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One- and two-electron reduction of chromium(VI) by polyaminocarboxylatocobaltate(II) complexes and the formation of chromium(V) and chromium(IV)

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Abstract The kinetics of the oxidation of $Co^{II}L^n$ complexes {where L = ethylenediaminetetraacetate (EDTA), diethylenetriaminepentaacetate (DTPA), or N-(2-hydroxyethyl)ethylenediaminetriacetate (HEDTA)} by Cr^{VI} were studied under pseudo-first-order conditions with $[Co^{II}L^n] \gg [Cr^{VI}]$. The kinetics showed first-order dependence on $[Cr^{VI}]$. The rate constant, k_{obs}, decreases with increasing concentration of $[Cr^{VI}]$. At constant $[H^+]$, ionic strength, and temperature, the rate law is described by Eq. (i)
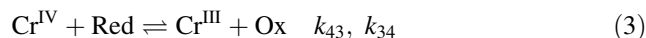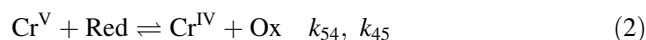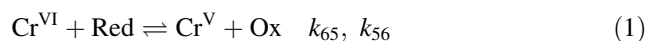
$$-d[Cr^{VI}]/dt = \left\{ k_2[Co^{II}L^n] + k_3[Co^{II}L^n]^2 \right\}[HCrO_4^-]$$
(i)

Both k_2 and k_3 showed acid-dependent and acid-independent pathways. The direct conversion $Co^{II}L^n$ to $Co^{III}L^m$ is ruled out by spectrophotometric and ESR spectroscopic measurements that showed the formation of initial reaction intermediate(s). The rate law is consistent with one-electron and concurrent two-electron transfers leading to the formation of Cr^V and Cr^{IV}, respectively. An inner-sphere process, at least for the first term, leading to the formation of a relatively stable Cr^V species is almost certain. The kinetic term showing second-order dependence on $[Co^{II}L^n]$, most likely, involves concurrent two-electron transfer leading to the formation of Cr^{IV}. The type of rate law and

the proposed mechanism, reported here, depart from the well-established rate laws observed and mechanisms proposed for the oxidation of one-electron reductants by Cr^{VI}.

Introduction

The oxidation of organic as well as inorganic compounds by Cr^{VI} has been a subject of long-standing interest. The mechanisms of these oxidations have been reviewed in detail by a number of investigators [1–5]. A general mechanism for the oxidation of one-electron reductants by Cr^{VI} has been proposed by King and co-workers [6, 7]. In this mechanism, a sequence of three one-electron transfer steps is involved in the reduction of Cr^{VI} to Cr^{III} as shown in Eqs. (1–3).

$$Cr^{VI} + Red \rightleftharpoons Cr^V + Ox \quad k_{65}, k_{56} \tag{1}$$

$$Cr^V + Red \rightleftharpoons Cr^{IV} + Ox \quad k_{54}, k_{45} \tag{2}$$

$$Cr^{IV} + Red \rightleftharpoons Cr^{III} + Ox \quad k_{43}, k_{34} \tag{3}$$

The general rate law is complicated and has been simplified by making assumptions: (i) A steady-state concentration of Cr^V intermediate exists and (ii) the rate of oxidation of Cr^{IV}–Cr^V is negligible.

With these assumptions, the general rate law is described by Eq. (4)

$$-d[Cr(VI)/dt] = \left(k_{65}k_{54}[Cr^{VI}][Red]^2 \right) \Big/ \left((k_{54}[Red] + k_{56}[Ox]) \right)$$
(4)

The complete form of the rate law has been observed in the oxidation of Np^{IV}–Np^V and in the oxidation of Fe^{II}–Fe^{III} [8, 9]. Limiting forms of the rate law have been

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observed in other studies. In the oxidation of V^{IV}–V^V, the rate law is given by Eq. (5) where inhibition by the product V^V was observed [10, 11]. This indicates that $k_{56} > k_{54}$.

$$-d[V(IV)]/dt = k_{54}K_{65}[Cr^{VI}][VO^{2+}]^2 \big/ [VO_2^+] \qquad (5)$$

The simple second-order rate of Eq. (6) has been observed with a number of reductants. These include $[Fe(phen)_3]^{2+}$ [7], V^{III} [12], $[Fe(bipy)_3]^{2+}$, $Fe(bipy)_2(CN)_2$, $[Fe(bipy)(CN)_4]^{2-}$, $[Fe(CN)_6]^{4-}$ [13], $[Ta_6Br_{12}]^{2+}$, and $[Ta_6Cl_{12}]^{2+}$ [14]. The kinetics of oxidation of $[Fe(CN)_6]^{4-}$ by Cr^{VI} are also reported to be retarded by the accumulation of the reaction product $[Fe(CN)_6]^{3-}$ and by its deliberate addition [15].

$$-d[Cr(VI)]/dt = k_{65}[Cr^{VI}][Red] \qquad (6)$$

In a previous report on the reaction between $Co^{II}L_1$ (L_1 = EDTA) and Cr^{VI}, it was claimed that both Cr^V and Cr^{IV} are formed. The formation of Cr^V was ascertained by ESR spectroscopy, but no direct or indirect evidence for the formation of Cr^{IV} was presented. It is claimed that Cr^V and Cr^{IV} are stabilized by L_1 [16]. There is no report in the literature on the isolation of Cr^V or Cr^{IV} by polyaminocarboxylates. In the oxidation of $Cr^{III}L_1$ by N-bromosuccinimide, however, the first product in the biphasic reaction is believed to be a $Cr^{IV} L_1$ species [17].

In this work, we report the kinetics of oxidation of Co^{II} complexes of the polyaminocarboxylate ligands, ethylenediaminetetraacetate (L_1), diethylenetriaminepentaacetate (L_2), and N-(2-hydroxyethyl)ethylenediaminetriacetate (L_3). It is shown in this report that both one-electron and concurrent two-electron processes are operative.

Experimental

Materials

The chemicals potassium dichromate (99.5% s.d. Fine-Chem), cobalt(II) nitrate hexahydrate, $Co(NO_3)_2 \cdot 6H_2O$, acetic acid, sodium acetate trihydrate, and perchloric acid were reagent grade (BDH) and were used as received. Ethylenediaminetetraacetate (L_1) (Sigma), diethylenetriaminepentaacetate (L_2) (GES), and N-(2-hydroxyethyl)ethylenediaminetriacetate (L_3) were used without further purification. Aqueous solutions of these chemicals were prepared by accurate weight. Fresh redistilled water was employed in all chemical preparations and experiments.

Chromium(VI) solution was prepared by dissolving a weighed amount of potassium dichromate in distilled water. Solutions of the complexes $Co^{II}L_1$, $Co^{II}L_2$, and $Co^{II}L_3$ were prepared by mixing solutions of L_1, L_2, and L_3 with a $Co(NO_3)_2.6H_2O$ solution of known concentration. For all three complexes, [ligand] was $1.2[Co^{II}]$ to ensure that virtually all Co^{II} was complexed by the ligands. Buffer solutions were prepared using acetic acid and sodium acetate solutions of known concentrations. A solution of $NaClO_4$ of known concentration was used to adjust ionic strength.

Instruments

UV–visible and pH measurements

The UV–visible absorption spectra of the reactions were measured using a Shimadzu spectrophotometer model 1800. The spectrophotometer was equipped with a thermostated cell holder. The pH of the reaction solution was measured using a Hanna pH meter model 211.

Kinetic procedures

The oxidations were carried out in an aqueous acidic medium. The pH was kept constant during the reaction using sodium acetate/acetic acid solutions of known concentrations. The ionic strength was maintained by adding sodium perchlorate solution of known concentration. The kinetic measurements for the oxidation of $[Co^{II}L^n]$ ($L = EDTA^{2-}$, $DTPA^{3-}$, or $HEDTA^-$) by Cr^{VI} were conducted under pseudo-first-order conditions, where $[Co^{II}L^n]$ was present in a large excess over $[Cr^{VI}]$ (more than tenfold). The course of the reaction was followed spectrophotometrically by recording the increase in absorbance of initial Co^{III} product at 550 nm as a function of time. The effects of various concentrations of the oxidant and complex, pH, and ionic strength on the rate of the reaction were investigated. At the completion of the kinetic runs, the solutions were examined spectrophotometrically. The values of the wavelength for the maximum absorbance and the molar absorption coefficient (ε) at the maxima were determined. By comparison with literature values, the ratio of ε at these maxima was used for the characterization of the products.

ESR measurements

ESR spectra were measured with an X-band ESR spectrometer (Bruker, EMX) at liquid nitrogen temperature (-60 °C) using a high sensitivity standard cylindrical resonator (ER 4119 HS) operating at 9.7 GHz. The ESR parameters were chosen to provide the maximum signal-to-noise ratio for non-distorted signals. Operating parameters for X-band ESR were as follows: power, 19.97 mW; modulation frequency, 100 kHz; modulation amplitude, 4.0 G; receiver gain, 5.02×10^4; conversion time, 81.92 ms; time constant, 20.48 ms; sweep time, 83.886 s;

center field, 3450 G; sweep width, 500 G; and number of scans, 4. All ESR measurements were taken using a reaction mixture of 6.0×10^{-3} M $Co^{II}L^n$ and 4.5×10^{-4} M of Cr^{VI}.

Results and discussion

The UV–visible absorption spectra of the initial products of the oxidation of $[Co^{II}L^n]$

The UV–Vis absorption spectra (over the 350–800 nm range) for the formation of the initial product of the oxidation were recorded as a function of time and are shown in Figs. 1, S1, and S2 (S indicates supplementary material).

The present study shows that the oxidation of $Co^{II}L^n$ by Cr^{VI} does not lead directly to the formation of $Co^{III}L^n$. In an earlier report of the oxidation of $Co^{II} L_1$ by Cr^{VI}, formation of Cr(V) and Cr(IV) has been proposed [16]. The ratio of the molar absorption coefficients (ε) at two maxima at the end of the oxidation reaction suggests that the final Co^{III} is not formed. In the literature, the ratio ($\varepsilon_{535}/\varepsilon_{382} = 322/230$ M^{-1} cm^{-1}) = 1.47 [18] is used to quantify the formation of $Co^{III}L_1$. However, the value of the ratio at these wavelengths after 10 days was 1.65. This shows that even after this long period of time the final product $Co^{III}L_1$ is not formed. In one experiment where $[Co^{II}L_1] = 2.4 \times 10^{-3}$ M and $[Cr^{VI}] = 9.95 \times 10^{-4}$ M at pH 3.40, the final absorbance at 534 nm was determined as 0.82 [16]. This value is higher than the calculated value of 0.77 calculated using the molar absorbance at this wavelength.
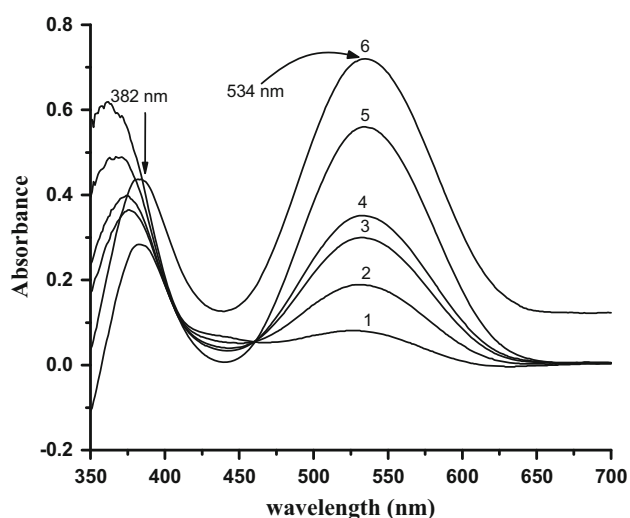
A similar behavior is shown in Figs. S1 and S2 where an increased reaction time caused a shift in the peak position and a decrease in the peak amplitude (below 400 nm) accompanied by an increase in peak amplitude (above 500 nm). This is consistent with the formation of an initial Co^{III} product which is very slowly converted to a final product.

The observation of isosbestic points (Figs. 1, S1, and S2) indicates the existence of species at equilibrium during the oxidation of $Co^{II}L^n$ by Cr^{VI}. For comparison, in one experiment H_2O_2 was used as an oxidant instead of Cr^{VI}, and no isosbestic point was observed, indicating the absence of species at equilibrium in this case. The final spectrum (curve 6) in each of the three figures does not pass through the isosbestic points.
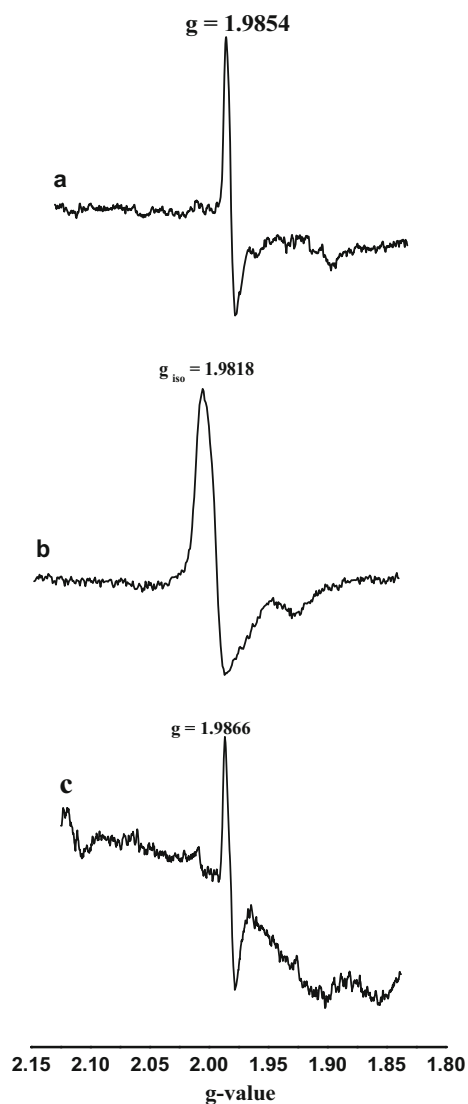
ESR of Cr^V species

Figure 2 shows the ESR spectra of the intermediates formed immediately after the initiation of the oxidation of $Co^{II}L^n$ by Cr^{VI}. The spectra are dominated by sharp single signals with the g-values 1.985, 1.982, and 1.987.

An ESR signal (g = 1.985) assigned to Cr^V species has already been reported [19]. The electronic configuration of Cr^V (d^1) makes it convenient for detection by ESR spectroscopy. Stabilization of Cr^V complexes is enhanced if a chelate ring is bonded to Cr^V [20]. Since in the present work the oxidation is not carried out in the presence of excess EDTA, the Cr^V species formed is not likely to be $Cr^V L_1$, but rather a Cr^V species coordinated to Co^{III} via an oxygen atom (L_1Co^{III}–O–Cr^V). In an earlier study, however, Cr^VL_1 is assumed to be formed in the oxidation of $Co^{II}L_1$ by Cr^{VI} [16]. The observation of a peak at 728 nm in the present study further supports the formation of a Cr^V species as it is the only absorbing species at 725 nm [21].

Variation of reaction rate with $[Cr^{VI}]$

Under pseudo-first-order conditions ($[Co^{II}L^n] \gg [Cr^{VI}]$), plots of $-\ln(A_\infty - A_t)$ versus time were found to be linear up to 90% of the reactions where A_∞ and A_t are absorbance values at infinity and time t, respectively. The values of pseudo-first-order constants (k_{obs}) were determined in each case from the slopes of the linear plots. It was found that the rate at which Cr^{VI} disappeared follows a first-order rate law. It was also observed (Tables 1, S1, and S2) that the values of k_{obs} decrease with increasing $[Cr^{VI}]_T$, i.e., initial gross Cr^{VI} concentration. This suggests that the acid chromate ion ($HCrO_4^-$) is probably the active oxidizing species. Such an observation in Cr^{VI} oxidation, which was first observed by Novick [22], has been reported by several other authors [23–25], and it was well explained by Wiberg [2]. The concentration of hydrogen chromate ion ($HCrO_4^-$)

Fig. 1 Change in absorbance as a function of time for the oxidation of $Co^{II}L_1$ by Cr^{VI}. The time periods are: (1) 20 min, (2) 30 min, (3) 40 min, (4) 1 h, (5) 2 h, and (6) 10 days

Fig. 2 X-band ESR spectrum of Cr^V intermediate complex formed immediately after the initiation of the oxidation of **a** $Co^{II}L_1$, **b** $Co^{II}L_2$, and **c** $Co^{II}L_3$ by Cr^{VI}, at −60 °C

may be calculated from Eq. (7) using $[Cr^{VI}]_T$ and the reported K_d value.

$$[HCrO_4^-] = \left\{ -1 + \left(1 + 4K_d[Cr^{VI}]_T\right)^{1/2} \right\} \Big/ 2K_d \qquad (7)$$

From Eq. (7), the ratio $[HCrO_4^-]/[Cr^{VI}]_T$ can be given by Eq. (8)

$$[HCrO_4^-]/[Cr^{VI}]_T = 2 \Big/ \left\{ 1 + \left(1 + 4K_d[Cr^{VI}]_T\right)^{1/2} \right\} \qquad (8)$$

It is clear from Eq. (8) that as $[Cr^{VI}]_T$ increases a progressively smaller portion of the total Cr^{VI} would be in $HCrO_4^-$ form. This explains the decreases in k_{obs} with increasing $[Cr^{VI}]_T$.

The plots of log $(k_{obs}[Cr^{VI}]_T)$ versus log $[HCrO_4^-]$ (Figs. 3, S3, and S4) gave straight lines with slopes equal to 0.42, 0.88, and 0.75 for each of the three complexes, respectively.
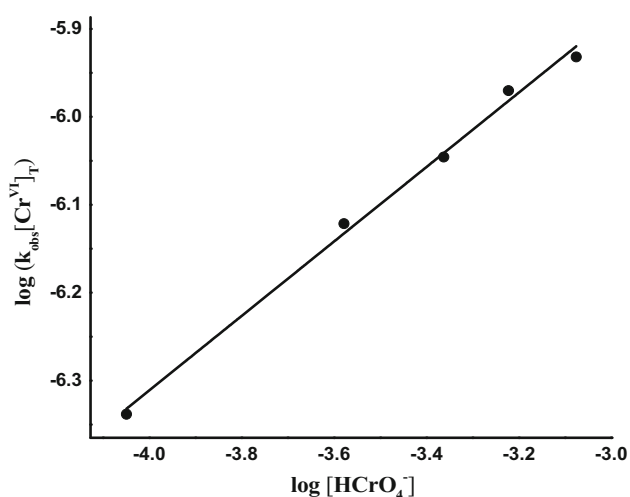
The rate of the reaction is given by Eq. (9), where $[Cr^{VI}]_T = [HCrO_4^-] + [Cr_2O_7^{2-}]$.

$$-d[Cr^{VI}]/dt = k_{obs}[Cr^{VI}]_T \qquad (9)$$

Data in Tables 1, S1, and S2 show that $k_{obs}[Cr^{VI}]_T/[HCrO_4^-]^{0.88}$, $k_{obs}[Cr^{VI}]_T/[HCrO_4^-]^{0.42}$, and $k_{obs}[Cr^{VI}]_T/[HCrO_4^-]^{0.75}$ are constants ($=k_{corrected}$). From these relations, $k_{obs}[Cr^{VI}]_T$ is equal to $k_{corr}[HCrO_4^-]^{0.88}$, $k_{corr}[HCrO_4^-]^{0.42}$, and $k_{corr}[HCrO_4^-]^{0.75}$, respectively. By substituting for $k_{obs}[Cr^{VI}]_T$ in Eq. (9), the rate is given by Eq. (10), which shows that the rate is proportional to $[HCrO_4^-]^m$, where m = 0.88, 0.42, or 0.75 for the oxidation of $Co^{II}L_1$, $Co^{II}L_2$, and $Co^{II}L_3$, respectively.

$$-d[Cr^{VI}]/dt = k_{cor}[HCrO_4^-] \qquad (10)$$

In the literature, the rate of oxidation of certain organic compounds by Cr^{VI} is reported to be proportional to $[HCrO_4^-]^X$. Thus, in the oxidation of α-hydroxy-iso-butyric acid by Cr^{VI} the rate was found to be proportional to $[HCrO_4^-]^{0.33}$ and varies as $[HCrO4^-]^{0.65}$ in the oxidation of oxalic acid [23, 26]. It is not obvious why the exponents vary with variation of the reductant. The fraction does not represent the order with respect to $[HCrO_4^-]$. In the present study, Eq. (10) shows that the rates of oxidation of $Co^{II}L^n$ complexes by Cr^{VI} are proportional to $[HCrO_4^-]$. It is well known that at very low concentration of dichromate solution, $[Cr^{VI}]_T \leq 4.0 \times 10^{-3}$ M, Cr^{VI} exists almost exclusively as $[HCrO_4^-]$ [27]. For this reason, in many studies of Cr^{VI} oxidations, its concentration was kept purposely very low to avoid the possibility of more complex rate

Table 1 Variation of k_{obs} with $[Cr^{VI}]$, for the oxidation of $[Co^{II}L_2]$ by $[Cr^{VI}]$, at $[Co^{II}L_2] = 6.00 \times 10^{-3}$ M, pH = 3.60, $\mu = 0.12$ M (acetate), and T = 25.0 °C

$10^4[Cr^{VI}]$ (M)	$10^3 k_{obs}$ (s^{-1})	$10^4[HCrO_4^-]$ (M)	$10^2 \dfrac{[HCrO_4^-]}{[Cr^{VI}]}$	$10^2 \dfrac{k_{obs}[Cr^{VI}]_T}{[HCrO_4^-]^{0.88}}$ (s^{-1})
5.46	2.77 ± 0.04	5.36	98.1	1.14
4.29	2.95 ± 0.03	4.23	98.5	1.18
1.95	3.39 ± 0.03	1.94	99.3	1.22
0.78	3.59 ± 0.04	0.76	99.7	1.16
0.39	3.88 ± 0.03	0.38	99.9	1.15

Fig. 3 Dependence of $\log (k_{obs}[Cr^{VI}]_T)$ on $\log[HCrO_4^-]$, for the oxidation of $[Co^{II}L_1]$ by $[Cr^{VI}]$, at $[Co^{II}L_1] = 9.60 \times 10^{-3}$ mol dm^{-3}, pH = 3.60, $\mu = 0.16$ mol dm^{-3} (acetate), and T = 25.0 °C

laws. It should be mentioned, however, that the fractional exponents to which the $[HCrO_4^-]$ is raised are not the order with respect to this species.

An alternative approach to the issue of the variation of k_{obs} with the initial $[Cr^{VI}]$ is to plot $1/k_{obs}$ versus $[Cr^{VI}]$. The results in Tables 1, S1, and S2 show that an inverse proportionality exists between k_{obs} and $[Cr^{VI}]$. These plots are linear with the intercept of each of the plots which gives the value of $1/k_{obs}$ at infinite dilution, namely when all the Cr^{VI} exists as the monomer $HCrO_4^-$. The reciprocal of the intercepts is in agreement with the values of k_{obs} at the lowest $[Cr^{VI}]$ used.

Dependence of reaction rate on $[Co^{II}L^n]$

In the oxidation of $Co^{II}L^n$ by Cr^{VI}, the variation in the rate constant with increasing complex concentration was investigated at constant reaction conditions. The results in Tables 2, 3S, and 4S show that the value of the observed rate constant, k_{obs}, increases nonlinearly with increasing concentration of $[Co^{II}L^n]$.

At constant reaction conditions, the dependence of k_{obs} on $[Co^{II}L_1]$ was found to fit a plot of k_{obs} versus $[Co^{II}L^n]$ using a polynomial fit of the second degree as shown in Figs. 4, S5, and S6.

The dependence of k_{obs} on $[Co^{II}L^n]$ is thus described by Eq. (11)

$$k_{obs} = k_2\left[Co^{II}L^n\right] + k_3\left[Co^{II}L^n\right]^2 \tag{11}$$

The rate law shows first- and second-order dependence on $[Co^{II}L^n]$. The plot of $k_{obs}/[Co^{II}L_1]$ versus $[Co^{II}L_1]$ was found to be linear with both intercept and slope (Fig. 5).

Effect of [H$^+$] on reaction rate

The results in Tables 2, 3S, and 4S show that for the oxidation of $Co^{II}L^n$ by Cr^{VI} the value of k_{obs} increased with increasing $[H^+]$. The effect of pH on the values of k_2 and k_3 was investigated by increasing $[Co^{II}L^n]$ and keeping all other variables constant at various pH values.

The results in Tables 3, 5S, and 6S show that both k_2 and k_3 increased with increasing $[H^+]$.

Plots of both k_2 and k_3 versus $[H^+]$ were found to be linear, each with an intercept (I_1 and I_2) and a slope (S_1 and S_2), respectively, as shown in Figs. 5 and 6 for the oxidation of $Co^{II}L_1$. Similar plots were found in the variation of k_2 and k_3 in oxidation of $Co^{II}L_2$ and $Co^{II}L_3$ and are shown in Figs. S7, S8, S9, and S10.

The dependences of k_1 and k_2 on $[H^+]$ are described by Eqs. (12) and (13), respectively.

$$k_2 = I_1 + S_1[H^+] \tag{12}$$

$$k_3 = I_2 + S_2[H^+] \tag{13}$$

By substituting for the values of k_2 and k_3 in Eq. (11), k_{obs} is given by Eq. (14)

$$k_{obs} = (I_1 + S_1[H^+])[Co^{II}L^n] + (I_2 + S_2[H^+])[Co^{II}L^n]^2 \tag{14}$$

From Eqs. (11) and (14), the experimental rate law for the oxidation of each of the three complexes $[Co^{II}L^n]$ by Cr^{VI} is given by Eq. (15)

$$-d[Cr^{VI}]/dt = \{ (I_1 + S_1[H^+])[Co^{II}L^n] + (I_2 + S_2[H^+])[Co^{II}L^n]^2\} \left[HCrO_4^-\right] \tag{15}$$

Generally, oxidations by Cr^{VI} are acid dependent and are accompanied by the transformation of $HCrO_4^-$ to $[Cr(H_2O)_6]^{3+}$, and this process consumes hydrogen ions. This can partially explain the increase in the rate with increasing $[H^+]$. It is also well documented that the Cr^{VI} reduction potential is relatively high in acidic media compared with neutral and basic media. Edwards has summarized observations on a large number of oxoanion reactions, noting that the rates of such reactions are usually accelerated by increasing $[H^+]$ [28].

The effect of ionic strength

The oxidation of $Co^{II}L^n$ by Cr^{VI} was investigated as a function of ionic strength (μ) at constant reaction conditions. The results in Table 4 show that k_{obs} increases with increasing the ionic strength.

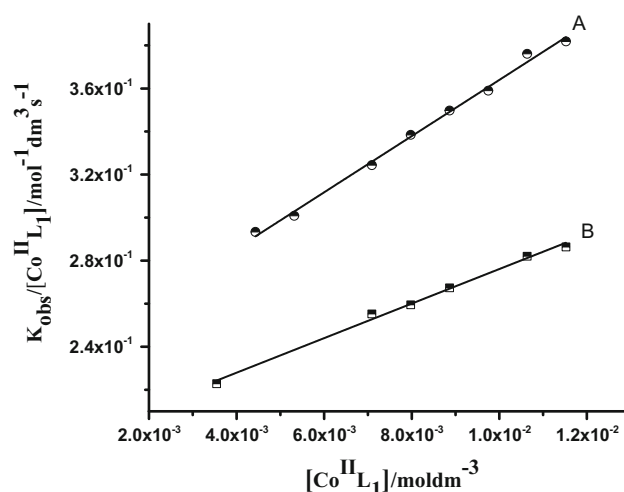Plots of $\log k_{obs}$ versus $\mu^{1/2}/(1 + \mu^{1/2})$ were found to be linear as shown in Fig. 7.

Table 2 Variation of k_{obs} with [Co^{II}L$_1$] for the oxidation of Co^{II}L$_1$ by Cr^{VI} at different pH values. Conditions: [Cr^{VI}] = 1.78 × 10^{-4} mol dm^{-3}, μ = 0.16 mol dm^{-3}, and T = 25.0 °C

10^3[Co^{II}L$_1$] (M)	$10^3 k_{obs}$/ s^{-1} at various pH values				
	4.18	3.97	3.67	3.50	3.38
11.50	3.30 ± 0.02	4.46 ± 0.05	–	7.83 ± 0.06	9.69 ± 0.09
10.65	2.98 ± 0.04	3.98 ± 0.06	6.41 ± 0.09	7.10 ± 0.03	8.51 ± 0.06
9.75	2.69 ± 0.03	3.55 ± 0.05	5.60 ± 0.05	6.40 ± 0.03	8.06 ± 0.09
8.85	2.38 ± 0.01	3.09 ± 0.04	5.23 ± 0.05	5.59 ± 0.05	6.87 ± 0.09
8.00	2.01 ± 0.01	2.68 ± 0.03	4.36 ± 0.05	5.37 ± 0.03	5.76 ± 0.09
7.10	1.78 ± 0.02	2.28 ± 0.02	3.48 ± 0.07	4.27 ± 0.04	5.37 ± 0.08
6.20	1.49 ± 0.01	1.84 ± 0.05	2.79 ± 0.05	3.41 ± 0.02	–
5.30	–	1.61 ± 0.00	2.35 ± 0.02	2.83 ± 0.02	3.50 ± 0.03
4.43	1.05 ± 0.01	1.29 ± 0.00	1.75 ± 0.01	2.22 ± 0.01	2.80 ± 0.03
3.55	0.80 ± 0.01	0.97 ± 0.00	1.43 ± 0.02	1.79 ± 0.02	2.00 ± 0.02
2.66	0.52 ± 0.01	–	1.03 ± 0.03	1.26 ± 0.01	1.42 ± 0.01
1.78	0.35 ± 0.01	0.45 ± 0.00	0.65 ± 0.03	–	0.87 ± 0.01
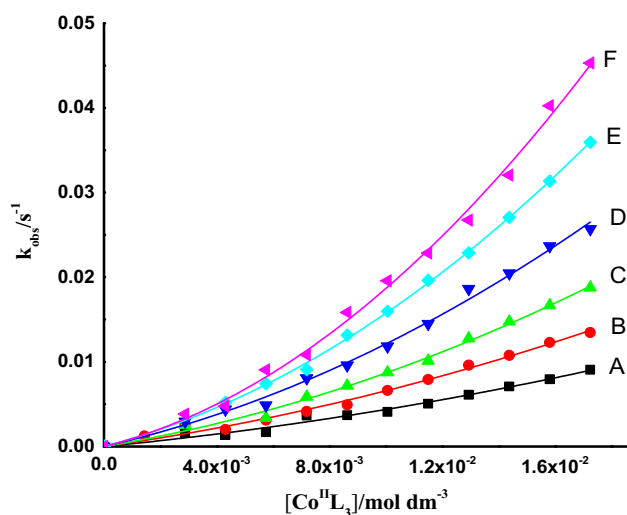
Fig. 4 Variation of k_{obs} with [Co^{II}L$_3$], for the oxidation of Co^{II}L$_3$ by Cr^{VI}, at six different pH values: A 4.33, B 4.13, C 3.82, D 3.55, E 3.45, F 3.33. Conditions: [Cr^{VI}] = 2.88 × 10^{-4} mol dm^{-3}, μ = 0.16 mol dm^{-3}, and T = 25.0 °C

Fig. 5 Variation of k_{obs} /[Co^{II}L$_1$] with [Co^{II}L$_1$] for the oxidation of Co^{II}L$_1$ by Cr^{VI} at Co^{II}L$_1$ = (12.00 − 4.00) × 10^{-3} mol dm^{-3}, [Cr^{VI}] = 1.78 × 10^{-4} mol dm^{-3}, μ = 0.16 mol dm^{-3}, T = 25.0 °C, and A pH = 3.97, B pH = 4.18

The increase in k_{obs} with increasing ionic strength is consistent with positive Bronsted–Debye salt effect, implying that the activated complex is composed of reactants of like charges (Fig. 8). Disagreement between the value of the slope and the product of charges ($Z_A Z_B$) was observed in all three cases. The failure to obtain the expected slope according to this law can be explained partially by considering the dimerization constant (K_d), which increases with μ. Increasing μ will favor the formation of Cr$_2$O$_7^{2-}$, and this will cause the equilibrium (2HCrO$_4^-$ ⇌ Cr$_2$O$_7^{2-}$ + H$_2$O) to shift toward Cr$_2$O$_7^{2-}$. Thus, an increase in μ decreases the rate of the reaction [29]. For this reason, it is recommended that oxidations by Cr^{VI} should always be performed at constant μ, to avoid such a conflict.

Table 3 Values of k_2 and k_3 at various [H$^+$] obtained from plots of k_{obs} versus [Co^{II}L$_2$]

10^4 [H$^+$], M	$10\ k_2$, M^{-1} s^{-1}	k_3, M^{-2} s^{-1}
10.50	5.56 ± 0.30	18.74 ± 0.21
4.17	2.50 ± 0.02	7.58 ± 0.82
2.80	2.09 ± 0.06	5.88 ± 0.32
2.14	1.68 ± 0.01	4.74 ± 0.40
1.07	1.13 ± 0.00	3.50 ± 0.65
0.66	0.97 ± 0.03	2.01 ± 0.16

A mechanism for the oxidation of Co^{II}L^n by Cr^{VI} consistent with the rate law may be described by Scheme 1. From Scheme 1, the rate law in Eq. (24) can be derived
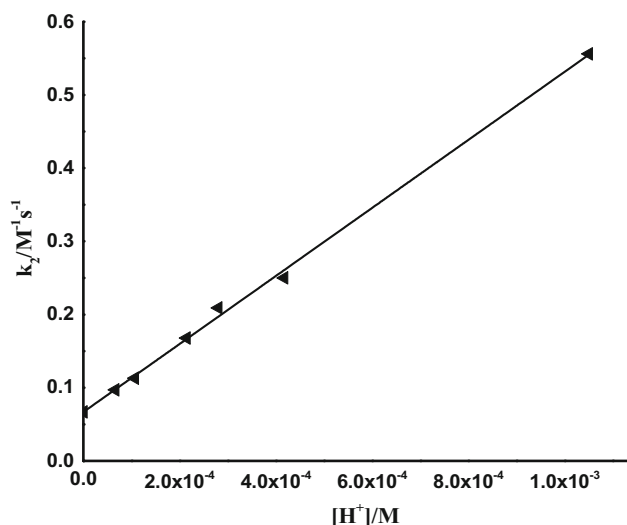
Fig. 6 Dependence of k_2 on [H$^+$] at 25 °C for the oxidation of Co^{II}L$_1$ by Cr^{VI}

Table 4 Variation of k_{obs} with ionic strength (μ) for the oxidation of Co^{II}L^n by Cr^{VI}, at [Co^{II}L$_3$] = 5.75 × 10^{-3} mol dm^{-3}, [Co^{II}L$_2$] = 6.65 × 10^{-3} mol dm^{-3}, [Co^{II}L$_1$] = 1.75 × 10^{-2} mol dm^{-3}, [Cr^{VI}] = 3.21 × 10^{-4} mol dm^{-3}, pH = 3.36, and T = 25.0 °C

μ, M	[Co^{II}L$_1$] 10^3 k_{obs}	[Co^{II}L$_2$] 10^3 k_{obs}	[Co^{II}L$_3$] 10^3 k_{obs}
0.29	2.06 ± 0.02	1.28 ± 0.02	2.81 ± 0.02
0.41	2.29 ± 0.02	1.46 ± 0.02	3.05 ± 0.02
0.61	2.59 ± 0.04	1.71 ± 0.03	3.38 ± 0.04
1.02	3.10 ± 0.03	2.21 ± 0.04	4.02 ± 0.03
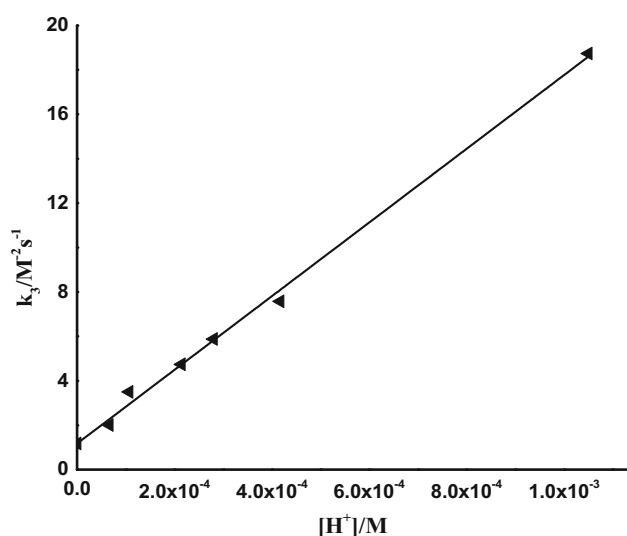
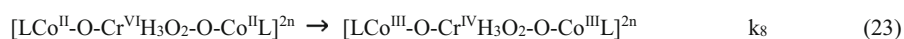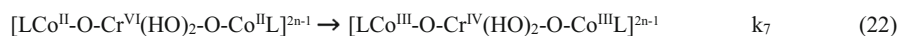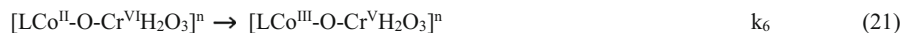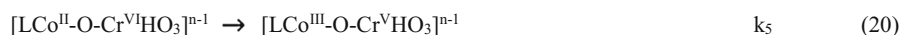**Fig. 7** Dependence of k_3 on [H$^+$] at 25 °C for the oxidation of Co^{II}L$_1$ by Cr^{VI}
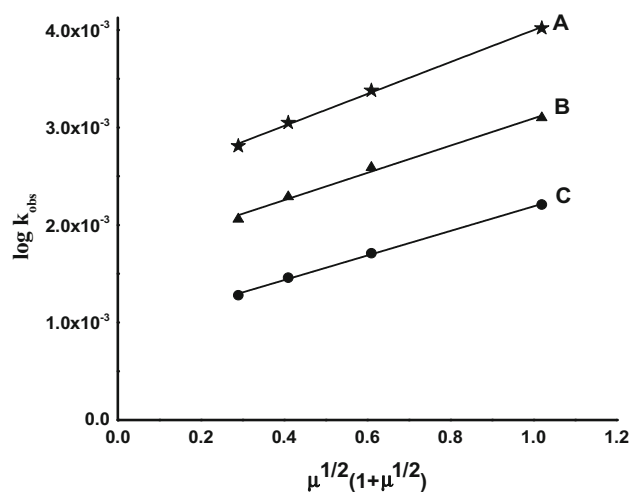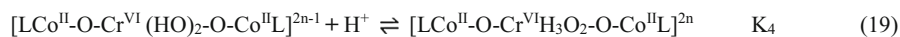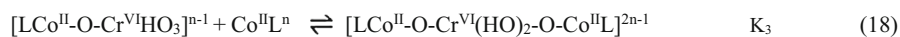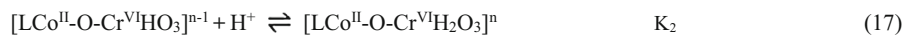

Fig. 8 Plots of logk_{obs} versus $\mu^{1/2}/(1 + \mu^{1/2})$ for the oxidation of A Co^{II}L$_3$, B Co^{II}L$_1$, and C Co^{II}L$_2$ by Cr^{VI}

$$-d[Cr^{VI}]/dt = \{(k_9 K_1 + k_{10} K_1 K_2 [H^+])[Co^{II}L^n] \\ + (k_{11} K_1 K_3 \\ + k_{12} K_1 K_3 K_{14} [H^+])[Co^{II}L^n]\}[HCrO_4^-] \quad (24)$$

From Eqs. (15) and (24), it can be seen that I1 = k5K1, S1 = k6K1k2, I2 = k7K1K3, S2 = k8K3K4. The derived rate law has the same form as the experimental one shown in Eq. (15).

In Eq. (16) of Scheme 1, it is proposed that HCrO$_4^-$ bonds to Co^{II} by an oxo group. The Co^{II}–Cr^{VI} species seems to undergo inner-sphere electron transfer which is either proton assisted [Eq. (21)] or not [Eq. (20)]. The existence of a pathway showing a second-order dependence on [Co^{II}L]^n necessitates the formation of Co^{II}–Cr^{VI} prior to attack by a second Co^{II}L^n species. It is well documented that termolecular reactions are very slow, and thus, it is very unlikely that two Co^{II}L^n species would simultaneously react with Cr^{VI}. Inner-sphere electron transfer may operate, following the bridging of a second Co^{II}L^{2-} ion, with concurrent two-electron transfer and the formation of a stabilized Cr^{IV} species. This electron transfer is also either proton assisted [Eq. (23)] or not [Eq. (22)]. The ESR detection of Cr^V species lends support to this mechanism. It has been noticed earlier that reactions of Cr^{VI} proceeding through Cr^V are those in which the primary reducing agent is an ion that can provide one electron such as V^{III} and Fe^{II} [27]. It is unfortunate that Cr^{IV} is ESR silent and its formation is not certain. An outer-sphere mechanism in the step involving the oxidation of two Co^{II} cannot be ruled out. This is shown in Scheme 2. A reaction pathway in which both inner- and outer-sphere electron transfers occur simultaneously is depicted in Eqs. (16)–(21) and Eqs. (25) and (26).

Scheme 1 Both the one- and the two-electron transfer reaction proceed by an inner-sphere mechanism

$$Co^{II}L^n + HCrO_4^- \rightleftharpoons [LCo^{II}\text{-}O\text{-}Cr^{VI}HO_3]^{n-1} \qquad K_1 \qquad (16)$$

$$[LCo^{II}\text{-}O\text{-}Cr^{VI}HO_3]^{n-1} + H^+ \rightleftharpoons [LCo^{II}\text{-}O\text{-}Cr^{VI}H_2O_3]^n \qquad K_2 \qquad (17)$$

$$[LCo^{II}\text{-}O\text{-}Cr^{VI}HO_3]^{n-1} + Co^{II}L^n \rightleftharpoons [LCo^{II}\text{-}O\text{-}Cr^{VI}(HO)_2\text{-}O\text{-}Co^{II}L]^{2n-1} \qquad K_3 \qquad (18)$$

$$[LCo^{II}\text{-}O\text{-}Cr^{VI}(HO)_2\text{-}O\text{-}Co^{II}L]^{2n-1} + H^+ \rightleftharpoons [LCo^{II}\text{-}O\text{-}Cr^{VI}H_3O_2\text{-}O\text{-}Co^{II}L]^{2n} \qquad K_4 \qquad (19)$$

$$[LCo^{II}\text{-}O\text{-}Cr^{VI}HO_3]^{n-1} \rightarrow [LCo^{III}\text{-}O\text{-}Cr^V HO_3]^{n-1} \qquad k_5 \qquad (20)$$

$$[LCo^{II}\text{-}O\text{-}Cr^{VI}H_2O_3]^n \rightarrow [LCo^{III}\text{-}O\text{-}Cr^V H_2O_3]^n \qquad k_6 \qquad (21)$$

$$[LCo^{II}\text{-}O\text{-}Cr^{VI}(HO)_2\text{-}O\text{-}Co^{II}L]^{2n-1} \rightarrow [LCo^{III}\text{-}O\text{-}Cr^{IV}(HO)_2\text{-}O\text{-}Co^{III}L]^{2n-1} \qquad k_7 \qquad (22)$$

$$[LCo^{II}\text{-}O\text{-}Cr^{VI}H_3O_2\text{-}O\text{-}Co^{II}L]^{2n} \rightarrow [LCo^{III}\text{-}O\text{-}Cr^{IV}H_3O_2\text{-}O\text{-}Co^{III}L]^{2n} \qquad k_8 \qquad (23)$$

Scheme 2 The one-electron transfer step proceeds by inner-sphere process and the two-electron process shows mixed inner-and outer-sphere mechanisms

$$[LCo^{II}\text{-}O\text{-}Cr^{VI}HO_3]^{n-1} + Co^{II}L^n \rightarrow [LCo^{III}\text{-}O\text{-}Cr^{IV}HO_3]^{n-1} + Co^{III}L^n \qquad k_9 \qquad (25)$$

$$[LCo^{II}\text{-}O\text{-}Cr^{VI}HO_3]^{n-1} + Co^{II}L^n + H^+ \rightarrow [LCo^{III}\text{-}O\text{-}Cr^{IV}H_2O_3]^n + Co^{III}L^n \qquad k_{10} \qquad (26)$$

A rate law having the same form as that given by Eq. (16) can be derived from Scheme 2.

$$\begin{aligned} -d[Cr^{VI}]/dt = &\{ (k_9 K_1 + k_{10}K_1 K_2[H^+])[Co^{II}L^n] \\ &+ (k_{11}K_1 K_3 \\ &+ k_{12}K_1 K_3 K_4[H^+])[Co^{II}L^n]^2 \}[HCrO_4^-] \end{aligned}$$
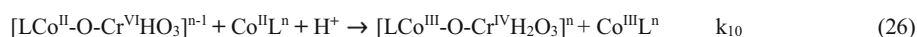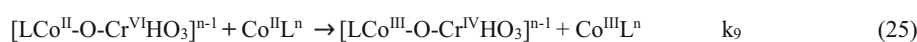(27)

The rate laws derived from Schemes 1 and 2 are similar to that obtained experimentally in Eq. (15). In the literature, a rate law with a term independent of [H$^+$] in oxidations by Cr^{VI} is very rare. It was observed in the oxidation of 2-deoxy-D-ribose [30], D- and L-rhamnose [31], and V^{IV} [27]. The path independent of [H$^+$] arises because of the low redox potential of Co^{III}/Co^{II} couple of the polyaminocarboxlate complexes. The formation of relatively stable Cr^{IV} and Cr^V complexes during reduction of Cr^{VI} has been observed earlier in a number of investigations [17, 19].

Conclusion

The oxidation of Co^{II}L^n complexes by Cr^{VI} does not lead directly to the formation of Co^{III}L^n. This is confirmed by the absorption spectra of the initial products as a function of time. The formation of Cr^V species is confirmed by ESR spectroscopy. The rate law of oxidation of the three Co^{II}L^n complexes by Cr^{VI} showed the same kinetic behavior. Evidence that supports the proposed mechanism included kinetic results, the ratio of the molar absorbance at the two maxima of Co^{III}L^n, the presence of isosbestic points, the existence of Cr^V species, and the observation of a peak at 728 nm.

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