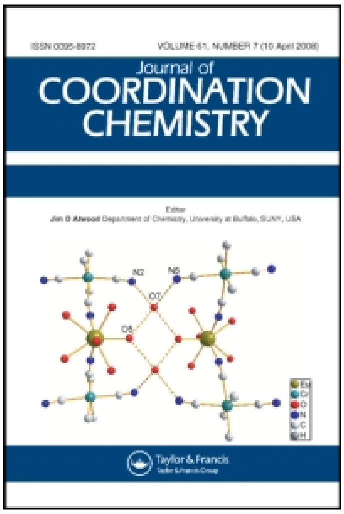

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# Mechanism of electron transfer reactions of ternary nitrilotriacetato cobaltate(II) complexes involving maleate and tartarate by periodate

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# Mechanism of electron transfer reactions of ternary nitrilotriacetato cobaltate(II) complexes involving maleate and tartarate by periodate

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The oxidation of $[Co^{II}NMa(H_2O)]^{3-} \cdot 4H_2O$ and $[Co^{II}NT(H_2O)]^{3-} \cdot 4H_2O$ by periodate have been studied kinetically in aqueous solution by periodate where, [N = nitrilotriacetate, Ma = maleic acid, and T = tartaric acid] over 25–45°C and a variety pH range. The oxidation of $[Co^{II}NMa(H_2O)]^{3-}$ by periodate, obeys the rate law,

$$\text{Rate} = [Co^{II}NMa(H_2O)^{3-}][H_5IO_6]\left\{k_{10}K_6 + \left(\frac{k_{11}K_7K_3}{H^+}\right)\right\}$$

while the reaction of $[Co^{II}NT(H_2O)]^{3-}$, with periodate follows the rate equation

$$\text{Rate} = \left\{\left(\frac{k_{12}K_8 + k_{13}K_3K_9}{[H^+]}\right)[H_5IO_6] + \left(\frac{k_{14}K_{10}K_8 + k_{15}K_{11}K_9K_3}{[H^+]}\right)[H_5IO_6]^2\right\}[Co^{II}NT(H_2O)^{3-}]$$

The thermodynamics activation parameters have been calculated.

*Keywords*: Periodate oxidation; Nitrilotriacetato cobaltate(II); Caffeic acid; Maleic acid; Tartaric acid

## 1. Introduction

Periodate oxidations have been reported to play an important role in biological determinants. They are used to degrade carbohydrate determinants in proteins without altering protein or lipid epitopes [1, 2]. Caffeic acid(3,4-dihydroxycinnamic acid) was oxidized by means of sodium periodate that mimics the mechanism of polyphenyleoxidase. The reaction leads to the formation of the antioxidant product 2-S-cysteinylecaffeic adduct which exhibits slightly improved antiradical activity in relation with the parent molecule (caffeic acid) [3]. Also, study of the kinetics of periodate oxidations on a series of dextran oligomers, polymers, some dimeric

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carbohydrates [4] and of chitosans with different chemical composition [5] were investigated to show the dependence of the kinetics on the molecular weight.

Oxidations of inorganic substrates by periodate are reported to proceed via an inner-sphere mechanism [6–8]. Also, oxidation of transition metal complexes, was found to proceed via the inner sphere mechanism [9–11]. This mechanism could be drawn from reactions of this oxidant with transition metal complexes. It was found that periodate readily oxidize either labile or inert complexes possessing at least one bridging ligand. Initial cobalt(III) products that were transformed to the final cobalt(III) products slowly were identified spectrophotometrically [9–11].

Oxidation of the binary complex diaqua(nitrilotriacetatocobaltate(II) $[Co^{II}nta(H_2O)_2]^-$ [12] and the ternary nitrilotriacetato cobaltate(II) complexes involving succinic acid, $[Co^{II}NS(H_2O)_2]^{3-}$ [13], and, malonic acid], $[Co^{II}NM(H_2O)_2]^{3-}$ [14], [where N = nitrilotriacetate, S = succinic acid, and M = malonic acid] by *N*-bromosuccinimide (NBS) has been studied in aqueous medium. These reactions proceeded via the formation of initial cobalt(III) products, which were converted slowly into final cobalt(III) products fitting an inner-sphere mechanism. It was found that succinate and malonate as a secondary ligand, make the ternary complexes more stable towards oxidation by NBS than the binary complex $[Co^{II}(nta)(H_2O)_2]^-$ [13, 14].

Ternary metal complexes might appear in biological fluids creating specific structure [15–17], most frequently manifesting themselves as enzyme-metal ion-substrate complexes [17–20]. This explains why ternary system has recently received increasing attention.

In this work, the kinetics of oxidation of $[Co^{II}NMa(H_2O)]^{3-} \cdot 4H_2O$ and $[Co^{II}NT(H_2O)]^{3-} \cdot 4H_2O$ where, [Ma = maleic acid, and T = tartaric acid] were studied. Choice of these ternary complexes was attributed to two considerations. Firstly, in order to study the effect of maleate and tartarate as a secondary ligand on the stability of $[Co^{II}nta(H_2O)_2]^-$ towards oxidation and the reaction pathways.

Secondly, transition metal ternary complexes have received particular focus and have been employed in mapping protein surfaces as probes for biological redox centers and in protein capture for both purification and study.

## 2. Experimental

### 2.1. *Materials and solutions*

All reagent grade or analar chemicals were used without further purification. $Co(NO_3)_2$ (BDH) solutions were standardized volumetrically with EDTA [21]. A stock solution of $(IO_4)^-$ was made up by weight and covered with aluminum foil to avoid photochemical decomposition [22]. Solutions of NaOAC, HOAC, and $NaNO_3$ were prepared by weighing.

HOAC/NaOAC buffers of known pH were used, and the ionic strength was adjusted with $NaNO_3$.

Potentiometric measurements were performed with a Metrohm 702 SM titrino. The titroprocessor equipped with a 728 dosimat (Switzerland-Herisau). The titroprocessor and electrode were calibrated with standard buffer solution [23].

The calculations were performed using computer program MINIQUAD-75 loaded on an IBM-550 computer. The solution containing 5 mL 0.1 M complex, 5 mL 0.8 M $NaNO_3$, 5 mL 0.05 M $HNO_3$ and 25 mL deionized water, was titrated with 0.01 M NaOH at 30°C.

$Na_3[Co^{II}NMa(H_2O)] \cdot 4H_2O$ and $Na_3[Co^{II}NT(H_2O)] \cdot 4H_2O$ were prepared using the same procedure as that for the preparation of $Na_3[Co^{II}NS(H_2O)_2]$ [13]. The elemental analysis data of these complexes are Found: C, 22.69; H, 3.01; N, 2.63. ($Na_3Co^{II}C_{10}H_{18}O_{15}N$). Calcd: C, 23.09; H, 3.46; N, 2.69 and Found: C, 20.92; H, 4.24; N, 2.76; ($Na_3Co^{II}C_{10}H_{20}O_{17}N$), Calcd: C, 21.67; H, 3.61; N, 2.53, respectively. To confirm the formula of the complexes, IR spectra and t.g.a. data were carried out.

In the IR spectra, bands in the (3514–3363) $cm^{-1}$ region, were attributed to $\nu(OH)$ of the water molecules. The OH of the carboxylic group disappeared and a new ($\nu COO^-$) appeared in the region (1464–1431) $cm^{-1}$ indicating that the carboxylic group of the ligands participates in the coordination with the metal ions through deprotonation.

All the spectra of the complexes studied showed asym- ($\nu$COO–Co) band in the region (1582–1658) $cm^{-1}$.

The thermogram of the complex $Na_3[Co^{II}NMa(H_2O)] \cdot 4H_2O$ shows that weight loss (13.63) at 87.55°C corresponds to the loss of four molecules of $H_2O$ of crystallization (Calcd 13.85), and a weight loss (3.61) at 145.8°C corresponds to the loss of one coordinated water molecule (Calcd 4.02). The thermogram of the complex $Na_3[Co^{II}NT(H_2O)] \cdot 4H_2O$ shows that weight loss (12.92) at 81.49°C corresponds to the loss of four molecules of $H_2O$ of crystallization (Calcd 13.01), and a weight loss (3.23) at 148.51°C corresponds to the loss of one coordinated water molecule (Calcd 3.73).

## 2.2. *Kinetic procedures*

During the oxidation, the pink aqueous solution of the complexes was gradually changed to blue. Reaction rates were measured by monitoring the initial $Co^{III}$-complexes absorbance at 595 nm on a Milton-Roy 601 spectrophotometer. All reactants, except $IO_4^-$, were equilibrated at required temperature for 15–20 min. The required amount of separately thermostated $IO_4^-$ stock solution was rapidly mixed, and then the recording of absorbance was started.

The pH of the reaction mixture was measured using a Chertsey, Surrey, 7065 pH-meter.

Pseudo-first order conditions were maintained in all runs by the presence of a large excess of $IO_4^-$ (>10-fold). The ionic strength was kept constant by addition of $NaNO_3$ solution. The pH of the reaction mixture was found to be always constant during the reaction run.

The error limits for results are calculated using Microcal™ Origin® (Version 6.0).

## 2.3. *Oxidation product*

The UV-Vis absorption spectra of the oxidation product of $[Co^{II}NMa(H_2O)^{3-}$ and $[Co^{II}NT(H_2O)]^{3-}$ by periodate were recorded on Schimadzu UV-160 IPC

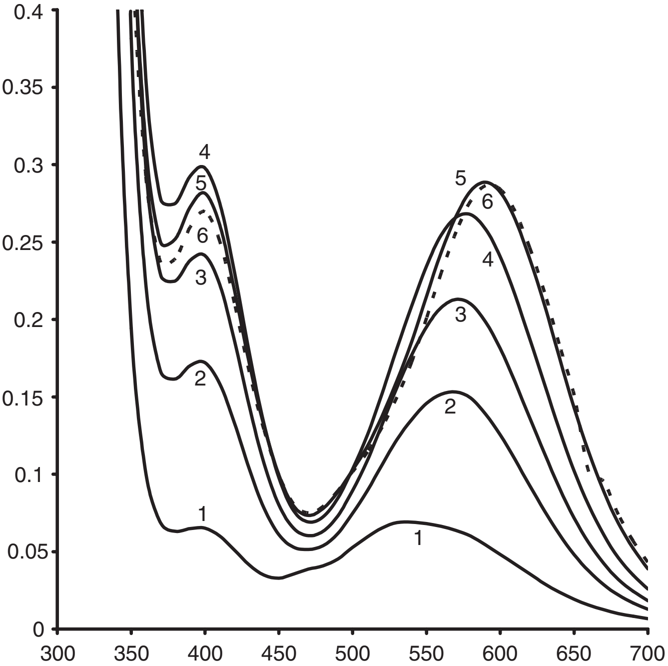

Figure 1. Change in absorbance as a function of time. Curves (1–5) were recorded at 5, 30, 60, 120, 180 and 240 min, respectively from the time of initiation of the reaction; The dotted curve (6) represents the final product. $[Co^{II}NMa(H_2O)]^{3-} = 2.0 \times 10^{-3}\,mol\,dm^{-3}$, $I = 0.25\,mol\,dm^{-3}$, $T = 30°C$, pH = 4.01 and $[IO_4^-] = 0.04\,mol\,dm^{-3}$.

spectrophotometer as a function of time over the 350–700 nm range (figures 1 and 2) respectively. Initial cobalt(III) products were formed and changed slowly to the final cobalt(III) products. Both initial and the final products were blue. The maxima and molar absorptivity coefficients of the final cobalt(III) product at pH 4.21 of oxidation of malice ternary complex were $\varepsilon_{max}^{398} = 135$ and $\varepsilon_{max}^{595} = 144\,dm^3\,mol^{-1}\,cm^{-1}$, while the coefficients of the tartarate ternary complex were $\varepsilon_{max}^{398} = 140$ and $\varepsilon_{max}^{595} = 152\,dm^3\,mol^{-1}\,cm^{-1}$.

The elemental analysis data of the oxidation products of both $[Co^{II}NMa(H_2O)]^{3-}$ and $[Co^{II}NT(H_2O)]^{3-}$, $[Na_3Co^{III}C_{10}H_{16}O_{14}N]$ and $[Na_3Co^{III}C_{10}H_{18}O_{16}N]$, were found (calculated): C, 22.88 (23.89); H, 3.31 (3.19); N, 2.90 (2.79) and C, 21.94 (22.39); H, 4.01 (3.36); N, 2.72 (2.61)%, respectively. The TGA curves of $[Na_3Co^{III}C_{10}H_{16}O_{14}N]$ show a two stages decomposition pattern. The weight loss (10.41%) at 88.56°C corresponds to the loss of $3H_2O$ of crystallization (Calcd 10.76%), and a weight loss (3.41%) at 147.20°C corresponds to the loss of one coordinated water molecule (Calcd 3.59%). While TGA of the complex $[Na_3Co^{III}C_{10}H_{18}O_{16}N]$ shows a weight loss (9.91%) at 82.81°C corresponds to the loss of $3H_2O$ of crystallization (Calcd 10.07%), and a weight loss (3.22%) at 150.01°C due to loss of one coordinated water molecule (Calcd 3.36%). The elemental and thermal analysis of $[Na_3Co^{III}C_{10}H_{16}O_{14}N]$ and $[Na_3Co^{III}C_{10}H_{18}O_{16}N]$ complexes agree with the formula $Na_3[Co^{III}NMa(H_2O)] \cdot 3H_2O$ and $Na_3[Co^{III}NT(H_2O)] \cdot 3H_2O$, respectively.

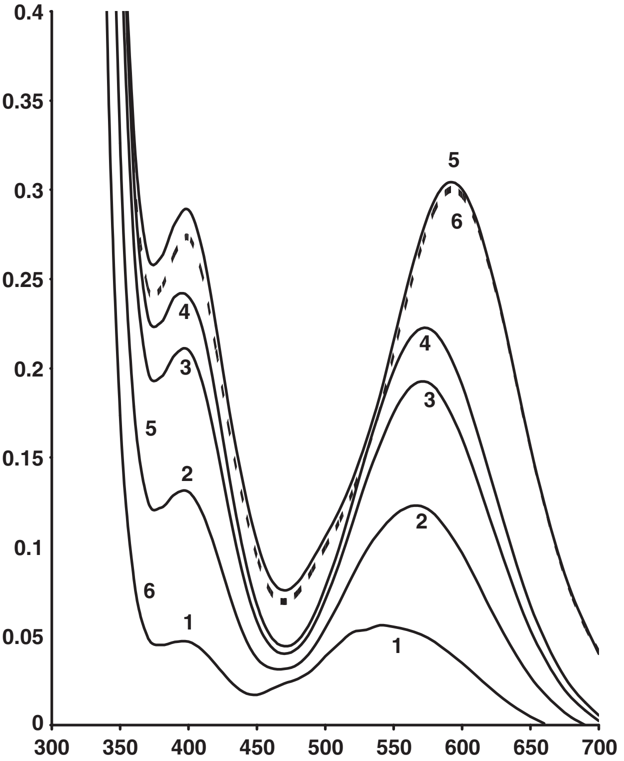

Figure 2. Change in absorbance as a function of time. Curves (1–5) were recorded at 15, 60, 120, 180 and 300 min, respectively from the time of initiation of the reaction; the dotted curve (6) represents the final product. $[Co^{II}NT(H_2O)]^{3-} = 2.0 \times 10^{-3}\,mol\,dm^{-3}$, $I = 0.25\,mol\,dm^{-3}$, $T = 25°C$, pH = 4.21 and $[IO_4^-] = 0.03\,mol\,dm^{-3}$.

## 3. Results

### 3.1. *Kinetics of $[Co^{II}NMa(H_2O)]^{3-}$*

Oxidation of $[Co^{II}NMa(H_2O)]^{3-}$ by $(IO_4)^-$ was studied over a pH range of (3.55–4.58), and ionic strength range of 0.25–0.50 M at 25–45°C using various $(IO_4)^-$ and complex concentrations.

Plots of in $(A_\alpha - A_t)$ *versus* time were linear up to 85% of reaction where $A_t$ and $A_\alpha$ are absorbance at time $t$, and infinity, respectively. Pseudo-first order rate constants, $k_{obs}$, obtained from the slopes of these plots, are collected in table 1. These data show that, $k_{obs}$, was unaffected when the concentration of the $Co^{II}$-complex was varied at constant $(IO_4)^-$ concentration indicating first order dependence on the complex concentration.

$$\frac{d[Co^{III}NMa(H_2O)]^{2-}}{dt} = k_{obs}\{[Co^{II}NMa(H_2O)]^{3-}\}_o \qquad (1)$$

Table 1. Dependence of the reaction rate constant, $10^4 k_{obs}$ (s$^{-1}$), on $[Co^{II}NMa(H_2O)]^{3-}$ [a], $[IO_4^-]$, $I^b$ and temperatures at pH = 4.21.

| | $10^4 k_{obs}$ (s$^{-1}$) | | |
|---|---|---|---|
| $10^2$ $[IO_4^-]$ (M) | $T = 25°$ | $T = 30°$ | $T = 35°$ |
| 5.0 | 7.66 | 12.55 | 18.63 |
| 4.5 | 7.22 | 10.56 | 15.51 |
| 4.0 | 6.33 | 9.85 | 14.46 |
| 3.5 | 5.56 | 8.55 | 12.74 |
| 3.0 | 4.83 | 7.91 | 11.02 |
| 2.5 | 4.08 | 5.68 | 8.56 |
| 2.0 | 3.40 | 4.75 | 7.32 |
| 1.5 | 2.61 | 3.60 | 5.55 |
| 1.0 | 1.75 | 2.66 | 3.58 |
| 0.5 | 0.98 | 1.50 | 2.03 |

[a] $[Co^{II}NT(H_2O)]^{3-} = 2.0 \times 10^{-3}$ mol dm$^{-3}$; $I^b = 0.25$ mol dm$^{-3}$, at $10^{3-}$ $[Co^{II}NT(H_2O)]^{3-} = 0.5$, 1.0, 3.0 and 4.0 mol dm$^{-3}$, 35°C, $I^b$ and $[IO_4^-] = 0.04$ mol dm$^{-3}$, $10^4 k_{obs} = 14.37$, 13.90, 14.16 and 14.32 s$^{-1}$, respectively. While at $(I) = 0.3$, 0.35, 0.4, and 0.5 mol dm$^{-3}$, 35°C, [a]$[Co^{II}NT(H_2O)]^3$ and $[IO_4^-] = 0.035$ mol dm$^{-3}$, $10^4 k_{obs} = 13.36$, 15.20, 16.01, and 17.11 s$^{-1}$, respectively.

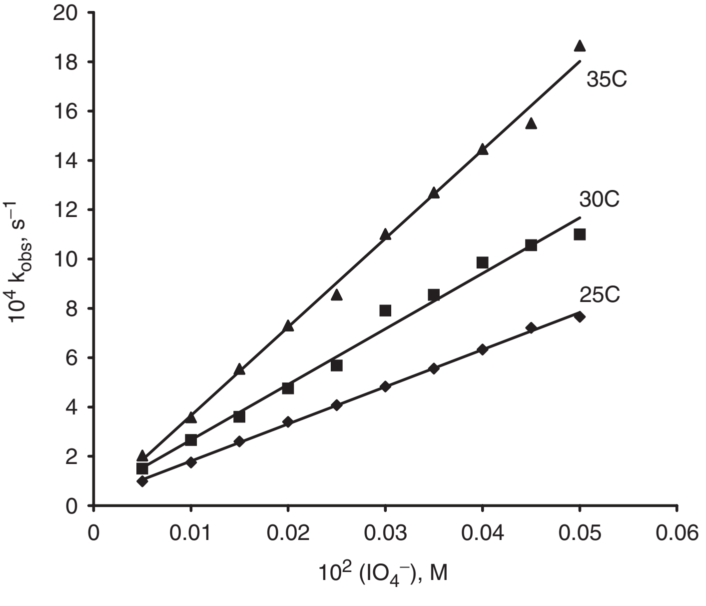

Figure 3. Variation of $k_{obs}$ *vs.* $[IO_4^-]$ at different temperatures for oxidation of $[Co^{II}NMa(H_2O)]^{3-}$.

Plots of $k_{obs}$ against $[IO_4^-]$ were found to be linear without intercept, figure 3. The dependence of $k_{obs}$ on $[IO_4^-]$, table 1, is described by

$$k_{obs} = k_1[IO_4^-] \tag{2}$$

The kinetics of the reaction was studied over pH range of (3.55–5.58) at different temperatures. Table 2 lists the variation of $k_1$ with $[H^+]$ at different temperatures which indicate that the reaction rate increased gradually with increasing pH. Plots of $k_1$ *versus*

Table 2. Variation of $k_1$ with pH at $[Co^{II}NMa(H_2O)]^{3-} = 2.0 \times 10^{-3}\,mol\,dm^{-3}$, $I = 0.25\,mol\,dm^{-3}$, different $[IO_4^-]$ and different temperatures.

| | $10^2 k_1$ ($M^{-1}\,s^{-1}$) | | | |
|---|---|---|---|---|
| pH | $T = 25°$ | $T = 30°$ | $T = 35°$ | $T = 45°$ |
| 3.55 | $1.01 \pm 0.03$ | $1.85 \pm 0.02$ | $2.23 \pm 0.15$ | $5.48 \pm 0.37$ |
| 3.85 | $1.43 \pm 0.07$ | $2.01 \pm 0.05$ | $2.77 \pm 0.05$ | $6.37 \pm 0.39$ |
| 4.21 | $1.49 \pm 0.02$ | $2.46 \pm 0.07$ | $3.68 \pm 0.05$ | $9.93 \pm 0.45$ |
| 4.58 | $2.49 \pm 0.08$ | $3.79 \pm 0.23$ | $5.12 \pm 0.33$ | $13.92 \pm 0.39$ |

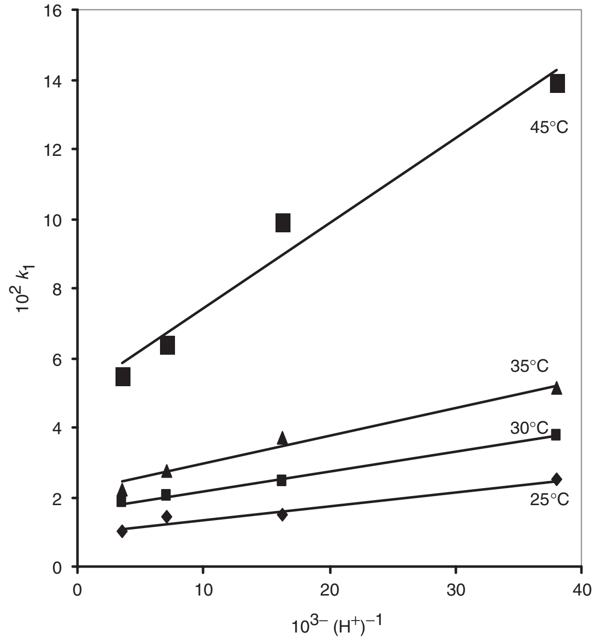

Figure 4. Variation of $k_1$ on pH of the reaction of $[Co^{II}NMa(H_2O)]^3$ with $[IO_4^-]$.

Table 3. Variation of $k_2$ and $k_3$ with temperatures at $[Co^{II}NMa(H_2O)]^{3-} = 2.0 \times 10^{-3}\,mol\,dm^{-3}$, $I = 0.25\,mol\,dm^{-3}$, and different $[IO_4^-]$.

| $T$ (°C) | $10^3 k_2$ ($M^{-1}\,s^{-1}$) | $10^7 k_3$ ($s^{-1}$) |
|---|---|---|
| 25 | $10.03 \pm 0.12$ | $3.83 \pm 0.06$ |
| 30 | $16.07 \pm 0.46$ | $5.75 \pm 0.22$ |
| 35 | $21.40 \pm 0.17$ | $8.24 \pm 0.35$ |
| 45 | $49.59 \pm 0.64$ | $24.01 \pm 0.31$ |

$[H^+]$ were linear, with intercepts as shown in figure 4. This behavior can be described by equation (3).

$$k_1 = \frac{k_2 + k_3}{[H^+]} \tag{3}$$

Values of $k_2$ and $k_3$ were calculated at different temperatures, and were listed in table 3. The thermodynamic activation parameters were calculated by using the transition state theory equation. The enthalpies of activation, $\Delta H_2^*$ and $\Delta H_3^*$ were reported as $59.0 \pm 3.0$ and $71.0 \pm 6.0\,\mathrm{kJ\,mol^{-1}}$, respectively. The corresponding entropies of activation, $\Delta S_2^*$ and $\Delta S_3^*$ were $-311.0 \pm 28.0$ and $-263.0 \pm 8.0\,\mathrm{JK^{-1}\,mol^{-1}}$, respectively.

Furthermore, the reaction rate increased with an increase in ionic strength, over a 0.25–0.50 M range as shown in table 1.

From equations (1–3) the experimental rate law was derived, as:

$$\text{Rate} = \left(\frac{k_2 + k_3}{[\mathrm{H}^+]}\right)\{[\mathrm{Co^{II}NMa(H_2O)}]^{3-}\}_{\mathrm{o}}[\mathrm{IO_4^-}]. \tag{4}$$

## 3.2. *Kinetics of oxidation of $[Co^{II}NT(H_2O)]^{3-}$*

The kinetics of oxidation of $[\mathrm{Co^{II}NT(H_2O)}]^{3-}$ by $\mathrm{IO_4^-}$ was studied over a pH range of (3.24–4.52), ionic strength range of 0.25–0.50 M, temperature range of 25–45°C range over a range of $(\mathrm{IO_4})^-$ concentration and complex concentrations.

Plots of $(A_\alpha - A_\mathrm{t})$ *versus* time were linear at up to 85% of reaction where $A_\mathrm{t}$ and $A_\alpha$ are absorbance at time $t$, and infinity, respectively. Pseudo-first order rate constants, $k_\mathrm{obs}$, obtained from the slopes of these plots, were recorded in table 4. The constancy of $k_\mathrm{obs}$, at a fixed periodate concentration, pH, ionic strength and temperature over a range of complex concentration was in agreement with a first-order dependence on $[\mathrm{Co^{II}NT(H_2O)}]^{3-}$.

The variation of $k_\mathrm{obs}$, with $[\mathrm{IO_4^-}]$, as evident from table 4, was not linear at the temperature range employed. However, a plot of $k_\mathrm{obs}/[\mathrm{IO_4^-}]$ *versus* $[\mathrm{IO_4^-}]$ was linear with an intercept and a slope as shown in figure 5. The dependence of $k_\mathrm{obs}$ on $[\mathrm{I^{VII}}]$ was thus described by equation (5),

$$k_\mathrm{obs} = k_4[\mathrm{IO_4^-}] + k_5[\mathrm{IO_4^-}]^2. \tag{5}$$

The value of $k_4$ and $k_5$ obtained from intercepts and the slopes respectively of plots in figure 3 were registered in table 5.

Table 4. Dependence of the rate constant, ($10^4$, $\mathrm{s^{-1}}\,k_\mathrm{obs}$) on $[\mathrm{Co^{II}NT(H_2O)}]^{3-}$ [a], $I^\mathrm{b}$, different $[\mathrm{IO_4^-}]$, and temperature at pH = 3.82.

| | $10^{-4}k_\mathrm{obs}$ ($\mathrm{s^{-1}}$) | | | | |
|---|---|---|---|---|---|
| $10^2$ $[\mathrm{IO_4^-}]$ (M) | $T = 25°$ | $T = 30°$ | $T = 35°$ | $T = 40°$ | $T = 45°$ |
| 5.0 | 7.02 | – | 17.92 | 26.66 | 35.50 |
| 4.5 | 6.17 | 9.66 | – | – | 28.99 |
| 4.0 | 5.15 | – | – | 19.46 | 24.50 |
| 3.5 | 4.33 | – | 10.75 | 15.33 | – |
| 3.0 | – | 5.87 | 8.40 | 12.67 | 16.73 |
| 2.5 | 3.05 | 4.47 | 6.78 | 9.33 | 12.54 |
| 1.5 | – | 2.23 | – | 4.50 | 6.28 |
| 1.0 | 0.93 | 1.33 | 2.26 | 2.88 | – |
| 0.5 | 0.42 | 0.63 | 0.92 | – | 1.60 |

[a] $[\mathrm{Co^{II}NT(H_2O)}]^{3-} = 2.0 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$; $I^\mathrm{b} = 0.3\,\mathrm{mol\,dm^{-3}}$, at $10^{3-}$ $[\mathrm{Co^{II}NT(H_2O)}]^{3-} = 0.5$, 1.0, and $3.0\,\mathrm{mol\,dm^{-3}}$, 40°C, $I^\mathrm{b}$ and $[\mathrm{IO_4^-}] = 0.03\,\mathrm{mol\,dm^{-3}}$, $10^4 k_\mathrm{obs} = 11.95$, 12.13 and $11.53\,\mathrm{s^{-1}}$, respectively. While at $(I) = 0.25$, 0.35, 0.4, and $0.5\,\mathrm{mol\,dm^{-3}}$, 40°C, [a]$[\mathrm{Co^{II}NT(H_2O)}]^{3-}$ and $[\mathrm{IO_4^-}] = 0.03\,\mathrm{mol\,dm^{-3}}$, $10^4 k_\mathrm{obs} = 7.76$, 14.41,14.93 and $16.31\,\mathrm{s^{-1}}$, respectively.

The effect of pH on both $k_4$ and $k_5$ was examined over the employed pH range. The results in (table 6) showed that both $k_4$ and $k_5$ depend on [H$^+$]. The dependence of $k_4$ and $k_5$ on [H$^+$] agreed with equations (6) and (7) as shown in figures 6 and 7

$$k_4 = \frac{k_6 + k_7}{[\mathrm{H}^+]} \tag{6}$$

$$k_5 = \frac{k_8 + k_9}{[\mathrm{H}^+]}. \tag{7}$$

The thermodynamic activation parameters were calculated by using the transition state theory equation. The enthalpies of activation, $\Delta H_4^*$ and $\Delta H_5^*$ were calculated as $49.0 \pm 2.0$ and $75.0 \pm 6.0\,\mathrm{kJ\,mol^{-1}}$, respectively. The corresponding entropies of activation, $\Delta S_4^*$ and $\Delta S_5^*$ were $-273.0 \pm 25.0$ and $-380.0 \pm 38.0\,\mathrm{JK^{-1}\,mol^{-1}}$, respectively.

The reaction rate increased with an increase in ionic strength, over a 0.25–0.50 M range as shown in table 4.

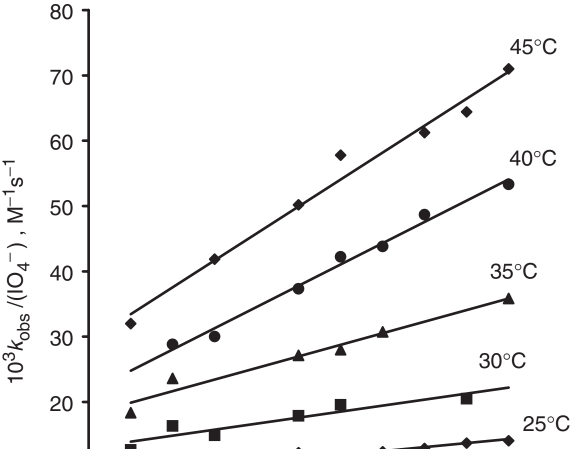

Figure 5. Plots of $k_{obs}/[\mathrm{IO_4^-}]$ *vs.* $[\mathrm{IO_4^-}]$ at various temperatures for oxidation of $[\mathrm{Co^{II}NT(H_2O)}]^{3-}$.

Table 5. Dependence of $k_4$ and $k_5$ on temperature at $[\mathrm{Co^{II}NT(H_2O)}]^{3-} = 2.0 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$, pH = 3.82 and $I = 0.3\,\mathrm{mol\,dm^{-3}}$.

| $T$ (°C) | $10^2 k_5$ | $10^3 k_4$ |
|---|---|---|
| 25 | $12.26 \pm 1.18$ | $8.20 \pm 0.40$ |
| 30 | $23.80 \pm 2.08$ | $11.46 \pm 0.53$ |
| 35 | $36.62 \pm 2.56$ | $17.64 \pm 0.77$ |
| 40 | $65.07 \pm 3.16$ | $21.53 \pm 1.01$ |
| 45 | $82.51 \pm 3.51$ | $29.03 \pm 1.18$ |

Table 6. Dependence of $k_4$ and $k_5$ on pH of the reaction, at $T = 40°C$, $[Co^{II}NT(H_2O)]^{3-} = 2.0 \times 10^{-3}$ mol dm$^{-3}$, and $I = 0.35$ mol dm$^{-3}$.

| pH | $10^2 k_5$ | $10^3 k_4$ |
|---|---|---|
| 3.24 | 59.90 ± 1.05 | 16.02 ± 0.32 |
| 3.55 | 68.78 ± 0.77 | 17.99 ± 0.23 |
| 3.94 | 78.91 ± 0.33 | 19.59 ± 0.10 |
| 4.15 | 103.9 ± 0.88 | 21.31 ± 0.28 |
| 4.43 | 139.1 ± 0.54 | 25.94 ± 0.16 |
| 4.52 | 168.6 ± 0.79 | 30.20 ± 0.24 |

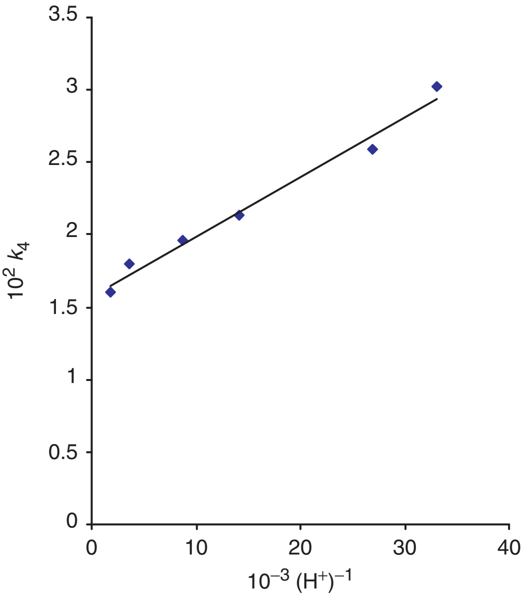

Figure 6. Dependence of $k_4$ on pH of the reaction of $[Co^{II}NT(H_2O)]^3$ with $[IO_4^-]$.

From the above results, the following experimental rate law was derived,

$$\text{Rate} = \left\{\left(\frac{k_6 + k_7}{[H^+]}\right)[IO_4^-] + \left(\frac{k_8 + k_9}{[H^+]}\right)[IO_4^-]^2\right\}[Co^{II}NT(H_2O)]_o^{3-}. \tag{8}$$

## 4. Discussion

Ternary cobalt(II) complex ions of N with maleic and tartaric acids may be formulated as $Na_3[Co^{II}NMa(H_2O)] \cdot 4H_2O$ and $Na_3[Co^{II}NT(H_2O)] \cdot 4H_2O$, where N is functioning as tridentate and both Ma and T, are bidentate ligands. The lability of cobalt(II) reactants and the inertness of cobalt(III) products could be utilized as a diagnostic tool for ascertaining inner-sphere electron transfer [6, 9–11]. Oxidation of some cobalt(II) complexes by periodate, where an initial cobalt(III) product was observed, was interpreted in terms of this mechanism.

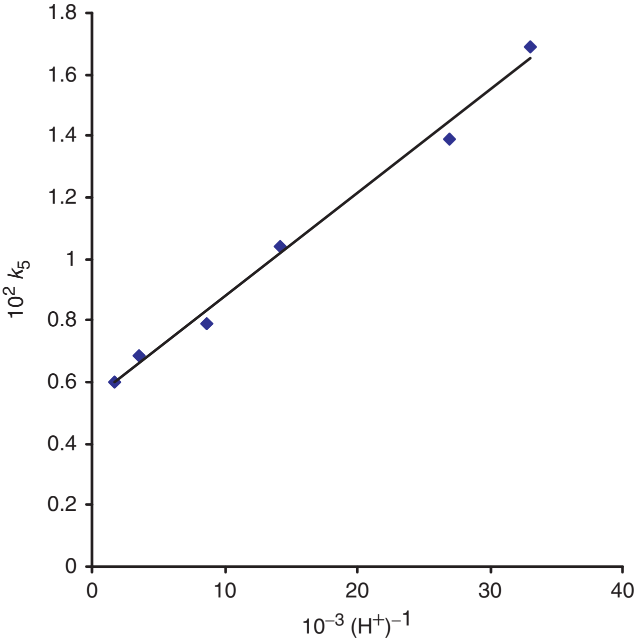

Figure 7. Dependence of $k_5$ on pH of the reaction of $[Co^{II}NMa(H_2O)]^3/[IO_4^-]$ system.

An inner-sphere mechanism is proposed for the bath way of oxidation of both two $Co^{II}$ complexes $Na_3[Co^{II}NMa(H_2O)] \cdot 4H_2O$ and $Na_3[Co^{II}NT(H_2O)] \cdot 4H_2O$. This proposal seems to be supported for the following reasons:

(a) Formation of the initial cobalt(III) products, which were slowly converted to the final cobalt products [9, 11, 24].
(b) Outer sphere electron transfer would lead directly to the formation of the final product [9].
(c) Periodate ion is capable of acting as a ligand, as evidenced from its coordination to copper(III) [25] and nickel [26].

In aqueous medium the $[Co^{II}NMa(H_2O)]^{3-}$ and $[Co^{II}NT(H_2O)]^{3-}$, complexes are in equilibria:

$$[Co^{II}NMa(H_2O)]^{3-} \leftrightarrow [Co^{II}NMa(OH)]^{4-} + H^+ \quad K_1 \tag{9}$$

$$[Co^{II}NT(H_2O)]^{3-} \leftrightarrow [Co^{II}NT(OH)]^{4-} + H^+ \quad K_2 \tag{10}$$

$K_1$ and $K_2$ were potentiometrically determined as $2.34 \times 10^{-6}$ and $9.3 \times 10^{-8}$, respectively. It was observed from values of $K_1$ and $K_2$ at the employed pH range that these equilibriums were not prevailing and the protonated $Co^{II}$-complex species was the predominant.

In aqueous solutions, periodate species are found in the equilibriums [27]

$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+ \quad (K_3 = 1.0 \times 10^{-3}) \tag{11}$$

$$H_4IO_6^- \rightleftharpoons 2H_2O + IO_4^- \quad (K_4 = 0.025) \tag{12}$$

$$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-} + H^+ \quad (K_5 = 5.0 \times 10^{-6}) \tag{13}$$

Thus, it may be concluded that over the pH range used, the periodate species likely to be present are $H_5IO_6$ and $H_4IO_6^-$.

The hydrogen ion dependence of the reaction rate of both complexes is in agreement with the involvement of both deprotonated and protonated forms of periodate in the rate determining steps, proceeded by a rapid deprotonation equilibrium and in which both forms are reactive.

The concomitant reaction rate increase with the increase of ionic strength may be attributed to that the reaction rate, in the rate determining step, occurred between two species of the same sign.

In view of the above considerations, kinetics of oxidation of $[Co^{II}NMa(H_2O)]^{3-}$ by periodate proceeds by one first-order pathway in each reactant. The mechanism could be described by the following equations (14–18).

$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+ \quad K_3$$

$$[Co^{II}NMa(H_2O)]^{3-} + H_5IO_6 \rightleftharpoons [Co^{II}NMa(H_5IO_6)]^{3-} + H_2O \quad K_6 \tag{14}$$

$$[Co^{II}NMa(H_2O)]^{3-} + H_4IO_6^- \rightleftharpoons [Co^{II}NMa(H_4IO_6)]^{4-} + H_2O \quad K_7 \tag{15}$$

$$[Co^{II}NMa(H_5IO_6)]^{3-} \longrightarrow [Co^{III}NMa(H_5IO_6)]^{2-} \quad k_{10} \tag{16}$$

$$[Co^{II}NMa(H_4IO_6)]^{4-} \longrightarrow [Co^{III}NMa(H_4IO_6)]^{3-} \quad k_{11} \tag{17}$$

From the above mechanism, the rate of the reaction can be described by equation (18),

$$\text{Rate} = k_{10}K_6[Co^{II}NMa(H_2O)^{3-}][H_5IO_6] + k_{11}K_7[Co^{II}NMa(H_2O)^{3-}][H_4IO_6^-]. \tag{18}$$

Substituting $[H_4IO_6^-]$ from equation (11) gives,

$$\text{Rate} = [Co^{II}NMa(H_2O)^{3-}][H_5IO_6] + \left\{k_{10}K_6 + \left(\frac{k_{11}K_7K_3}{[H^+]}\right)\right\} \tag{19}$$

which is identical to the experimental rate law, equation (4), and therefore,

$$k_{obs} = \left\{k_{10}K_6 + \left(\frac{k_{11}K_7K_3}{[H^+]}\right)\right\}[H_5IO_6] \tag{20}$$

Comparison of equations (20) and (2), gives

$$k_1 = k_{10}K_6 + \left(\frac{k_{11}K_7K_3}{[H^+]}\right). \tag{21}$$

Values of $k_2$ and $k_3$ were obtained by comparison of equations (21) and (3), as follows:

$$k_2 = k_{10}K_6 \quad \text{and} \quad k_3 = (k_{11}K_7K_3)$$

In case of $[Co^{II}NT(H_2O)]^{3-}$,the pathway that is first-order in each reactant, almost certainly, proceeds via inner-sphere electron transfer. This is necessitated by the pathway that is second order in $[IO_4^-]$, as a rapid preequilibrium between $[Co^{II}NT(H_2O)]^{3-}$ and $IO_4^-$ is required to account for the termolecular reaction [28]. The existence of initial cobalt(III) product renders further support for this mechanism. The oxidation process that is second-order in $[IO_4^-]$, probably, also proceeds via an inner sphere mechanism. This would be in agreement with the hypotheses that periodate is an inner sphere oxidant. Two periodate ions could substitute the coordinated water molecule and a free carboxylate arm of (NTA) nitrilotriacetate. A second-order dependence on $[IO_4^-]$ in its reaction with V(IV) [7], $Co^{II}$HEDTA, $Co^{II}$EDDA [10] and the precursor complexes $VO(IO_4^-)_2$, $[HEDTA\text{-}Co^{II}\text{-}(OIO_3)_2]^{3-}$ and $[EDDA\text{-}Co^{II}\text{-}(OIO_3)_2]^{2-}$ was proposed respectively. The second-order dependence in $[IO_4^-]$ could not result from a dimerization of periodate as this occurs only at higher pH values [29].

In comparison, entry of the second periodate ion occurring in case of $[Co^{II}NT(H_2O)]^{3-}$ not in $[Co^{II}NMa(H_2O)]^{3-}$ may be explained as in $[Co^{II}NT(H_2O)]^{3-}$. The hydroxyl group of tartaric acid was a withdrawing group making it more acidic than maleic acid, and leaving more effective negative charge on carboxyl group of tartarate leading to stronger bond with cobalt. This result, in addition to the already first present $IO_4^-$, leads to weakening the adjacent arm of NTA. This arm is set free, so substitution of the second $IO_4^-$ takes place. The free carboxylate arm, on the entry of the second $IO_4^-$ may be protonated.

$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+ \quad K_3$$

$$[Co^{II}NT(H_2O)]^{3-} + H_5IO_6 \rightleftharpoons [Co^{II}NT(H_5IO_6)]^{3-} + H_2O \quad K_8 \tag{22}$$

$$[Co^{II}NT(H_2O)]^{3-} + H_4IO_6^- \rightleftharpoons [Co^{II}NT(H_4IO_6)]^{4-} + H_2O \quad K_9 \tag{23}$$

$$[Co^{II}NT(H_5IO_6)]^{3-} + H_5IO_6 \rightleftharpoons [Co^{II}NT(H_5IO_6)_2]^{3-} \quad K_{10} \tag{24}$$

$$[Co^{II}NT(H_4IO_6)]^{4-} + H_4IO_6^- \rightleftharpoons [Co^{II}NT(H_4IO_6)_2]^{5-} \quad K_{11} \tag{25}$$

$$[Co^{II}NT(H_5IO_6)]^{3-} \longrightarrow [Co^{III}NT(H_5IO_6)]^{2-} \quad k_{12} \tag{26}$$

$$[Co^{II}NT(H_4IO_6)]^{4-} \longrightarrow [Co^{II}NT(H_4IO_6)]^{3-} \quad k_{13} \tag{27}$$

$$[Co^{II}NT(H_5IO_6)]^{3-} \longrightarrow [Co^{III}NT(H_5IO_6)_2]^{2-} \quad k_{14} \tag{28}$$

$$[Co^{II}NT(H_4IO_6)_2]^{5-} \longrightarrow [Co^{III}NT(H_4IO_6)_2]^{4-} \quad k_{15} \tag{29}$$

From the above mechanism, the rate of the reaction can be described by equation (30),

$$\begin{aligned} \text{Rate} = {} & k_{12}K_8[Co^{II}NT(H_2O)^{3-}][H_5IO_6] + k_{13}K_9[Co^{II}NT(H_2O)^{3-}][H_4IO_6^-] \\ & + k_{14}K_{10}K_8[Co^{II}NT(H_2O)^{3-}][H_5IO_6]^2 + k_{15}K_{11}K_9[Co^{II}NT(H_2O)^{3-}][H_4IO_6^-]^2 \end{aligned} \tag{30}$$

Substituting $[H_4IO_6^-]$ from equation (11) gives,

$$\begin{aligned} \text{Rate} = {} & \left\{ \left( \frac{k_{12}K_8 + k_{13}K_3K_9}{[H^+]} \right)[H_5IO_6] + \left( \frac{k_{14}K_{10}K_8 + k_{15}K_{11}K_9K_3}{[H^+]} \right)[H_5IO_6]^2 \right\} \\ & \times [Co^{II}NT(H_2O)^{3-}] \end{aligned}$$

which is identical to the experimental rate law, equation (8), and therefore,

$$k_{\text{obs}} = \left( \frac{k_{12}K_8 + k_{13}K_3K_9}{[H^+]} \right)[H_5IO_6] + \left( \frac{k_{14}K_{10}K_8 + k_{15}K_{11}K_9K_3}{[H^+]} \right)[H_5IO_6]^2. \tag{31}$$

Comparison of equations (31) and (5), gives

$$k_4 = \left(\frac{k_{12}K_8 + k_{13}K_3K_9}{[\mathrm{H}^+]}\right) \quad \text{and} \quad k_5 = \left(\frac{k_{14}K_{10}K_8 + k_{15}K_{11}K_9K_3}{[\mathrm{H}^+]}\right)$$

$$k_6 = k_{12}K_8, \quad k_7 = k_{13}K_3K_9, \quad k_8 = k_{14}K_{10}K_8, \quad k_9 = k_{15}K_{11}K_9K_3$$

In comparison, $k_2$, $k_3$ with $k_6$, $k_7$ indicates that the secondary ligand Ma, and T has the same effect on the stability of CoNTA towards oxidation by $IO_4^-$.

The enthalpy of activation reported for the two pathways are composite figures. The relatively low heat of activation calculated for the $k_4$ process is probably, due to the formation of $[LCo^{II}–OIO_3]$, being exothermic. The entry of a second periodate probably is endothermic and therefore, the pathway second-order in $[IO_4^-]$ showed a relatively high heat of activation.

The initial cobalt(III) product of oxidation of $[Co^{II}NMa(H_2O)]^{3-}$ by $IO_4^-$ may be converted to final products according to the equation (32),

$$[N(Ma)Co^{III}–OIO_3]^{2-} + H_2O \longrightarrow [Co^{III}NMa(H_2O)]^{2-} + I^{VI} \qquad (32)$$

While the conversion of the initial products of oxidation of $[Co^{II}NT(H_2O)]^{3-}$ to the final products may proceed via two steps:

$$[N(T)Co^{III}–OIO_3]^{2-} + H_2O \longrightarrow [Co^{III}NT(H_2O)]^{2-} + I^{VI} \qquad (33)$$

$$[N(T)Co^{III}–(OIO_3)_2]^{2-} + H_2O \longrightarrow [NTCo^{III}–(OIO_3)(H_2O)]^{2-} + I^{VI} \qquad (34)$$

$$[NTCo^{III}–(OIO)_3(H_2O) \longrightarrow [Co^{III}NT(H_2O)]^{2-} + I^{VII} \qquad (35)$$

Then fast reaction takes place between $I^{VI}$ radicals,

$$2I^{VI} \longrightarrow IO_4^- + IO_3^- \qquad (36)$$

In both reactions, $[Co^{III}NMa(H_2O)]^{2-}$ and $[Co^{III}NT(H_2O)]^{2-}$, an $I^{VI}$ in the initial product is probably substituted by a water molecule with a very slow rate due to inertness of $Co^{III}$ and $Co^{II}–OIO_3$ bond is being stronger than $Co–H_2O$ bond. Substitution of the carboxylate arm free for $IO_4^-$ in the initial product of oxidation of $[Co^{II}NT(H_2O)]^{3-}$ may be much slower than that of the water molecule because this closing arm is protonated and a proton has to be lost prior to coordination [30, 31].

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