffer 0.05 M); scan rate = 200 mV s^{-1}; T = 25°C. Inset: titration plots showing the parallel decay and formation of the aqua and dmso ruthenium(II) species and the equivalence point, indicative of a quantitative reaction.

equilibrium with Ru^{III}A, and using a scan rate of 200 mV/s, practically all the Ru^{III}S complex would be reduced within 0.15 s, which is the time elapsed in passing from the base line to the voltammetric peak. During this time interval, formation of Ru^{III}S from the reaction of Ru^{III}A and dmso, at a concentration below 0.1 M, is practically negligible, corroborating the hypothesis assumed in the evaluation of the equilibrium constant.

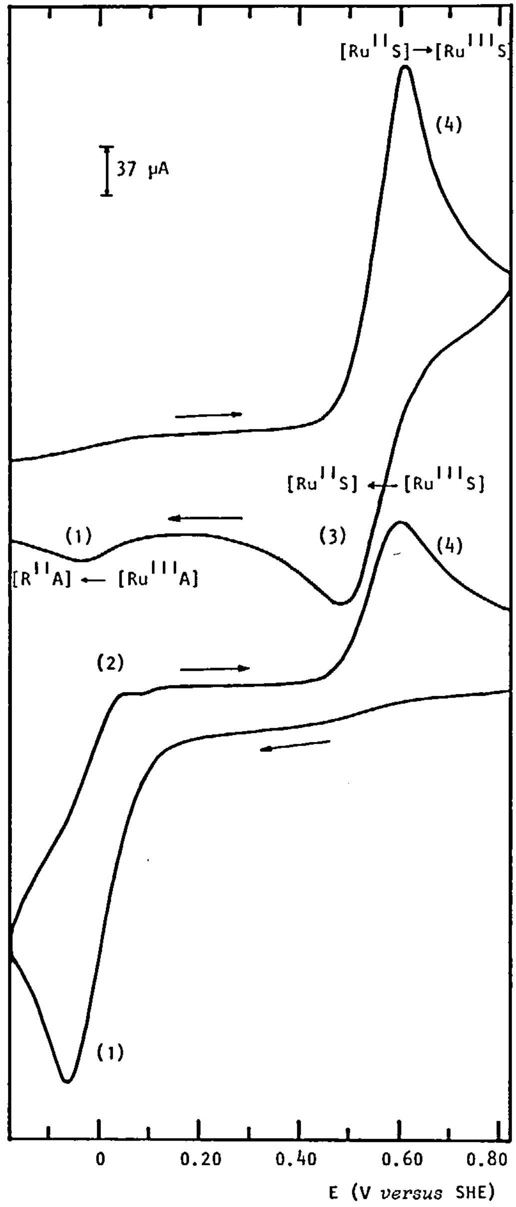

FIGURE 3 (A): Electrochemical oxidation of [Ru(II)(EDTA)(dmso)$^{2-}$ (5 mM), [dmso] = 0.5 M, followed by the aquation of the [Ru(III)(EDTA)(dmso)]$^{-}$ complex, and (B): electrochemical reduction of [Ru(III)(EDTA)(H_2O)]$^{-}$ followed by the formation of the [Ru(II)(EDTA)(dmso)]$^{2-}$ complex, at a potential scan rate = 200 mV s^{-1}; [dmso] = 0.025 M; [NaTFA] = 0.25 M; pH 4.5 (acetate buffer 0.05 M); T = 25°C.

In the second case, one can start from the $\mathrm{Ru^{III}A}$ complex at 0.9 v using a typical concentration of dmso, *e.g.* 0.025 M, where the concentration of the $\mathrm{Ru^{III}S}$ product is negligible (Figure 3.B). By starting the potential scan and reversing, for instance at -0.2 V, the electrochemical reduction of $\mathrm{Ru^{III}A}$ is followed by reaction of $\mathrm{Ru^{II}A}$ with dmso, yielding $\mathrm{Ru^{II}S}$. The situation approaches the scheme discussed by Shain and Nicholson,[18] involving a reversible electrochemical step followed by an irreversible chemical reaction,

$$\mathrm{Ru^{III}A} + e^- \rightleftharpoons \mathrm{Ru^{II}A}$$

$$\mathrm{Ru^{II}A} + \mathrm{dmso} \longrightarrow \mathrm{Ru^{II}S}$$

and can be analysed in terms of the appropriate formalisms as a function of the switching potential, E_λ. The ratio of anodic to cathodic peak current, $ip_a(2)/ip_c(1)$, corresponds to the quotient $[\mathrm{Ru^{II}A}]/[\mathrm{Ru^{III}A}]$, and depends on the time interval (τ) from $E_{1/3}$ to the switching potential E_λ, according to the working curve elaborated by Shain and Nicholson.[17] The evaluation of $ip_a(2)$ was carried out as recommended in the literature,[19] or alternatively, from $ip_c(1)$ minus $ip_a(4)$, taking into account the material balance $[\mathrm{Ru^{III}A}]_{t=0} = [\mathrm{Ru^{II}A}] + [\mathrm{Ru^{II}S}]$ and the similar diffusion constants expected for the complexes. The calculated rate constant based on the theoretical working curve,[18] using several values of E_λ in the range -200 to -500 mV ([dmso] = 0.025) was $1.07\ s^{-1}$, yielding a second order rate constant, $k_f = 43 \pm 6\ M^{-1}\,s^{-1}$.

Based on the equilibrium constant and redox potential for the $\mathrm{Ru^{III}S}$ complex, the following thermodynamic cycle can be solved,

$$\begin{tikzcd}[column sep=huge, row sep=huge]
\mathrm{Ru^{III}A} \arrow[r, shift left, harpoon, "E_0 = -0.01\ \mathrm{V}"] \arrow[d, shift left, harpoon, "+\ \mathrm{dmso}\quad K^{III} = 1.8\ M^{-1}"] & \mathrm{Ru^{II}A} \arrow[l, shift left, harpoon] \arrow[d, shift left, harpoon] \\
\mathrm{Ru^{III}S} \arrow[u, shift left, harpoon] \arrow[r, shift left, harpoon, "E_0 = 0.56\ \mathrm{V}"] & \mathrm{Ru^{II}S} \arrow[l, shift left, harpoon] \arrow[u, shift left, harpoon, "+\ \mathrm{dmso}\quad K^{II}"']
\end{tikzcd}$$

yielding an association constant (K^{II}) for the $\mathrm{Ru^{II}S}$ complex of $7.7 \times 10^9\ M^{-1}$.

The $\mathrm{Ru^{II}S}$ complex is more stable than the corresponding $\mathrm{Ru^{III}S}$ species by 9 orders of magnitude in K. This large difference is indicative of strong π-backbonding interactions in the $\mathrm{Ru^{II}S}$ complex. Since the formation rate constant is known, *i.e.*, $k_f = 43\ M^{-1}\,s^{-1}$, the dissociation rate constant for the $\mathrm{Ru^{II}S}$ complex can be calculated as $k_r = k_f/K^{II} = 5.6 \times 10^{-9}\ s^{-1}$.

It is interesting to notice that the $[\mathrm{Ru(EDTA)(dmso)}]^-$ complex differs from the $[\mathrm{Ru(NH_3)_5(dmso)}]^{3+}$ analogue by the greater stability of the $\mathrm{Ru^{III}S}$ isomer with respect to the $\mathrm{Ru^{III}O}$ species, and by the pronounced lability of the $\mathrm{Ru^{III}}$–S bond. As a matter of fact, the *S*-bound $[\mathrm{Ru(NH_3)_5(dmso)}]^{3+}$ complex is relatively inert ($k_d = 7.7 \times 10^{-5}\ s^{-1}$), but thermodynamically unstable with respect to the *O*-bound isomer,[15] undergoing intramolecular isomerization with a rate constant of $7 \times 10^{-2}\ s^{-1}$.In the case of the $[\mathrm{Ru(EDTA)(dmso)}]^-$ complex, the formation of the

$Ru^{III}O$ isomer is not thermodynamically favoured, and aquation, instead of isomerization, has been observed.

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