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Inorganica Chimica Acta 225 (1994) 245–250

Inorganica Chimica Acta

# The reduction of pentaammine(phenanthroline-2-carboxamido-*N*)cobalt(III) by titanium(III) and vanadium(II)

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Received 29 March 1994

## Abstract

Pentaammine(phenanthroline-2-carboxamido-*N*)cobalt(III) (I) reacts with $Ti^{3+}$(aq.) in two separable steps. The first step involves rapid formation of a binuclear intermediate with $Ti^{3+}$ forming a chelate with the carboxamido oxygen and the adjacent ring nitrogen. The rate law is $k_{obs}=k_1[Ti^{3+}]+k_r[H^+]$ where $k_1=240\pm10$ and $k_r=6.7\pm0.4$ $M^{-1}$ $s^{-1}$ at 25 °C and $I=1.0$ M (LiCl). The second reaction involves electron transfer and follows the rate law $k_{obs}=a[H^+]^{-1}[Ti^{3+}]+b[H^+]^{-1}$ where $a=0.0046\pm0.0005$ $s^{-1}$ and $b=(1.3\pm0.1)\times10^{-4}$ $M^{-1}$ $s^{-1}$. The first term in the rate law of the second step is assigned to outer-sphere reduction by $Ti(OH)^{2+}$ of the binuclear precursor formed in the first reaction. The second term involves intramolecular electron transfer within the conjugate base of the binuclear precursor with $k_{et}$ estimated as 0.13 $s^{-1}$. The factors affecting intramolecular electron transfer within Co(III)- and Ru(III)–Ti(III) intermediates are discussed. The reaction of I with $V^{2+}$(aq.) also occurs in two distinct reactions. The first reaction follows the same rate law as the analogous $Ti^{3+}$ reaction with $k_1=2010\pm100$ and $k_r=600\pm50$ $M^{-1}$ $s^{-1}$ at 25 °C, $I=1.0$ M ($LiClO_4$). The second reaction is first-order in $[V^{2+}]$ and independent of $[H^+]$ with a second-order rate constant of $0.36\pm0.02$ $M^{-1}$ $s^{-1}$. The latter redox reaction is thought to involve outer-sphere reduction of the binuclear precursor formed in the first step.

*Keywords:* Kinetics and mechanism; Reduction; Cobalt complexes; Ammine complexes; Carboxamido complexes

## 1. Introduction

The reductions of pentaamminecobalt(III) and pentaammineruthenium(III) complexes by titanium(III) often feature pathways involving loss of $H^+$ from the titanium(III) centre [1–15]. When no suitable bridging group is available on the oxidant, reaction occurs via $TiOH^{2+}$ in an outer-sphere mechanism. For inner-sphere reactions, the loss of $H^+$ is thought to occur from $Ti^{3+}$ within a binuclear precursor complex prior to intramolecular electron transfer. In many systems the rate-limiting process is substitution on Ti(III) and little information is obtained regarding the redox reaction [4,7–9,11,12]. In only two cases, the reduction of a cobalt(III) complex containing a pendant β-diketone group, $[(NH_3)_5Co(NCacac)]^{2+}$ [2], and the reduction of $[(trien)CoQ]^+$ ($Q^{2-}$ is the dianion of 2,5-dihydroxy-1,4-benzoquinone) [1], has the intermediate binuclear precursor complex been observed. For the former reaction, electron transfer occurs in the deprotonated precursor, $[(NH_3)_5CoNCacacTi(OH)]^{4+}$, at an estimated rate of 6 $s^{-1}$. In the latter case, reduction occurs without loss of $[H^+]$ within the binuclear complex $[(trien)CoQTi]^{4+}$. For both systems the rapid formation of a stable precursor presumably is enhanced by chelation of titanium(III) to the hard oxygen donors.

In order to investigate the details of this type of mechanism and in particular the generality of intramolecular electron transfer via an $[H^+]^{-1}$ pathway, we report here the reduction by titanium(III) of complex I (see p. 246) containing a pendant phenanthroline group. This complex has been shown to form binuclear complexes with $Co^{2+}$(aq.), $Ni^{2+}$(aq.) and $Fe^{2+}$(aq.) by initial chelation at the carbonyl oxygen and the adjacent phenanthroline nitrogen [16]. It was anticipated that $Ti^{3+}$ would form a stable precursor within which intramolecular electron transfer could be observed. We also report here the reduction of I by vanadium(II).

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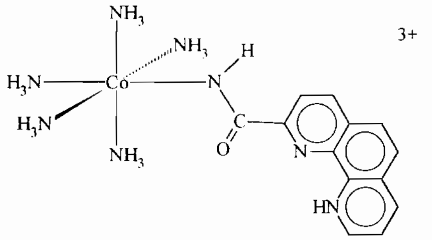
*SSDI* 0020-1693(94)04053-X



I

## 2. Experimental

Pentaammine(phenanthroline-2-carboxamido-*N*)-cobalt(III) perchlorate, $[Co(NH_3)_5(NHCOphen)](ClO_4)_2$ was prepared as previously described [17]. **Caution!** Perchlorate salts are potentially explosive and should be handled with care. The complex was purified by cation exchange chromatography on CM-Sephadex.

A standard titanium(III) solution was prepared by dissolving titanium metal in 1.0 M HCl with gentle warming. Oxygen was excluded during dissolution by passing argon over the surface of the reaction mixture. The titanium(III) concentration was determined by adding an aliquot of the titanium(III) solution to a known volume of standard iron(III). The amount of iron(III) remaining was determined iodometrically. The acid concentration of the stock titanium(III) solution was determined by passing a known volume through a Dowex column ($H^+$) under anaerobic conditions. The $H^+$ concentrations were calculated by taking the difference in the known concentration of Ti(III) (assuming each Ti(III) liberates three $H^+$ ions) and the total amount of $H^+$ obtained from the column.

Standard vanadium(II) solutions were obtained by reduction of a standard vanadyl perchlorate solution. $VO(ClO_4)_2$ was prepared by dissolving $VOSO_4$ in 0.1 M $HClO_4$ and adding a stoichiometric amount of $Ba(ClO_4)_2$. The $BaSO_4$ produced was removed by filtration through a 0.85 μm millipore filter. These solutions were reduced with Zn(Hg) amalgam just prior to use since $V^{2+}$(aq.) slowly reduces perchlorate. Vanadium(II) concentrations were determined as for titanium(III).

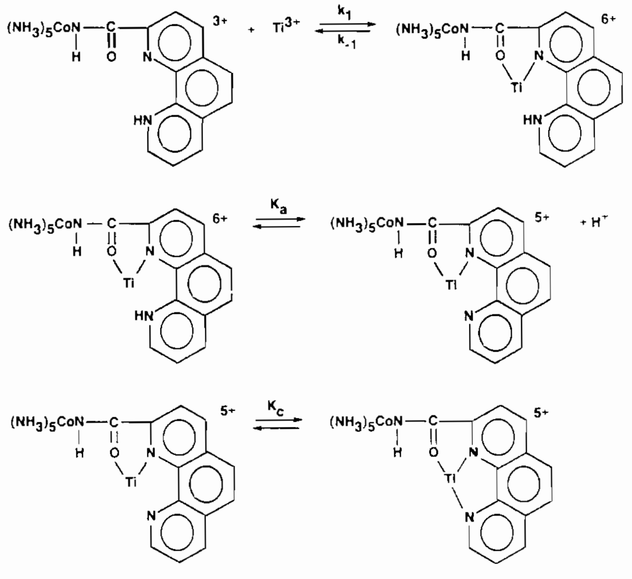
The perchloric acid standard solutions were prepared by dilution of 70% $HClO_4$ (G.F. Smith) and titrated with standardised NaOH. The lithium perchlorate (G.F. Smith) stock solutions were prepared from anhydrous $LiClO_4$ and standardised by passing an aliquot through Dowex ($H^+$) ion exchange resin and titrating the $H^+$ liberated.

Rate constants for the reduction of the cobalt(III) complex were measured spectrophotometrically at 330 nm using a Dionex D-110 stopped-flow apparatus interfaced with a DASAR digital storage unit. Curve fitting was performed by matching experimental traces with a calibrated exponential curve generator. Data were also collected with the stopped-flow interfaced to a computer. In this case rate constants were determined using the OLIS Kinfit routines (ON-Line Instrument Systems, Jefferson, GA). Rate constants determined by both methods were in good agreement and precise to at least 10%. Spectrophotometric measurements were performed on a Beckman Acta C111 spectrophotometer or a Hewlett Packard 8452A diode array spectrophotometer.

Table 1
Kinetic data for the reaction of $(NH_3)_5CoNHCOphenH^{3+}$ with $Ti^{3+}$-substitution step[a]

| $[Ti^{3+}]\times 10^2$ (M) | $[H^+]$ (M) | $k_{obs}$ ($s^{-1}$) |
|---|---|---|
| 0.450 | 0.320 | 3.3 (3.2)[b] |
| 0.900 | 0.320 | 4.0 (4.3) |
| 1.80 | 0.320 | 6.4 (6.4) |
| 4.50 | 0.320 | 13 (13) |
| 0.900 | 0.220 | 3.6 (3.6) |
| 2.25 | 0.220 | 6.6 (6.9) |
| 4.50 | 0.220 | 12 (12) |
| 0.450 | 0.110 | 1.6 (1.8) |
| 0.900 | 0.110 | 2.7 (2.8) |
| 2.25 | 0.110 | 5.9 (6.1) |
| 4.50 | 0.110 | 11 (11) |

[a] $T$ = 25.0 °C, $I$ = 1.00 M (LiCl, HCl), λ = 330 nm.
[b] Calculated according to Eq. (1).



Scheme 1.

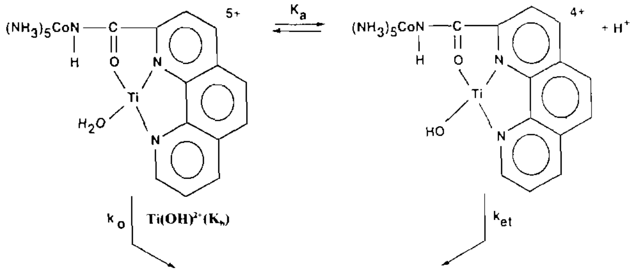
## 3. Results and discussion

The reaction of $Ti^{3+}$ with $(NH_3)_5CoNHCOphenH^{3+}$ occurs in two separable reactions. The first reaction is

Table 2
Kinetic data for the reaction of $(NH_3)_5CoNHCOphenH^{3+}$ with $Ti^{3+}$-redox step[a]

| $[Ti^{3+}]\times10^2$ (M) | $[H^+]$ (M) | $k_{obs}\times10^3$ ($s^{-1}$) |
|---|---|---|
| 0.900 | 0.0500 | 3.4 (3.4)[b] |
| 2.25 | 0.0500 | 4.7 (4.7) |
| 3.40 | 0.0500 | 5.8 (5.7) |
| 0.900 | 0.0850 | 2.2 (2.0) |
| 2.25 | 0.0850 | 2.8 (2.7) |
| 4.50 | 0.0850 | 4.0 (3.9) |
| 0.900 | 0.110 | 1.7 (1.6) |
| 2.25 | 0.110 | 2.1 (2.1) |
| 3.40 | 0.110 | 2.7 (2.6) |
| 4.50 | 0.110 | 3.1 (3.1) |
| 6.75 | 0.110 | 4.0 (4.0) |
| 0.900 | 0.220 | 0.50 (0.78) |
| 4.50 | 0.220 | 1.0 (1.5) |
| 4.50 | 0.220 | 1.2 (1.5) |
| 9.00 | 0.220 | 1.7 (2.5) |
| 9.00 | 0.220 | 1.5 (2.5) |

[a] $T=25.0$ °C, $I=1.00$ M (LiCl, HCl), $\lambda=330$ nm.
[b] Calculated according to Eq. (4).



Scheme 2.

rapid and is complete in less than 2 s. The second slower reaction has half-times in the range 2–20 min. Reaction mixtures were analysed for the presence of cobalt(II) at various time intervals by quenching the reaction with potassium monoperoxysulfate. Tests for cobalt(II) were negative for reaction mixtures quenched at times corresponding to completion of the first reaction (immediately after initial mixing of reactants, within 5–10 s). Analysis for cobalt(II) after the second reaction was complete indicated a stoichiometric amount of cobalt(II) based on initial concentrations. Thus it is reasonable that the first reaction (no redox) corresponds to rapid formation of a precursor by complexation of $Ti^{3+}$ at 2-carboxamidophenanthroline within the cobalt(III) complex. The subsequent reaction involves reduction of cobalt(III). Both reactions are conveniently monitored at 330 nm where the first reaction corresponds to a large absorbance increase and the second reaction produces a smaller absorbance decrease. This behaviour is similar to that observed for the reduction of cobalt(III) complexes containing pendant acac groups.

For the first reaction, with $Ti^{3+}$ in excess over the Co(III) complex, the observed rate constants show a linear dependence on $[Ti^{3+}]$ with a finite intercept at a given acid concentration thus indicating an equilibrium situation. The value of the intercept is directly dependent on $[H^+]$ and the rate law can be expressed as Eq. (1).

$$k_{obs}=k_1[Ti^{3+}]+k_r[H^+] \tag{1}$$

The data are collected in Table 1. The value of $k_r$ was obtained from the slope of a plot of the intercepts versus $[H^+]$. At 25 °C, $I=1.0$ M (LiCl), $k_1=240\pm10$ and $k_r=6.7\pm0.4$ $M^{-1}$ $s^{-1}$. A mechanism consistent with the data is given in Scheme 1. In this mechanism the initial chelation at the carboxamido oxygen and the adjacent ring nitrogen is rate-determining. It is to be expected that the hard $Ti^{3+}$ species would favour complexation to the hard oxygen as part of chelate formation. We favour the latter over monodentate coordination by analogy to the $Fe^{2+}$ complexation reaction with the same complex [16]. The two equilibria represented by $K_a$ and $K_c$ are rapidly maintained and satisfy the first-order dependence of $k_r$ on $[H^+]$. The experimentally determined value of $k_r$ can be expressed as Eq. (2).

$$k_r=\frac{k_{-1}}{K_aK_c} \tag{2}$$

Using the Irving–Williams order as a guide and the kinetically determined formation constants for $Co^{2+}$ and $Ni^{2+}$ with I [16], one can estimate the formation constant for $Fe^{2+}$ as 100 $M^{-1}$. This value gives $K_c\sim40$ for the $Fe^{2+}$ system which is thought to follow the mechanism in Scheme 1. Making the reasonable assumption that this value is an upper limit for $Ti^{3+}$, $k_{-1}$ is approximately 0.07 $s^{-1}$ for the $Ti^{3+}$ reaction. On this basis the kinetically determined formation constant is $\geq3\times10^3$ $M^{-1}$. This is at least an order of magnitude larger than for $Co^{2+}$ and $Ni^{2+}$ as might be anticipated for the increased charge on $Ti^{3+}$.

The second reaction observed produced a quantitative amount of Co(II) and involves reduction of the oxidant via both first-order and bimolecular processes. Plots of the observed rate constants versus $[Ti^{3+}]$ gave straight lines with finite intercepts where both the slopes and the intercepts were dependent on the hydrogen-ion concentration. The data (Table 2) are consistent with a rate law of the type (3)

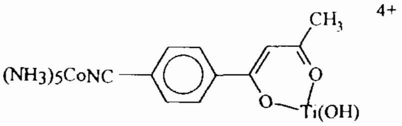
$$k_{obs}=\frac{a[Ti^{3+}]}{[H^+]}+\frac{b}{[H^+]} \tag{3}$$

Assuming all of the cobalt(III) is present as the binuclear complex (large formation constant in the first reaction), the inverse acid dependencies can be accounted for by the mechanism in Scheme 2. This

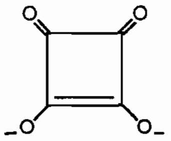
$$k_{obs}=\frac{k_0K_b[Ti^{3+}]}{[H^+]+K_b}+\frac{k_{et}K_a}{[H^+]+K_a} \tag{4}$$

Table 3

Intramolecular electron transfer rate constants for Ti(III) precursors at 25 °C

| Binuclear complex | $k_{et}$ ($s^{-1}$) | Intermediate observed (I), assumed from rate law (R) | Reference |
|---|---|---|---|
| $[(NH_3)_5CoNCacacTi(OH)]^{4+}$ | 6 | I | [2] |
|  | 1.2 | I | [20] |
| $[(NH_3)_5CoNHCOphenTi(OH)]^{4+}$ | 0.13 | I | this work |
| $[(en)_2CoSQTi(OH)]^{3+}$ [a] | $\leq 10^{-2}$ [b] | R | [1] |
| $[(trien)CoQTi]^{4+}$ [c] | 0.49 $s^{-1}$ | I | [1] |
| $[(pd)_2RufpdTi(OH)]^{2+}$ | $\geq 10^4$ | R[d] | [13] |
|  | 20 | I[d] |  |
| $[Ru_2^{III,II}(OAc)_2(ox)_2Ti(OH)]^+$ | 30 | R | [14] |
| $[(trien)RuCQTi]^{4+}$ [e] | 110 | R | [1] |

[a] $SQ^{2-}$ is the dianion of squaric acid,



[b] Assuming $k_4 \leq 40$ $M^{-1}$ $s^{-1}$ in Ref. [1].

[c] $Q^{2-}$ is the dianion of 2,5-dihydroxy-1,4-benzoquinone.

[d] Two relaxations are observed in this system. The value of $10^4$ ensues if the faster relaxation involves the formation of a binuclear intermediate followed by rate-determining electron transfer within the conjugate base of the intermediate. The slow relaxation then corresponds to a Ti(IV) substitution reaction. The value of 20 results if the faster relaxation corresponds to intermediate formation from $Ti(OH)^{2+}$ and $[(pd)_2Rufpd]$.

[e] $CQ^{2-}$ is the dianion of chloranilic acid, 3,6-dichloro-2,5-dihydroxy-1,4-benzoquinone.

mechanism leads to the rate law (4), which is of the same form as Eq. (3) when $[H^+] \gg K_b$, $K_a$. Since both $K_b$ and $K_a$ are expected to have values $\leq 10^{-3}$ M under these conditions, the data are consistent with Eq. (3). The values of $k_0K_b$ and $k_{et}K_a$ determined from the data are $0.0046 \pm 0.0005$ $s^{-1}$ and $(1.3 \pm 0.1) \times 10^{-4}$ M $s^{-1}$, respectively. Using $K_b = 4 \times 10^{-3}$ M [18,19], and an estimate of $K_a = 10^{-3}$ M, $k_0 = 1.1$ $M^{-1}$ $s^{-1}$ and $k_{et} = 0.13$ $s^{-1}$, respectively. Although the current mechanism involving rapid formation of a precursor complex followed by intramolecular electron transfer within the conjugate base of the binuclear intermediate has been proposed previously, most Ti(III)–Co(III) redox systems do not react via separable formation and reduction steps. In many cases the reaction resulting in reduction is controlled by substitution on $Ti^{3+}$. The large majority of rate constants for this situation are in the range of 50 to 500 $M^{-1}$ $s^{-1}$ [7–9,11,12] and compare favourably with the substitution value of 240 $M^{-1}$ $s^{-1}$ determined for formation of the precursor complex in this work.

The redox reaction outlined in Scheme 2, where the intramolecular electron transfer occurs within the conjugate base of the precursor complex, appears to be of general mechanistic applicability. If formation of a stable precursor is rapid, several factors should affect the electron transfer reaction within the binuclear intermediate: (i) the reduction potential of $Ti^{3+}$ versus that of $Ti(OH)^{2+}$, (ii) the ability of the $t_{2g}$ orbitals on $Ti^{3+}$ or $Ti(OH)^{2+}$ to mix effectively with empty ligand orbitals (LUMO) of appropriate symmetry and the energy of these LUMOs (the 'reducibility' of the ligand), (iii) the symmetry of the acceptor metal orbitals on the oxidant. It is difficult to separate these factors for different metal complexes but a few comments are in order. Known values of intramolecular electron transfer rate constants for Co(III)- and Ru(III)–Ti(III) binuclear intermediates are collected in Table 3. For the cobalt(III) complexes, the relatively small values of $k_{et}$ can be related to the symmetry mismatch of donor–acceptor orbitals ($t_{2g}$–$e_g$). Also, since the ligands (with the exception of Q [1]) are not reduced by $Ti^{3+}$ or $Ti(OH)^{2+}$ the ligand LUMOs are too high in energy to effectively mix with $t_{2g}$ donor orbitals. For this situation deprotonation of $Ti^{3+}$ in the binuclear complex occurs presumably because there is now a greater driving force for the reduction (the reduction potentials of $Ti^{3+}$ and $Ti(OH)^{2+}$ are approximately +0.03 and −0.08 V [18]). For $[(trien)CoQTi]^{4+}$ where the LUMOs are of appropriate energy to form out-of-phase combinations [21] with the Ti(III) orbitals, the electron transfer still

Table 4
Kinetic data for the reaction of $(NH_3)_5CoNHCOphenH^{3+}$ with $V^{2+}$ [a]

| $[V^{2+}]\times 10^3$ (M) | $[H^+]$ | $k_{obs}$ ($s^{-1}$) |
|---|---|---|
| First reaction | | |
| 1.60 | 0.0500 | 30 (33)[b] |
| 4.30 | 0.0500 | 34 (39) |
| 6.90 | 0.0500 | 45 (44) |
| 8.50 | 0.0500 | 43 (47) |
| 11.90 | 0.0500 | 54 (54) |
| 13.70 | 0.0500 | 55 (58) |
| 27.30 | 0.0500 | 80 (85) |
| 4.30 | 0.100 | 70 (67) |
| 8.50 | 0.100 | 83 (77) |
| 13.70 | 0.100 | 90 (88) |
| 6.90 | 0.150 | 98 (100) |
| 13.70 | 0.150 | 120 (120) |
| 27.30 | 0.150 | 140 (150) |
| Second reaction | | |
| 6.80 | 0.0500 | 2.5 (2.5)[c] |
| 27.30 | 0.0500 | 9.8 (9.8) |
| 6.80 | 0.100 | 2.2 (2.5) |
| 9.30 | 0.100 | 2.6 (3.3) |
| 27.30 | 0.100 | 10.0 (9.8) |
| 6.80 | 0.200 | 2.5 (2.5) |
| 27.30 | 0.200 | 9.8 (9.8) |

[a] 25.0 °C, $I = 1.0$ M ($LiClO_4$), $\lambda = 350$ nm.
[b] Calculated according to Eq. (1).
[c] $k_{obs} = 0.36[V^{2+}]$.

appears to be limited by the symmetry mismatch ($k_{et} = 0.49$ $s^{-1}$) but the donor-bridge electronic interaction is more favourable and $Ti^{3+}$ is the effective electron donor.

The Ru(III)–Ti(III) reactions are symmetry matched ($t_{2g}$–$t_{2g}$) and should be dominated by the interaction of the donor–acceptor $t_{2g}$ orbitals with the LUMOs of the ligands. This cross-bridge interaction would be expected to be small for oxalate and formylpentane-2,4-dionato (fpd), both of which are difficult to reduce, and only a modest increase in rate might be anticipated with respect to cobalt(III). This is what is observed if, in the fpd complex, the value of 20 $s^{-1}$ is taken. This value rather than $10^4$ $s^{-1}$ results if the rate law is taken to imply rapid formation of a precursor complex from $[(pd)_2Rufpd]$ and $Ti(OH)^{2+}$, after which electron transfer ensues [13]. It is difficult to rationalise the 'small' $k_{et}$ for $[(trien)RuCQTi]^{4+}$ since CQ has low energy LUMOs of symmetry appropriate to form out-of-phase combinations with the metal $t_{2g}$ orbitals [1]. Furthermore, for pyrazine-bridged diruthenium complexes, intramolecular electron transfer rates are $10^6$–$10^7$ $s^{-1}$ larger [22,23]. If inner-sphere pathways can be observed for the $Ti^{3+}$ reaction with pyrazine complexes of cobalt(III) and ruthenium(III) some of these effects may be clarified.

We have also studied the reduction of complex I with $V^{2+}$. As with $Ti^{3+}$, two resolvable reactions are observed. The first reaction obeys the same rate law (1) as for the $Fe^{2+}$ reaction [16] and the first $Ti^{3+}$ reaction. The data, collected in Table 4, give $k_1 = 2010 \pm 100$ and $k_r = 600 \pm 50$ $M^{-1}$ $s^{-1}$. The mechanism of Scheme 1 would appear to be applicable. However, the value of $k_1$ is 20 times larger than the upper limit for substitution on $V^{2+}$ ($\sim 10^2$ $M^{-1}$ $s^{-1}$) [24]. We suggest that the anomalously high rate of substitution is due to a neighbouring group assistance by the nucleophilic carboxamido oxygen which forms an H bond to a water molecule on the incoming vanadium(II). This 'semi-deprotonated' water molecule labilises a neighbouring water molecule on vanadium and thus accelerates the substitution reaction. A similar mechanism has been proposed for aquation of chloride in a macrocyclic complex of cobalt(III) [25]. In this case the chloride is labilised by a *cis* water molecule which is H bonded to a nearby carboxylate group. Furthermore, evidence for the participation of the carboxamido oxygen in nucleophilic reactions is provided by the complex $(NH_3)_5CoNHC(O)–C_6H_4–2\text{-}CN^{2+}$. In this case the carboxamido oxygen promotes a novel intramolecular amide-N to nitrile-bonded isomerisation in acidic solution by nucleophilic attack at the nearby nitrile [26].

The second reaction produces cobalt(II) (1 mol per mole of cobalt(III) complex) and is first-order in $[V^{2+}]$ and independent of $[H^+]$. The second-order rate constant for reduction is $0.36 \pm 0.02$ $M^{-1}$ $s^{-1}$ at 25 °C and $I = 1.0$ M ($LiClO_4$). Since this reaction is dependent on $[V^{2+}]$, it must involve outer-sphere reduction of either reactant complex I or the binuclear intermediate formed in the first fast reaction.

## Acknowledgement

The authors thank the Natural Sciences and Engineering Research Council of Canada for an operating grant in support of this research.

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