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# The Kinetics and Mechanism of the Oxidation of Titanium(III) by Thiocyanatopentaamminecobalt(III) and Azidopentaamminecobalt(III) Ions

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*The kinetics of the oxidation of titanium(III) by* $Co(NH_3)_5SCN^{2+}$ *and* $Co(NH_3)_5N_3^{2+}$ *ions at 25 °C in aqueous chloride medium of 1 M ionic strength (NaCl or LiCl) was studied as a function of acidity and the concentration of the reactants. Much faster rates of the two Co(III) complexes as compared to the rate of the* $Co(NH_3)_5NCS^{2+}$ *complex, the N-bonded thiocyanato isomer, offer evidence for an inner-sphere mechanism. This evidence is supported by the nature of the acidity dependence of the reactions. A differentiation between two more detailed inner-sphere mechanisms operative for the reduction of the thiocyanato and azido complex is discussed.*

## Introduction

An interest in titanium(III) as a reducing agent for cobalt(III)–ammine complexes has recently arisen [1–4]. The question of inner-sphere *vs.* outer-sphere mechanism in the reaction of cobalt chloroammine complexes came out unanswered at first [1] and our attention was turned toward titanium(III) reduction of cobalt(III) pentaamminepseudohalides. For these oxidizing agents a simple and useful approach was developed to make a distinction between the two mechanisms [5]. In the meantime kinetic data for a number of cobalt(III) complexes have been obtained, revealing an operation of both modes of oxidation of titanium(III) [2–4].

Here we report a kinetic study of the oxidation of titanium(III) by thiocyanato- and azidopentaamminecobalt(III) ions as a function of acidity in an aqueous chloride medium of unimolar ionic strength. The reactivities of the two oxidizing agents compared with the very slowly reacting analogous isothiocyanato complex give an evidence in favor of the inner-sphere mechanism, while the acidity dependence offers an insight into more subtle mechanistic differences between the thiocyanato- and azido-complexes. While this work was in progress data on the oxidation of titanium(III) by azidopentaamminecobalt(III) ion in 0.5 *M* ionic strength were published [3].

## Experimental

### Materials

$[Co(NH_3)_5NCS](SCN)_2$ [6], $[Co(NH_3)_5N_3](NO_3)_2$ [7] and $[Co(NH_3)_5SCN]Cl_2\cdot3/2H_2O$ [8], were prepared by the published procedures. The former two complexes were purified and converted to the chloride salts by the method described previously [9]. The purity of chloride salts of the three cobalt(III) complexes was ascertained by the comparison of their visible–u.v. spectra with the literature data [8–11].

Titanium(III) solution in chloride medium was prepared by dissolving titanium metal (Alfa Inorganic m3N+sponge) in 3 *M* HCl at 50–60 °C. It was filtered and stored at 0 °C. The solution kept in this way was found stable for several months as proved by the lack of an appearance of Ti(IV) absorption in the 300 nm spectral region [12]. The stock solution was standardized by oxidation of an aliquot to titanium(IV) with an excess of chromium(VI), followed by addition of an excess of iron(II) and back-titration with chromium(VI) in 1 *M* $H_2SO_4$ using N-phenylanthranilic acid as the indicator. The concentration of $H^+$ was calcualted by subtracting 3[Ti(III)] from the known concentration of hydrochloric acid used to dissolve titanium metal. Air oxygen was excluded from the contact with titanium(III) by the use of an atmosphere of purified nitrogen gas. All the solutions were purged with $N_2$ prior to addition of Ti(III).

Lithium chloride from two sources ("Baker Analyzed" and Merck "Suprapur") and sodium chloride (Merck, reagent grade) were used without further purification.

Doubly distilled water was used throughout.

## Kinetic Measurements

The kinetics of the reactions were followed with a Cary 17 spectrophotometer equipped with thermostatted cell compartment and cell holder. Decreases of absorption were measured at 302 nm or 518 nm for $Co(NH_3)_5N_3^{2+}$ ion, at 288 nm for $Co(NH_3)_5SCN^{2+}$

TABLE 1. Rate Constants for the Titanium(III) Reduction of the $Co(NH_3)_5SCN^{2+}$ Ion at 25 °C in Aqueous Chloride Medium of $\mu = 1.0$ *M*.[a]

| $[H^+] \times 10^3$ *M* | $[Co(NH_3)_5SCN^{2+}] \times 10^5$ *M* | $[Ti(III)] \times 10^5$ *M* | $k_{SCN} \times 10^{-1}$ $M^{-1}$ $s^{-1}$ |
|---|---|---|---|
| 1000 | 19.1 | 175 | 1.17[b] |
| 1000 | 16.6 | 175 | 1.21[c] |
| 1000 | 1.06 | 175 | 1.18 |
| 1000 | 1.19 | 24.0 | 1.24 |
| 1000 | 46.5 | 118 | 1.20[b] |
| 750 | 1.2 | 59.0 | 1.62 |
| 500 | 1.2 | 24.0 | 2.36 |
| 500 | 1.2 | 23.6 | 2.23[d] |
| 250 | 1.2 | 35.4 | 4.15 |
| 200 | 1.2 | 22.8 | 5.65 |
| 100 | 1.2 | 23.2 | 9.45 |
| 100 | 1.2 | 22.8 | 9.8[d] |
| 81.5 | 1.2 | 15.7 | 12.8 |
| 75.5 | 1.2 | 22.8 | 12.0 |
| 57.5 | 1.2 | 15.7 | 18.0 |
| 47.0 | 0.89 | 15.7 | 20.6 |
| 33.8 | 1.03 | 11.8 | 26.5 |
| 23.4 | 1.03 | 11.8 | 33.5 |
| 18.3 | 1.03 | 10.5 | 39.5 |
| 15.2 | 0.52 | 11.8 | 44.5 |
| 10.0 | 0.52 | 10.5 | 55.0 |
| 6.65 | 1.2 | 11.8 | 68.5[d] |
| 5.0 | 1.2 | 11.8 | 80.5 |
| 4.20 | 1.2 | 11.8 | 78.5 |
| 3.58 | 1.2 | 11.8 | 75.5 |
| 3.10 | 1.2 | 11.8 | 74.0 |
| 2.78 | 1.2 | 11.8 | 86.0 |
| 2.63 | 1.2 | 11.8 | 87.0 |
| 2.48 | 1.2 | 11.8 | 84.5 |

[a] Determined at 288 nm at the ionic strength adjusted by NaCl, unless noted otherwise. [b] 510 nm. [c] 350 nm. [d] $\mu$ adjusted by LiCl.

ion and at 306 nm for $Co(NH_3)_5NCS^{2+}$ ion, wavelengths of absorption maxima of the Co(III) complexes. The reactions were initiated by adding a titanium(III) solution to the other reaction components contained in a deoxygenated and thermostatted 10 cm cell. Cobalt(III) solutions were handled under semidarkened conditions as a routine precaution due to their photochemical sensitivity [13, 14]. Most of the runs were performed under pseudo first order conditions with 10 to 200 fold excess of titanium(III) over the complex. Two runs were performed under second order conditions with 0.56 and 1.98 concentration ratios between Ti(III) and $Co(NH_3)_5N_3^{2+}$. Specific rates were calculated from the slopes of standard plots for pseudo first order or second order reactions. Plots for both conditions were linear up to at least 90% of the reaction. All reactions were studied in chloride anionic medium which was shown not to interfere with the kinetics of reactions of titanium(III). Ionic strength was adjusted to 1 *M* by LiCl or NaCl.

## Stoichiometry

Stoichiometry was checked for a number of runs by analyzing unreacted Ti(III) and Co(II) produced in the reaction solution after the reaction was 99% or more completed. Ti(III) concentration was determined by the oxidation to Ti(IV) with an excess of Cr(VI) in 1 *M* HCl followed by the spectrophotometric determination of Cr(VI) at 355 nm ($\epsilon_{355} = 2.50 \times 10^3$ $mol^{-1}$ l $cm^{-1}$ in the range $(6.9–120) \times 10^{-5}$ *M* of Cr(VI) concentration in 1 *M* HCl). No reaction between $N_3^-$ and Cr(VI) was detected under the conditions employed.

Co(II) concentration was determined by Kitson's method [15].

For the reduction of the $Co(NH_3)_5N_3^{2+}$ ion attempts were made to determine the released azide ion spectrophotometrically as $FeN_3^{2+}$ at 460 nm [16, 17]. 1 *M* chloride medium interfered with these attempts and stoichiometric runs in $10^{-2}$–$10^{-3}$ *M* HCl were performed by omitting LiCl or NaCl as the

TABLE II. Rate Constants for the Titanium(III) Reduction of the $Co(NH_3)_5N_3^{2+}$ Ion at 25 °C in Aqueous Chloride Medium of $\mu = 1.0$ *M*.[a]

| $[H^+] \times 10^3$ *M* | $[Ti(III)] \times 10^5$ *M* | $[Co(NH_3)_5N_3^{2+}] \times 10^5$ *M* | $k_{N_3}$ $M^{-1}s^{-1}$ |
|---|---|---|---|
| 990 | 36.5 | 65.6 | 2.43 |
| 984[b] | 222 | 16.7 | 2.53 |
| 984[b,c] | 222 | 15.8 | 2.67 |
| 984 | 262 | 1.67 | 2.43 |
| 984[c] | 256 | 1.78 | 2.74 |
| 984 | 256 | 1.78 | 2.59 |
| 980 | 375 | 1.78 | 2.39 |
| 800 | 380 | 2.16 | 3.16 |
| 700[d] | 387 | 2.15 | 3.32 |
| 600 | 94.0 | 2.15 | 4.20 |
| 500 | 86.3 | 2.15 | 5.22 |
| 500[d] | 91.0 | 2.15 | 5.29 |
| 400 | 76.2 | 2.15 | 6.84 |
| 300 | 90.3 | 2.15 | 8.93 |
| 300[d] | 85.9 | 2.15 | 8.02 |
| 200 | 89.5 | 2.15 | 10.9 |
| 157[d] | 85.5 | 2.15 | 13.4 |
| 144 | 71.4 | 2.15 | 14.5 |
| 125 | 71.4 | 2.15 | 17.5 |
| 100[e] | 406 | 2.04 | 18.9 |
| 100 | 96.6 | 1.99 | 18.6 |
| 100 | 76.3 | 2.07 | 16.9 |
| 100[f] | 35.7 | 2.07 | 17.5 |
| 100 | 22.8 | 2.07 | 17.1 |
| 100[d] | 369 | 1.77 | 17.0 |
| 100[d] | 245 | 1.77 | 17.3 |
| 100[d] | 61.3 | 1.77 | 18.2 |
| 50.2 | 26.3 | 2.15 | 29.6 |
| 40.0[d] | 53.4 | 1.99 | 28.7 |
| 36.4 | 58.0 | 1.99 | 33.2 |
| 33.3[d] | 58.4 | 1.99 | 31.0 |
| 29.8 | 26.3 | 2.15 | 33.6 |
| 20.1 | 33.8 | 2.15 | 38.8 |
| 17.5[e] | 48.8 | 1.77 | 39.6 |
| 16.6[d] | 53.0 | 1.99 | 39.6 |
| 13.5[e] | 255 | 129 | 45.1 |
| 13.4[d] | 56.9 | 1.99 | 41.3 |
| 12.3 | 60.8 | 2.07 | 40.4 |
| 12.0 | 52.0 | 1.77 | 40.5 |
| 10.3[d] | 48.0 | 1.99 | 40.3 |
| 8.36[e] | 102 | 2.04 | 39.4 |
| 6.75[e] | 128 | 2.04 | 42.5 |
| 6.26[e] | 76.7 | 2.04 | 39.1 |
| 4.34[e] | 51.1 | 2.21 | 38.4 |
| 4.18[e] | 51.1 | 2.04 | 38.9 |

[a] $\lambda = 302$ nm, $\mu$ adjusted with LiCl (Baker Analyzed). [b] $\lambda = 518$ m. [c] Added $[HN_3] = 1.0 \times 10^{-3}$ *M*. [d] $\mu$ adjusted with NaCl. [e] $\mu$ adjusted with LiCl Merck "Suprapur". [f] Added $[HN_3] = 2.7 \times 10^{-3}$ *M*.

supporting electrolyte. Absorption curves calibrated with the known concentrations of Fe(III) and $N_3^-$ ions were used in this determination.

## Results

Analyses of Co(II) produced, of $N_3^-$ released, and of unreacted Ti(III) after the kinetic runs confirmed the stoichiometries 1 and 2:

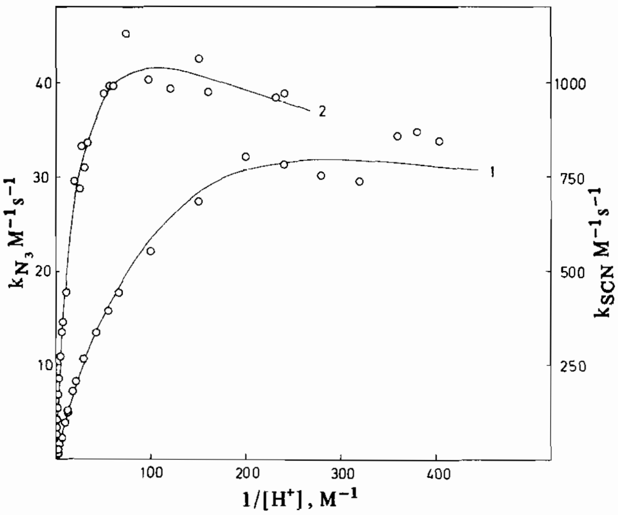

Figure 1. The second order rate constants for the oxidation of titanium(III) by $Co(NH_3)_5SCN^{2+}$ (1) and $Co(NH_3)_5N_3^{2+}$ (2) at 25 °C, $\mu = 1.0\ M$.

$$Co(NH_3)_5SCN^{2+} + Ti(III) \xrightarrow{H^+} Co(II) + 5NH_4^+ + SCN^- + Ti(IV) \quad (1)$$

$$Co(NH_3)_5N_3^{2+} + Ti(III) \xrightarrow{H^+} Co(II) + 5NH_4^+ + HN_3 + Ti(IV) \quad (2)$$

Neither azide nor thicyanate are reduced by titanium(III) under the conditions employed.

Reactions 1 and 2 were found to be of the first order with respect to both Co(III) and Ti(III). The kinetic data are presented in Table I for $Co(NH_3)_5SCN^{2+}$ and in Table II for $Co(NH_3)_5N_3^{2+}$. The second order rate constants $k_{SCN}$ for the reduction of $Co(NH_3)_5SCN^{2+}$ and $k_{N_3}$ for the reduction of $Co(NH_3)_5N_3^{2+}$ are graphically shown in Figure 1 as functions of inverse acid concentration. The curve 1, for $Co(NH_3)_5SCN^{2+}$, levels off in the range of (5–2.5) × $10^{-3}$ $M$ of $H^+$ concentration and if it is assumed that the behaviour comes from the hydrolytic equilibrium 3 then for $TiOH^{2+}$ being the

$$Ti^{3+} \rightleftharpoons TiOH^{2+} + H^+ \quad K_a \quad (3)$$

reacting species the data can be fitted according to equation 4

$$k_{SCN} = \frac{k_{-1}^{SCN} K_a[H^+]^{-1}}{1 + K_a[H^+]^{-1}} \quad (4)$$

with an average deviation of 4.2% of the experimental from the calculated $k_{SCN}$ values. However, the equilibrium constant $K_a = 1.1 \times 10^{-2}\ M$ obtained in this way shows an unrealistically high value [1, 18, 19]. Thus, equilibrium 3 is not the only step of reaction 1 in which proton is involved and equation 4 is inadequate for a description of the $k_{SCN}$ dependence on $[H^+]$. This is even more obvious for the Ti(III) reduction of $Co(NH_3)_5N_3^{2+}$. Curve 2 in Figure 1 shows a more peculiar dependence of $k_{N_3}$ on $[H^+]$, and its treatment according to equation 4 would give still a higher value for $K_a$ ($5.9 \times 10^{-2}\ M$).

New sets of literature data on the acid dissociation constant of $Ti^{3+}$ put the value of $K_a$ in the range of (1.6–4.6) × $10^{-3}$ $M$ at 25 °C. Potentiometric titrations in 3 $M$ ionic strength by Krentzien and Brito [18] yielded $K_a = 1.6 \times 10^{-3}\ M$ (in KCl) and those by Paris and Gregoire [19] yielded $K_a = 2.8 \times 10^{-3}\ M$ (in KBr). Kinetic data [1] for the reduction of $Co(NH_3)_5Cl^{2+}$ in 1 $M$ LiCl gave $K_a = 4.6 \times 10^{-3}\ M$. The value of $K_a = 2 \times 10^{-3}\ M$ seems a good approximation for the conditions employed in this work. Incidentally, $K_a$ for $V(H_2O)_6^{3+}$ and $Fe(H_2O)_6^{3+}$ have very similar values.

The acid dependences of $k_X$ in Figure 1 are explained by the operation of a two-step mechanism in which, in addition to equilibrium 3, proton has a role in the second step. The data are well represented by equation 5

$$k_X = \frac{a[H^+]}{(K_a + [H^+])(b + [H^+])} \quad (5)$$

which is an expanded form of equation 4, $k_X = q/(K_a + [H^+])$.

The treatment of $k_{SCN}$ and $k_{N_3}$ from Tables I and II according to equation 5 by a non-linear least squares program with $1/k_X^2$ weighting and $K_a = 2 \times 10^{-3}$ $M$ yielded $a_{SCN} = 11.0 \pm 0.2\ s^{-1}$ and $b_{SCN} = (5.29 \pm 0.31) \times 10^{-3}\ M$ for Ti(III) reduction of $Co(NH_3)_5SCN^{2+}$ and $a_{N_3} = 2.69 \pm 0.33\ s^{-1}$ and $b_{N_3} = (4.35 \pm 0.29) \times 10^{-2}\ M$ for the reduction of $Co(NH_3)_5N_3^{2+}$. The uncertainties quoted are standard deviations. The curves in Figure 1 are constructed from the computed values of $k_{SCN}$ and $k_{N_3}$. According to equation 5 the plots of $k_X$ *vs.* $1/[H^+]$ should exhibit a maximum, its position on $1/[H^+]$ scale depending on the relative values of a, b, and $K_a$. The experimental $k_{N_3}$ data and the calculated curve 2 hint to the existence of such a maximum in the acidity range studied.

Attempts were made to measure the rate of Ti(III) reduction of $Co(NH_3)_5NCS^{2+}$ ion, the N-bonded isomer. At 25 °C the reaction was found to be extremely slow as compared to the rate of reduction of $Co(NH_3)_5N_3^{2+}$ and $Co(NH_3)_5SCN^{2+}$, the S-bonded isomer. Rough estimates put the rate slower by many orders of magnitude and the reaction was not further quantitatively studied.

## Discussion

The reaction of $Co(NH_3)_5NCS^{2+}$ ion being slower by many orders of magnitude as compared to the reactions of $Co(NH_3)_5N_3^{2+}$ and $Co(NH_3)_5SCN^{2+}$ ions

TABLE III. Comparison of Rate Constants for the Reduction of Co(NH$_3$)$_5$X$^{2+}$ Ions by Titanium(III) According to Two Different Inner-Sphere Mechanisms at 25 °C, $\mu$ = 1.0 *M*.

| X | $k_1$ $M^{-1}$ s$^{-1}$ | $k_4$ $M^{-1}$ s$^{-1}$ | $k_3k_2^{-1}$ *M* | $k_5k_6^{-1}$ *M* | $K_a$ *M* |
|---|---|---|---|---|---|
| SCN$^-$ | $2.1 \times 10^3$ | $5.5 \times 10^3$ | $5.3 \times 10^{-3}$ | $5.3 \times 10^{-3}$ | $2 \times 10^{-3}$[a] |
| N$_3^-$ | 62 | $1.3 \times 10^3$ | $4.4 \times 10^{-2}$ | $4.4 \times 10^{-2}$ | $2 \times 10^{-3}$ |

[a] $K_a$ was held fixed at this value.

offers the straight-forward suggestion that their reduction by titanium(III) proceeds by an inner-sphere mechanism [5]. Titanium(III) is a hard metal center and the difference between the two sets of rates is principally due to the increased stability of Ti(III)–nitrogen bond over Ti(III)–sulfur bond in the precursor complexes. A higher reactivity of Co(NH$_3$)$_5$SCN$^{2+}$ over that of Co(NH$_3$)$_5$N$_3^{2+}$ is also observed, as expected on the basis of free energy considerations [20].

The acidity dependence of the reactions 1 and 2, indicative of proton involvement in steps additional to 3, also supports assignment of the inner-sphere mechanism. Birk [3] has previously proposed two mechanisms consistent with the acidity dependence given by 5:

*Mechanism I*

$$\mathrm{Ti^{3+} + Co(NH_3)_5X^{2+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Co(NH_3)_5XTiOH^{4+} + H^+}$$

$$\mathrm{Co(NH_3)_5XTiOH^{4+} \xrightarrow{k_3} Co^{2+} + 5NH_3 + HX + TiO^{2+}}$$

*Mechanism II*

$$\mathrm{TiOH^{2+} + Co(NH_3)_5X^{2+} \underset{k_5}{\overset{k_4}{\rightleftharpoons}} Co(NH_3)_5XTiOH^{4+}}$$

$$\mathrm{Co(NH_3)_5XTiOH^{4+} + H^+ \xrightarrow{k_6} Co^{2+} + 5NH_3 + HX + TiO^{2+} + H^+}$$

Here, the binuclear Co(NH$_3$)$_5$XTiOH$^{2+}$ complex, which is precursor to the electron transfer step, is present in a steady state concentration. The second order rate constant, defined as $k_X$ = Rate/[Co(NH$_3$)$_5$X$^{2+}$] [Ti(III)], has then the form 6 according to mechanism I,

$$k_X = k_1k_3k_2^{-1}\,[H^+]/(k_3k_2^{-1} + [H^+])(K_a + [H^+]) \qquad (6)$$

and the form 7 according to mechanism II,

$$k_X = k_4K_a[H^+]/(k_5k_6^{-1} + [H^+])(K_a + [H^+]) \qquad (7)$$

Though 6 and 7 have the same general form 5 and are kinetically indistinguishable, it appears that the data obtained in this work offer some insights for speculative differentiations between the two. Table III lists the corresponding rate constants calculated from the data in Tables I and II according to expressions 6 and 7 by a non-linear least-squares program.

Path $k_1$, the substitution in Ti$^{3+}$, involves formation of a titanium–nitrogen bond in the reactions of the –SCN and –N$_3$ complexes and is expected to proceed by similar rates for the two oxidants. The same applies for path $k_4$, the substitution in TiOH$^{2+}$. The calculated $k_1$ values in Table III are very different, strongly suggesting that at least one of the two oxidants does not react by Mechanism I. The $k_4$ values are much closer, what would be consistent with both oxidants reacting by Mechanism II. However, a comparison of $k_5k_6^{-1}$ for the two oxidants tends to reject this possibility, too. Namely, path $k_5$ represents breaking of the Ti(III)–nitrogen bond in the Co(NH$_3$)$_5$XTiOH$^{4+}$ precursors and is likely to have similar rates for Co$^{III}$–SCN–Ti$^{III}$ and Co$^{III}$–NNN–Ti$^{III}$ complexes. The difference in $k_5k_6^{-1}$ comes mostly from different $k_6$. It is reasonable to assume that path $k_2$ involves an attack of proton of the hydroxy ligand bound to titanium(III) in the binuclear precursor complex yielding back the original mononuclear reagents, while path $k_6$ involves an attack of proton on the bridging ligand of the same precursor, causing a catalyzed electron transfer step. Path $k_6$ is then expected to be more effective for the reduction of Co(NH$_3$)$_5$N$_3^{2+}$ over that of Co(NH$_3$)$_5$SCN$^{2+}$, since azide is a much more basic ligand than tiocyanate. The calculated $k_5k_6^{-1}$ values in Table III for the two oxidants show an opposite trend to the expected one, suggesting that they are not reduced by the same mechanism, Mechanism II.

The consideration is reconciled by the assignment of Mechanism I for the titanium(III) reduction of the Co(NH$_3$)$_5$SCN$^{2+}$ ion and of Mechanism II for the reduction of Co(NH$_3$)$_5$N$_3^{2+}$ ion. It appears reasonable that a "normal" electron transfer step ($k_3$), operative for the binuclear complex of the former oxidizing reactant containing an acidic bridging ligand, is being prevailed by the proton catalyzed electron transfer step ($k_6$), operative for the binuclear complex of the latter oxidizing reactant containing a basic bridging ligand.

According to the proposed mechanisms water ligand is substituted by Co(NH$_3$)$_5$SCN$^{2+}$ in the coordination sphere of $Ti^{3+}$ ion with $k_1 = 2.1 \times 10^3$ $M^{-1}$ $s^{-1}$, while substitution by the $Co(NH_3)_5N_3^{2+}$ ion in the coordination sphere of the $TiOH^{2+}$ ion proceeds with $k_4 = 1.3 \times 10^3$ $M^{-1}$ $s^{-1}$. These similar rates agree with observations made by Diebler that substitutions on titanium(III) show lack of dependence on acidity [21]. This is consistent with contention [22] that substitution on titanium(III) proceeds by an associative mode of activation. The substitution rate constants quoted above are not inconsistent with the rate constant $10^5$ $s^{-1}$ for the exchange of water ligand bound to Ti(III) and the rate constant $10^4$ $M^{-1}$ $s^{-1}$ at 8 °C for the formation of monothiocyanatotitanium(III) complex [23, 24].

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