Pyridyl to Amido and Amido to Pyridyl Isomerisation in an Isonicotinamide Complex of Ruthenium(III)

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The reaction of $[Ru^{III}(edta)(H_2O)]^-$ (edta = ethylenediamine-*N*,*N*,*N*',*N*'-tetraacetate) with isonicotinamide (isna) was studied spectrophotometrically at different pH (6–10), isonicotinamide concentrations and ionic strengths. The pyridyl-*N*-co-ordinated complex $[Ru(edta)(isna)]^-$ is stable at low pH (6.0), but undergoes intramolecular isomerisation at high pH (9.6) to yield the amido-*N*-co-ordinated $[Ru(edta)(isna)]^{2-}$. Upon acidification, the amido-*N*-bonded species isomerises back to the pyridyl-*N*-co-ordinated isomer.

The chemistry of carboxamidoruthenium complexes is of continued interest[1–5] in its own right and in the context of metal–peptide chemistry.[6] However, the knowledge of these systems is mostly limited to pentaammineruthenium amido complexes. Owing to our continued interest[7] in Ru–edta (edta = ethylenediamine-*N*,*N*,*N*',*N*'-tetraacetate) chemistry, we wanted to examine the reactions of Ru–edta with some amides which have not been studied so far. Although kinetic data for the substitution of $[Ru^{III}(edta)(H_2O)]^-$ with isonicotinamide (isna) at pH 5.0 were reported long ago,[8] we have undertaken the present work to investigate the possibility of isomerisation in the Ru^{III}–edta–isna system at high pH. Hence, we have re-examined the reactions of $[Ru^{III}(edta)(OH)]^{2-}$ with isna at high pH and since comparable data would be useful for substantiating the formation of amido-*N*-co-ordinated $[Ru^{III}(edta)(isna)]^{2-}$, we also studied the reaction of $[Ru(edta)(H_2O)]^-$ with benzamide. Here, we report spectrophotometric and kinetic evidence for pyridyl to amido and amido to pyridyl linkage isomerisation in $[Ru(edta)(isna)]^{2-}$. To the best of our knowledge, this is a unique reaction of its kind in Ru^{III}–edta chemistry.

Experimental

The salt $K[Ru^{III}(Hedta)Cl]\cdot 2H_2O$ was prepared by the published procedure[9] and characterised. It is rapidly aquated[8] when dissolved in water and at pH 5–6 exists predominantly as $[Ru(edta)(H_2O)]^-$. At higher pH (>8) the complex $[Ru(edta)(H_2O)]^-$ hydrolyses, to give corresponding hydroxo-species (pK_2 = 7.6 at 25 °C).[8] All other chemicals used were of A. R. grade. Double distilled water was used throughout the experiments. The absorption spectra of the experimental solutions were recorded on a Shimadzu-160 UV/VIS spectrophotometer equipped with a TCC 240A temperature controller. Kinetic measurements were carried out on a HI-TECH (SF-51) stopped-flow spectrophotometer coupled with an Apple IIe data analyser. All the reactions were monitored in the wavelength region 360–380 nm where reasonable spectral differences between the reactant and product exist. The instrument was thermostatted at ±0.1 °C. Rate constant data (each rate constant is an average from two or three separate experimental determinations performed under constant reaction conditions) were measured under pseudo-first-order conditions of an excess (10–100 fold) of nucleophile. Acetic acid–acetate, phosphate and borate buffers were used to adjust the pH of the kinetic solutions, whereas $NaClO_4$ was used to control the ionic strength. pH Measurements were carried out with a Digisun pH meter.

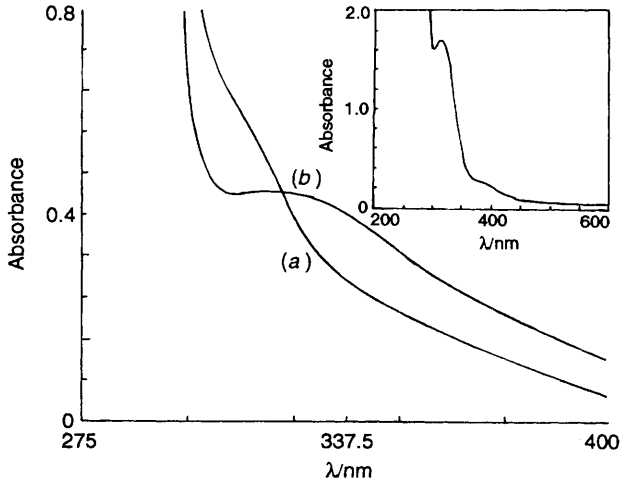

Fig. 1 Absorption spectra of a solution containing Ru^{III}–edta (2.5×10^{-4} mol dm^{-3}) and isonicotinamide (5×10^{-3} mol dm^{-3}): (*a*) at pH 5.5, (*b*) at pH 10.1. Inset: spectrum of a solution containing Ru^{III}–edta (1×10^{-3} mol dm^{-3}) and benzamide (1×10^{-2} mol dm^{-3}) at pH 9.6

Results and Discussion

Absorption Spectra.—The spectrum of $[Ru(edta)(isna)]^-$ at pH 5.2 is shown in Fig. 1. Formation of the pyridyl-*N*-co-ordinated $[Ru(edta)(isna)]^-$ complex (hereafter designated as Ru^{III}–N_{py}) in the reaction of $[Ru(edta)(H_2O)]^-$ with isonicotinamide at low pH (≈5) was established earlier.[8] The spectrum of Ru^{III}–N_{py} [Fig. 1(*a*)] does not show any peak or shoulder above 300 nm. However, a new peak at 320 nm (ε_{max} = 1800 ± 100 dm^3 mol^{-1} cm^{-1}) is developed [Fig. 1(*b*)] by increasing the pH from 5.2 to 10.1. A similar spectrum (λ_{max} = 323 nm, ε_{max} = 1720 ± 50 dm^3 mol^{-1} cm^{-1}) was also obtained (inset, Fig. 1) by mixing a solution of Ru^{III}–edta (1×10^{-3} mol dm^{-3}) with a solution of benzamide (1×10^{-2} mol dm^{-3}) at pH 9.6. The spectral pattern [Fig. 1(*b*) and inset] observed in our systems at high pH resembles those observed for pentaammineruthenium amide complexes.[5c] Ruthenium(III) carboxamido complexes usually show a ligand-to-metal charge

transfer (l.m.c.t.) band (in the range 320–400 nm)[1a,2d] which is associated with charge transfer from the nitrogen lone pair of deprotonated NH_2 group to the half-empty d orbital of Ru^{III}. It is important to note here that all the pyridyl-*N*-co-ordinated complexes of $[Ru^{III}(edta)L]$ (L = pyridine, pyrazine or isonicotinamide) do not show any clear band above 300 nm.[8] This may be explained in terms of very poor ligand-to-metal charge transfer through the pyridyl N atom. On the basis of the above spectral observations and comparison of spectral data to those reported for pentaammineruthenium analogues, it can be presumed that the reaction of Ru^{III}–edta with $RCONH_2$ (R = C_5H_4N or Ph) results in the formation of an amido-*N*-co-ordinated Ru^{III}–edta–amide complex (hereafter designated as Ru^{III}–N_{am}) at high pH (≈9).

Kinetic Studies.—Ru^{III}–N_{py} *to* Ru^{III}–N_{am} *isomerisation.* In a typical experiment a solution (I) containing Ru^{III}–edta (5×10^{-4} mol dm^{-3}) and isonicotinamide (5×10^{-3} mol dm^{-3}) at pH 5.2 (adjusted by NaOH) was allowed to mix with buffer solutions of different pH (6–10) in a stopped-flow mixing chamber and corresponding kinetic traces (growth at 380 nm) were found to be single exponential in all cases. At a constant pH, the observed rate constant (k_{obs}) was found to be independent of [isna] (total concentration of isonicotinamide present in solution I) and the ionic strength (I) of the medium. The effect of pH on k_{obs} at 25 °C (I = 0.2 mol dm^{-3}) shown in Fig. 2(*a*) may be analysed in terms of the acid-dissociation equilibrium (1) and reaction (2). The rate equation (3) predicts limiting

$$[(edta)Ru^{III}\text{–}NC_5H_4CONH_2)]^- \overset{K_a}{\rightleftharpoons} [(edta)Ru^{III}\text{–}NC_5H_4CONH]^{2-} + H^+ \quad (1)$$

$$[(edta)Ru^{III}\text{–}NC_5H_4CONH]^{2-} \xrightarrow{k} [(edta)Ru^{III}\text{–}NHCOC_5H_4N]^{2-} \quad (2)$$

values of k_{obs} at high pH ($k_{obs} = k$) and the value of k thus obtained is 0.18 s^{-1}. The inflection in the curve [Fig. 2(*a*)] occurs at pH 8.3 which is very close to the value of pK_a (8.2) determined spectrophotometrically. Further, a rate *vs.* pH profile (calculated by considering the value of k = 0.18 s^{-1} and pK_a = 8.2) is superimposable on that obtained experimentally [Fig. 2(*a*)]. This substantiates the validity of the rate expression (3).

$$k_{obs} = kK_a/(K_a + [H^+]) \quad (3)$$

In order to gain more mechanistic information regarding the Ru^{III}–N_{py} to Ru^{III}–N_{am} isomerisation, we have re-examined the ligand-substitution reaction of $[Ru(edta)(H_2O)]^-$ with isonicotinamide over the range pH 6–10 in a second set of experiments. The most important and remarkable observation was two consecutive kinetic traces (both for growth at 380 nm) at high pH. The observed rate constant (k_0) for the first step showed a similar ligand concentration and pH dependence as that reported earlier.[8] The k_0 *versus* pH profile (in the range 6–10) at 25 °C (I = 0.2 mol dm^{-3}) for this step is shown in Fig. 2(*b*). The values of k_b[8] {second-order rate constant for the substitution of $[Ru(edta)(H_2O)]^-$ by isna} and k_c[8] {second-order rate constant for the substitution of $[Ru(edta)(OH)]^{2-}$ by isna} are 8500 ± 200 and 370 ± 20 dm^3 mol^{-1} s^{-1}, respectively.

Analysis of the second kinetic trace yielded a rate constant which was independent of [isna] and the ionic strength of the medium. Moreover, the plot of pH *versus* observed rate constant at 25 °C (I = 0.2 mol dm^{-3}) was identical to that [Fig. 2(*a*)] shown for the isomerisation of Ru^{III}–N_{py} to Ru^{III}–N_{am}.

The above experimental results suggest that the reaction of Ru^{III}–edta with isonicotinamide at high pH proceeds through

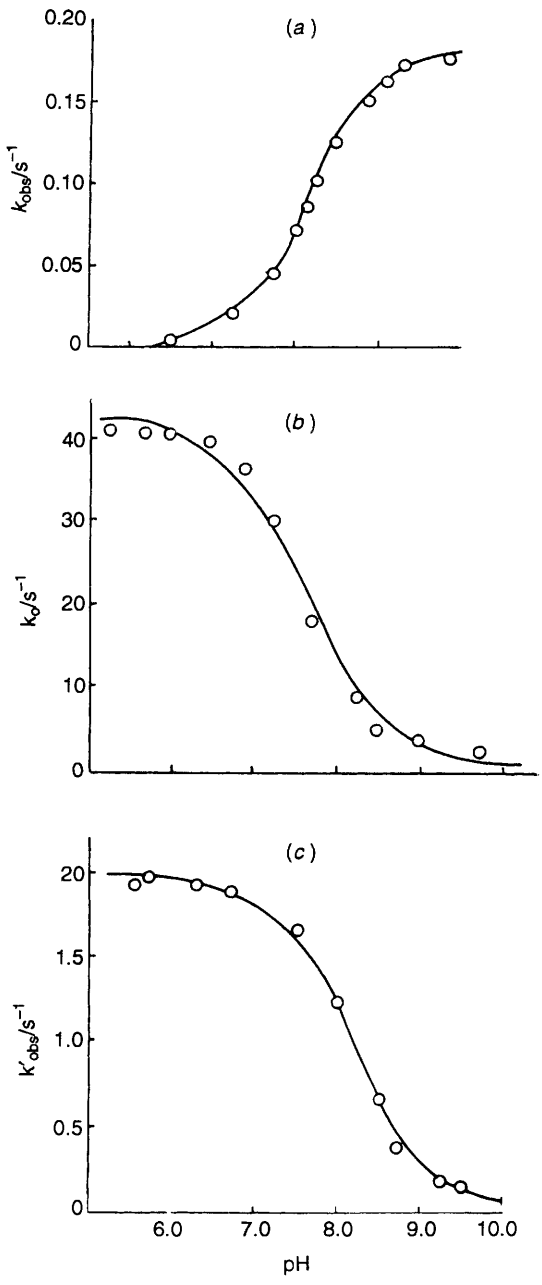

Fig. 2 The pH dependence of the observed rate constants for (*a*) Ru^{III}–N_{py} to Ru^{III}–N_{am} isomerisation, (*b*) substitution of $[Ru(edta)(H_2O)]^-$ by isonicotinamide and (*c*) isomerisation of Ru^{III}–N_{am} to Ru^{III}–N_{py}. (○) Experimentally observed values, (–) calculated by using resolved rate constants at 25 °C and I = 0.2 mol dm^{-3}

the formation of a pyridyl-*N*-co-ordinated Ru^{III}–N_{py} species in a rapid substitution step followed by its conversion into the Ru^{III}–N_{am} isomer in a slower step. It may be noted here that, as expected, the substitution of the Ru^{III}–edta complex with benzamide did not show more than one kinetic trace (single exponential) over the pH range studied (6–10). The second-order rate constant determined from the kinetic measurements at various benzamide concentrations is 18 ± 2 dm^3 mol^{-1} s^{-1} at 25 °C (pH 9.6, I = 0.2 mol dm^{-3}).

Ru^{III}–N_{am} *to* Ru^{III}–N_{py} *isomerisation.* The kinetics of amido to pyridyl (Ru^{III}–N_{am} to Ru^{III}–N_{py}) isomerisation was studied by mixing a solution (II) containing Ru^{III}–edta (5×10^{-4} mol dm^{-3}) and isonicotinamide (5×10^{-3} mol dm^{-3}) at pH 10.1 (adjusted by NaOH) with buffer solution of different pH (9.6–5.0). The

Table 1 Rate and activation parameters for the isomerisation reactions

	Ru^{III}–N_{py} to Ru^{III}–N_{am}			Ru^{III}–N_{am} to Ru^{III}–N_{py}		
T/°C	k/s^{-1}	$\Delta H_1^{\ddagger}$/kJ mol^{-1}	$\Delta S_1^{\ddagger}$/J K^{-1} mol^{-1}	k'/s^{-1}	$\Delta H_2^{\ddagger}$/kJ mol^{-1}	$\Delta S_2^{\ddagger}$/J K^{-1} mol^{-1}
25	0.180 ± 0.003			1.98 ± 0.02		
35	0.322 ± 0.004	39 ± 1	−127 ± 5	3.11 ± 0.05	24 ± 1	−126 ± 4
45	0.524 ± 0.004			5.00 ± 0.04		

reaction was monitored by the decrease in absorbance at 380 nm. The kinetic traces (decay) were found to be single exponentials in all cases. The observed rate constant (k'_{obs}) was independent of [isna] (total concentration of isonicotinamide present in solution II) and the ionic strength of the medium. The pH dependence for the conversion of the amido into the pyridyl isomer at 25 °C (I = 0.2 mol dm^{-3}) is shown in Fig. 2(*c*). The value of k'_{obs} drops to half the maximum value (1.98 s^{-1}) at pH 7.9. The results may be explained in terms of the following protonation equilibrium (4) and isomerisation (5) for which the

$$[Ru^{III}\text{–}N_{am}]^{2-} + H^+ \overset{K'_a}{\rightleftharpoons} [Ru^{III}\text{–}N_{am}H]^- \quad (4)$$

$$[Ru^{III}\text{–}N_{am}H]^- \xrightarrow{k'} [Ru^{III}\text{–}N_{py}]^- \quad (5)$$

rate equation (6) is derived where $K''_a = 1/K'_a$. The calculated

$$k'_{obs} = k'[H^+]/(K''_a + [H^+]) \quad (6)$$

rate *vs.* pH profile is superimposable on that obtained experimentally [Fig. 2(*c*)]. This underlines the validity of the rate expression (6). Under limiting conditions ($[H^+] \gg K''_a$), equation (6) reduces to $k'_{obs} = k'$ and the value of k' thus obtained is 1.98 s^{-1}.

Activation parameters for both isomerisation processes are summarised in Table 1. The almost identical values of $\Delta S^{\ddagger}$ may be suggestive that the structures of the activated complexes are similar and there appear to be specific orientational and vibrational requirements. However, the pathway through which the ruthenium(III) centre 'walks' to reach the two different *N* atoms is not clear. We speculate the intermediacy of an aromatic ring-bonded ruthenium(III) isomer as reported for the corresponding isomerisation of $[Ru^{II}(NH_3)_5(isna)]^{2+}$.[5b]

In conclusion, we provide spectral and kinetic evidence of Ru^{III}–N_{py} to Ru^{III}–N_{am} and Ru^{III}–N_{am} to Ru^{III}–N_{py} isomerisation reactions. Amido complexes of Ru^{III}–edta are exemplified.

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