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THE KINETICS AND MECHANISM OF THE FORMATION OF THIOCYANATO-BRIDGED DINUCLEAR COMPLEX ION $[Ru_2(NH_3)_8(SCN)_3]^{3+}$

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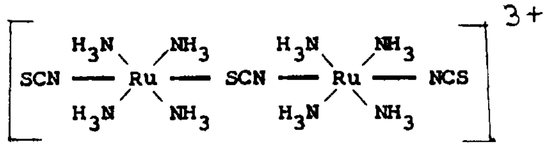
Abstract—Formation of a thiocyanato-bridged dinuclear complex $[Ru_2(NH_3)_8(SCN)_3]^{3+}$ by the interaction of $[Ru(NH_3)_5Cl]^{2+}$ and SCN^- was investigated in aqueous solution between 48 and 59°C. The reaction proceeds in two stages. First stage proceeds with ion-pair formation between the reacting species giving $[Ru(NH_3)_4(SCN)Cl]^+$ with the loss of one coordinated ammonia. The second stage comprises "ion-aggregation" of this tetraamine complex with another SCN^- ion leading to the formation of the SCN^- bridged dinuclear complex ion. Activation parameters ($\Delta H^\ddagger$ 96 ± 8 and 56 ± 8 kJ mol^{-1} and $\Delta S^\ddagger$ -17 ± 20 and -125 ± 21 J K^{-1} mol^{-1} respectively for the first and second stages of reaction) are consistent with other similar processes and support the mechanism proposed.

Formation and dissociation of ruthenium(II)/(III) complexes received a good deal of attention from the kineticists over the last decade or two. Ruthenium has a good tendency to form bridged complexes and a number of oxo,[1] peroxo,[2] dinitrogen,[3] oxalato,[4] cyanide and cyanogen,[5] 4-4′-dipyridyl[5] and thiocyanato[6] bridged complexes are known owing to the various oxidation states of this metal ion. However, mechanistic studies on the formation and dissociation of such bridged complexes of this metal ion have till now received little attention.[1,7] Ruthenium(III), a second series transition metal ion, differs in many ways from cobalt (III) and chromium(III) and mechanistic studies with the complexes of this metal ion may reveal interesting results. In this communication we are reporting the formation of a thiocyanato bridged dinuclear complex $[Ru_2(NH_3)_8(SCN)_3]^{3+}$ by the interaction of $[Ru(NH_3)_5Cl]^{2+}$ and SCN^- in the temperature range 48–60°C. The temperature range under investigation is narrow, however, beyond this range, both above and below, other simultaneous reactions are likely to occur with the formation of thiocyanato substituted trinuclear and mononuclear species.[6] Treatment of such simultaneous reactions requires a complicated rate law which is avoided in the present study.

The structure of the dinuclear complex may be presented as



EXPERIMENTAL

Preparation of complexes

Pentaamminechlororuthenium(III) chloride, tetraammineiodothiocyanatoruthenium(III) iodide and the dinuclear complex octaamminotrithiocyanatodiruthenium(III) chloride were prepared according to literature methods.[6,8] Reagent grade chemicals were used in all the experimental procedures. A "Sicospek 100" spectrophotometer was used for monitoring the kinetic runs. A PYE-UNICAM SP 8-150 UV/visible spectrophotometer was used for recording spectra of the complexes. A

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requisite amount of the complex was transferred to the reaction vessel containing an appropriate amount of ammonium thiocyanate and sodium *para*-toluene sulphonate (for maintenance of ionic strength) in thermostated double distilled water. Perchlorates could not be used for the maintenance of ionic concentration as the dinuclear complex perchlorate is insoluble in water and deposits as a residue on the bottom of the reaction vessel. The reaction vessel was shaken well and placed on the thermostat. Sample quenching technique[9] was adopted for absorbance measurements at suitable time intervals. The kinetics were followed at 516 nm corresponding to the maxima of the formed complex, although at other wavelengths too similar results are obtained. All the kinetic runs were carried out under pseudo-first-order conditions. No experimental difference could be detected for parallel runs in presence or absence of oxygen.

RESULTS AND DISCUSSION

The visible absorption spectra of both the dinuclear and the mononuclear complexes were found to be rather insensitive to the ionic environment, being within the experimental error of water and of 0.395 mol dm^{-3} solutions of NH_4SCN or NaPTS. Figure 1 shows the spectra of these two complexes along with the spectral scanning of the formation reaction. The spectra were remarkably insensitive to temperature changes. The topmost curve in Fig. 1 represents the stage of apparent completion of the reaction, and no further changes were noted over the next 2–3 days. At this final stage there was a maximum at 516 nm (log ε 3.98) (calculated on the basis of the known concentration of $Ru(NH_3)_5Cl^{2+}$) and the spectrum matched very closely with that of the freshly prepared solution of the dinuclear complex $[Ru_2(NH_3)_8(SCN)_3]^{3+}$ (λ_{max} 516 nm; log ε_{max} 4.02). However, it is necessary to point out at this stage that the double salt $[Ru(NH_3)_4(NCS)_2]$ $[Ru(NH_3)_2(NCS)Cl_3]$ also has a similar spectrum with only a little difference in the absorption peak position in the visible range (522 nm), ε_{max} and peak positions in the ultraviolet region are all the same. So, it was necessary to identify the products by other means also. After completion of the reaction (4–5 h), the reaction mixture was loaded on to a column of ion-exchanger (DOWEX-50 × W, 100–200 mesh) in Na^+ form and first eluted with water. A portion of the reaction mixture (reddish–pink) remains absorbed on the column and a minute amount of a violet–red coloured solution passes through it. If the reaction mixture is allowed to stand for long (2–3 days), the amount of this violet–red compound increases. This compound was identified as the double salt $[Ru(NH_3)_4(NCS)_2]$ $[Ru(NH_3)_2(NCS)Cl_3]$. When the absorbed portion was eluted with 1.0 mol dm^{-3} $NaNO_3$, the reddish–pink compound elutes out. It was acidified with conc. HCl, concentrated on a rotary evaporator and by partial crystallization the dinuclear complex $[Ru_2(NH_3)_8(SCN)_3]Cl_3$ was obtained. It was identified by UV/visible (λ_{max} at 232, 340 and 516 nm) and IR spectra (2045 sb, 2005 sb and 787 s). The reaction does not follow a simple first-order plot. However, a plot of log $(A_t - A_\infty)$ *vs* "time" (A_t and A_∞ denotes absorbances at time t and after completion of the reaction) gives a biphasic plot[10] indicating that there are two reactions taking place consecutively. The rate constants for the slow reaction was determined from the later linear portion of the plot and that of the fast reaction was determined from a plot of log $\{A_t - A_\infty) - (A_t - A_\infty)'\}$ *vs* "time", where $(A_t - A_\infty)'$ denotes the extrapolated $(A_t - A_\infty)$ value to time "zero", The two rate constants, $k_{1(obs)}$ and $k_{2(obs)}$ thus obtained are given in Table 1. It was simultaneously observed that while $k_{1(obs)}$ does not change with concentration of the complex employed, $k_{2(obs)}$ changes with it. The rate constants at three different complex concentrations but at a particular concentration of ammonium thiocyanate are given in Table 1. Plots of $k_{1(obs)}$

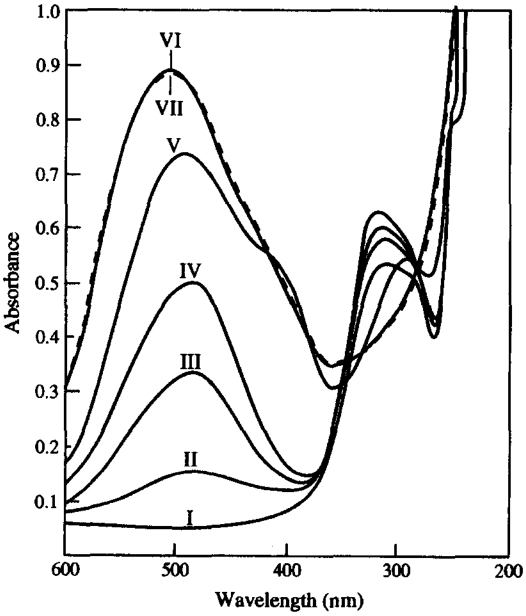


Fig. 1. Spectral scanning of the reaction between $[Ru(NH_3)_5Cl]^{2+}$ and $[SCN^-]$; complex = 7.5×10^{-4} mol dm^{-3}, $[SCN^-]$ 0.079 mol dm^{-3}. I, spectrum of $[Ru(NH_3)_5Cl]^{2+}$; II, 5 min after mixing; III, 20 min; IV, 40 min; V, 90 min; VI, 1 day; VII, spectrum of $[Ru_2(NH_3)_8(SCN)_3]^{3+}$.

Table 1. Formation of $[Ru_2(NH_3(SCN)_3]Cl_3$ by the reaction $[Ru(NH_3)_5Cl]^{2+}$ and SCN^- in aqueous solution ($I = 0.3950$ mol dm^{-3} NaPTS)

[Complex] × 10^4 (mol dm^{-3})	[NH_4SCN] (mol dm^{-3})	$10^5k_{1(obs)}$(s^{-1})			$10^4k_{2(obs)}$(s^{-1})		
		48°	55°	59°	48°	55°	59°
7.5	0.079	7.47	13.91	27.12	3.11	—	8.9
7.5	0.158	12.19	26.22	40.94	5.62	10.00	12.62
7.5	0.237	14.30	30.00	47.33	7.50	13.20	15.71
7.5	0.316	19.10	33.54	58.00	8.80	14.10	18.52
15.0	0.316	18.92	33.00	57.20	11.30	18.58	21.79
22.5	0.316	19.07	33.23	57.49	13.23	20.20	24.07
7.5	0.395	18.35	39.34	60.02	9.55	16.00	20.20
15.0	0.395	19.84	39.47	59.71	12.30	19.00	23.00
22.5	0.395	19.63	39.95	59.22	13.82	20.79	24.90

vs [SCN^-] and $k_{2(obs)}$ *vs* [SCN^-] at a particular concentration of the complex are all curved, tending to a limiting value at higher concentration of [SCN^-]. However, reciprocal plots of $1/k_{1(obs)}$ *vs* $1/[SCN^-]$ and $1/k_{2(obs)}$ *vs* $1/[SCN^-]$ are all linear having positive slope and positive intercept on the rate axis. The nature of the plot of $k_{1(obs)}$ *vs* [SCN^-] indicates that ion-pair formation is extensive, and the reaction proceeds through ion-pair formation. This ion-pair formation may be one of the causes that makes the spectra of the complex insensitive to change in an ionic environment as mentioned at the beginning of this discussion. The mechanistic pathways of the first stage of the reaction may be shown as:

$$[Ru(NH_3)_5Cl]^{2+} + SCN^- \overset{K_1}{\rightleftharpoons} \underset{\text{(ion-pair)}}{[Ru(NH_3)_5Cl]^{2+}SCN^-} \quad (1)$$

$$[Ru(NH_3)_5Cl]^{2+}SCN^- \xrightarrow{k_1} SCN\text{–}Ru(NH_3)_4Cl^+ + NH_3. \quad (2)$$

The rate of the reaction is then given by the equation

$$-\frac{d[\text{complex}]}{dt} = \frac{k_1K_1[\text{complex}][SCN^-]}{1+K_1[SCN^-]} = k_{1(obs)}[\text{complex}] \quad (3)$$

and

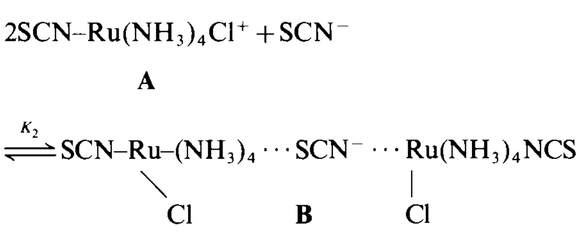
$$1/k_{1(obs)} = 1/k_1K_1[SCN^-] + 1/k_1. \quad (4)$$

The values of k_1 and K_1 are obtained from the intercept ($1/k_1$) and slope ($1/k_1K_1$) of the plot of $1/k_{1(obs)}$ *vs* $1/[SCN^-]$ and are collected in Table 2. In eq. (2) one coordinated ammonia is lost instead of the chloride which is of considerable interest since NH_3 ligands are generally extremely inert when complexed to cobalt(III). In their preparation of ruthenium(III) ammine complexes Prashad *et al.* were able to replace successive ammonia molecules, up to a maximum of three, with thiocyanate ion without removal of the coordinated chloride ion.[6] They were also able to isolate a complex ion $[Ru(NH_3)_4(SCN^-)X]^+$ (X^- represents a halide ion) in the solid crystalline form. *Trans* labilization of the chloride ion causes removal of the coordinated ammonia opposite to it. Halpern *et al.* also observed that sulphur bonded sulphite ligand in $[Co(NH_3)_5(SO_3)]^+$ labilizes an ammonia in the *trans* position.[11] However, in the present situation approach of the SCN^- ion is to a position opposite to the chloride ion. In such a situation release of ammonia is very unlikely in an I_d process and entry of the thiocyanate in the coordination sphere seems important for having a driving force for the "ammonia". This model will present an "associative character" for the process. The second stage of the reaction which is more important as regard to the formation of the final complex is given by the reaction steps (5) and (6). At a particular concentration of NH_4SCN employed, $1/k_{2(obs)}$ *vs* 1/[complex] gives a linear plot. Again, at a particular complex concentration, $1/k_{2(obs)}$ *vs* $1/[SCN^-]$ plot is also linear. These dependencies lead to a system of "ion association" or "ion aggregation" with the reacting species giving the intermediate species as:

Table 2. Rate constants, ion-pair and ion-association constants and activation parameters

Temp. (°C)	48	55	59	$\Delta H\ddagger$ (kJ mol^{-1})	$\Delta S\ddagger$ (J K^{-1} mol^{-1})
$10^4 k_1$ (dm^3 mol^{-1} sec^{-1})	2.57 ± 0.24	5.21 ± 0.30	9.89 ± 0.30	96 ± 8	-17 ± 21
K_1	5.72 ± 0.35	5.48 ± 0.20	5.26 ± 0.30		
$10^3 k_2$ (dm^3 mol^{-1} sec^{-1})	1.74 ± 0.26	2.53 ± 0.17	3.33 ± 0.20	56 ± 8	-125 ± 21
K_2	$(1.31 \pm 0.15) \times 10^4$	$(1.24 \pm 0.10) \times 10^4$	$(1.19 \pm 0.20) \times 10^4$		

Second stage of reaction



$$\underset{\mathbf{A}}{2\mathrm{SCN\text{-}Ru(NH_3)_4Cl^+ + SCN^-}} \underset{}{\overset{K_2}{\rightleftharpoons}} \mathrm{SCN\text{-}Ru\text{-}(NH_3)_4} \cdots \underset{\mathbf{B}}{\mathrm{SCN^-}} \cdots \mathrm{Ru(NH_3)_4NCS}$$

(ion association) (5)

$$\xrightarrow{k_2} \mathrm{SCN\text{-}Ru(NH_3)_4\text{-}SCN\text{-}Ru(NH_3)_4NCS^{3+} + 2Cl^-}. \quad (6)$$

C

The rate of formation of the final product **C** is given by

$$\frac{d[\mathrm{C}]}{dt} = k_{2(\mathrm{obs})}\{2[\mathbf{A}] + [\mathbf{B}]\}$$

$$= k_2[\mathbf{B}] = k_2 K_2 [\mathbf{A}]^2[\mathrm{SCN^-}] \quad (7)$$

but ion-association constant,

$$K_2 = \frac{[\mathbf{B}]}{[\mathbf{A}]^2[\mathrm{SCN^-}]} \quad (8)$$

from eqs (7) and (8),

$$k_{2(\mathrm{obs})} = \frac{k_2 K_2 [\mathbf{A}]^2[\mathrm{SCN^-}]}{2\mathbf{A} + K_2[\mathbf{A}]^2[\mathrm{SCN^-}]}$$

and,

$$1/k_{2(\mathrm{obs})} = \frac{2}{k_2 K_2 [\mathrm{SCN^-}][\mathbf{A}]} + \frac{1}{k_2} \quad (9)$$

From eq. (9) it is apparent that at any particular concentration of the species **A**, a plot of $1/k_{2(\mathrm{obs})}$ *vs* $1/[\mathrm{SCN^-}]$ gives a linear plot with intercept $1/k_2$ and slope $2/[\mathbf{A}]k_2K_2$, with a known amount of complex employed, K_2, the ion-association or the "ion-aggregation" constant can be determined and the values thus determined in the present case are given in Table 2. The enthalpy of the reaction (for k_2) is also given there. This type of "ion-aggregation" has been observed in the cleavage of an hydroxo-bridged complex $[(\mathrm{NH_3})_5\mathrm{Co \cdot OH \cdot Co(NH_3)}_5^{5+}]$.[12] Thiocyanate ion with its ambidentate characteristics forms bonds with two ruthenium atoms, giving the bridged dinuclear complex ion. Ruthenium(III) being moderately soft interacts with the thiocyanate ion, while cobalt(III), a hard acid, cannot do so and no thiocyanato bridged complex has been obtained.

Loss of ammonia from cobalt–ammine complexes indicates a high enthalpy of reaction in each case; for $\mathrm{Co(NH_3)}_6^{3+}$, $\Delta H^{\ddagger}$ is 146 kJ mol^{-1} and for the dibridged complex cation, $[(\mathrm{NH_3})_4\mathrm{Co}(\mu\text{-OH},\mu\text{-NH_2})\mathrm{Co(NH_3)}]_4^{4+}$, $\Delta H^{\ddagger}$ is 105 kJ mol^{-1}.[13] Nevertheless, in the case of ruthenium(III), the enthalpy of the reaction 96 kJ mol^{-1} is smaller due to the loss of ammonia. The ruthenium–nitrogen bond in ruthenium–ammine complexes is weaker than the cobalt–nitrogen bond in cobalt–ammine complexes. This may be the reason for the observed lower enthalpy for the ruthenium complex. The small negative entropy accompanying the first step of the reaction indicates that entry of the $\mathrm{SCN^-}$ ion is in the position of the lost ammonia, with minimum stereochemical disturbance. As already emphasized earlier the thiocyanate ion occupies the position held by one of the "ammonia" ligands when attacking the complex species. The opposite charges on the reacting species may also render a less negative entropy value. Nevertheless, because of ion-pairing this effect is less prominent. The $\Delta H^{\ddagger}$ value for the second stage of the reaction is smaller for usual substitutions on the ruthenium(III) complex. *Trans* labilization is at least partially responsible for this observed lower $\Delta H^{\ddagger}$ value. However, "ion-association" favours the formation of the final complex with a smaller $\Delta H^{\ddagger}$ value.

An attempt was made to proceed with the second stage of the reaction independently starting from the complex species $[\mathrm{Ru(NH_3)_4(SCN)Cl}]^+$.

However, this species could not be isolated in the pure form in the solid state. So, we proceeded with the similarly constituted "iodo" complex $[Ru(NH_3)_4(SCN)I]^+$, but the "iodo" complex fails to give the thiocyanato bridged dinuclear complex and only a simple substitution reaction sets in resulting in the formation of the $[Ru(NH_3)_4(SCN)_2]^+$ complex ion. This is because of high *trans* labilization by the iodide. No further attempt was made to study this substitution reaction.

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