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Kinetics and mechanism of the oxidation of L-ascorbic acid by *cis*-diaqua cobalt(III) ammine complexes

Kamaluddin Abdur-Rashid,[a] Tara P. Dasgupta *[,a] and John Burgess[b]

[a] *Department of Chemistry, University of the West Indies, Kingston 7, Jamaica, West Indies*
[b] *Department of Chemistry, University of Leicester, Leicester LE1 7RH, UK*

The kinetics of oxidation of L-ascorbic acid by *cis*-diaquacobalt(III) complexes, $[CoL_4(H_2O)_2]^{3+}$ (L_4 = $(NH_3)_4$, $(en)_2$ or tren; en = ethane-1,2-diamine, tren = tris(2-aminoethyl)amine] was studied as a fuction of pH, L-ascorbic acid concentration, temperature, ionic strength and methanol content of the solvent using stopped-flow and conventional spectrophotometry. The results indicated that only the ascorbate monoanion, HA^-, is involved in the redox process with the cobalt(III) species. The rate constants for the $[Co(tren)(H_2O)_2]^{3+}$ and $[Co(tren)(H_2O)(OH)]^{2+}$ species (k_2 and k_5) are 0.26 ± 0.09 and 1.25 ± 0.03 dm^3 mol^{-1} s^{-1} respectively at 30 °C, and the corresponding activation parameters are $\Delta H_2^\ddagger = 124 \pm 9$ kJ mol^{-1}, $\Delta S_2^\ddagger = 137 \pm 30$ J K^{-1} mol^{-1} and $\Delta H_5^\ddagger = 82 \pm 2$ kJ mol^{-1}, $\Delta S_5^\ddagger = 26 \pm 6$ J K^{-1} mol^{-1}. The variations in the rate constants and thermodynamic parameters for the series of complexes is discussed. The Marcus cross-relationship for electron transfer has been applied to the redox process to confirm the outer-sphere mechanism and to estimate the self-exchange rate constant for the $[CoL_4(H_2O)(OH)]^{2+/+}$ couple.

Oxidation of the reduction functionality of L-ascorbic acid is its single most important reaction, producing a variety of chemical species depending on the nature of the solvent, the duration of the reaction and the strength of the oxidising agent. Much interest has been shown in the kinetics and mechanisms of metal-ion-catalysed oxidation by molecular oxygen,[1–5] primarily involving iron(III) and copper(II) complexes.[2–6] Electron-transfer reactions involving cobalt(III) complexes have been investigated and are still being paid a lot of attention because of the possibility of studying spin-multiplicity changes and ligand-reorganisation energies.[7–10] These studies are necessary in order to obtain thermodynamic and reactivity parameters for L-ascorbic acid, which are useful in understanding its role in biological systems, especially respiratory-related reactions. The kinetics of the oxidation of L-ascorbic acid by tetraamminediaquacobalt(III) in acidic aqueous solution has been reported by Martinez *et al.*[11] The proposed mechanism indicates that there is no significant difference in reactivity of the $[CoL_4(H_2O)_2]^{3+}$ and $[CoL_4(H_2O)(OH)]^{2+}$ ($L = NH_3$) species. We report here the kinetics and mechanism of the oxidation of L-ascorbic acid by *cis*-$[Co(NH_3)_4(H_2O)_2]^{3+}$ as well as the analogous ethylenediamine (en) and tris(2-aminoethyl)amine (tren) complexes over the range pH 3.8–5.8. The reduction of $[Co(NH_3)_4(H_2O)_2]^{3+}$ was also studied over the range pH 7.1–9.0.

Experimental

Materials

All chemicals were either Reagent or Analar grade. Distilled water was obtained from a Corning all-glass distillation unit. Deionised water was obtained by passing distilled water through a Milli-Q reagent grade water system (Millipore Corporation, Bedford, MA) and used to make up all solutions. Nitrogen was obtained from Jamaica Oxygen and Acetylene Limited. Lithium ascorbate stock solution (0.25 mol dm^{-3}) was prepared by partially neutralising ascorbic acid with the stoichiometric amount of lithium carbonate in nitrogen-purged deionised water. Dissolved carbon dioxide was removed by bubbling nitrogen through the solution. The ascorbate concentration was accurately determined by iodometric titration.

Preparation of complexes

cis-Tetraamminediaquacobalt(III) perchlorate, *cis*-aquabis(ethane-1,2-diamine)hydroxocobalt(III) dithionate and aquahydroxo[tris(2-aminoethyl)amine]cobalt(III) perchlorate were prepared as previously described.[12–14] The purity of the three complexes were determined from their absorption coefficients at the respective λ_{max} of their UV/VIS spectra in 0.12 mol dm^{-3} perchloric acid: $\varepsilon_{504} = 52$ (lit.,[13] = 53), $\varepsilon_{492} = 79$ (lit.,[13] = 78.5) and $\varepsilon_{512} = 110$ dm^3 mol^{-1} cm^{-1} (lit.,[14] = 110 dm^3 mol^{-1} cm^{-1}) respectively.

Stoichiometry

The stoichiometry of the reactions was determined by spectrophotometric titrations and cobalt(II) analysis using ammonium thiocyanate in acetone.[15]

Proton equilibrium constant for L-ascorbic acid in methanol–water

The first acid-dissociation constant for L-ascorbic acid in methanol–water mixtures was determined by pH titrations at 25 °C. In a typical titration 10 cm^3 of 0.01 mol dm^{-3} L-ascorbic acid in the cosolvent mixture, which was previously purged with nitrogen, was pipetted into a thermostatted container fitted with a rubber septum seal through which an electrode was passed. The solution was again purged with nitrogen for 20 min. Aliquots of a 0.02 mol dm^{-3} sodium hydroxide solution, containing the appropriate quantity of methanol, were injected into the L-ascorbic acid solution. The pK_a values were calculated using the equation pK_a = pH + log([H_2A]/[HA^-]) and making appropriate volume corrections.

Kinetic measurements

The reactions were studied using stopped-flow and conventional spectrophotometry as a function of the decrease in absorbance with time. All runs were done under pseudo-first-order conditions. The reactions were monitored at the λ_{max} for each complex at an ionic strength, I, of 0.5 mol dm^{-3} for the ammine complex, while I = 0.3 mol dm^{-3} was used for the en and tren complexes. This was necessary because the complexes react very slowly with acetate ions of the buffer. This was more significant for the en and tren complexes, the lower ionic strength ensured that this secondary reaction was relatively insignificant under the conditions. The supporting electrolyte used throughout this study was standard lithium perchlorate solution. The total ascorbate concentration, $[A]_T$, was in the range 0.01–0.05 mol dm^{-3}, while $3.7 \leqslant pH \leqslant 5.8$ using acetic acid–sodium acetate buffer and $20 \leqslant T \leqslant 40$ °C. The reduction of the ammine complex was also studied over the range pH 7.1–9.0.

For the reactions in methanol–water mixtures the methanol was present in the same concentration in both solutions so that no temperature or density changes would occur on mixing. Compositions are expressed as volume percent which refers to the volume before mixing, regardless of the contraction in volume on mixing. For example, mixing 30 cm^3 methanol with 70 cm^3 water gives '30% MeOH'. Each k_{obs} value cited is an average of at least two runs. The error in each k_{obs} value was less than 2%.

The previously reported literature values for the acid-dissociation constants of L-ascorbic acid[7–11,16–20] and the cobalt(III) complexes[11,13,14,21–27] at various temperatures and ionic strengths were used.

All pH measurements were obtained using an Orion Research Expandable Ion Analyser (model EA920) digital pH meter fitted with a Cole-Parmer combination electrode. The pH meter was calibrated using standard buffer solutions. The $[H^+]$ was computed from the pH by using the appropriate activity coefficient of H^+ at the particular temperature and ionic strength.[28]

Results and Discussion

Nature of the reactions

The reaction of the complexes with L-ascorbic acid is accompanied by a decrease in absorbance, culminating in the pink colouration of the respective cobalt(II) complexes. The results of cobalt(II) analysis following the reaction of $[Co(NH_3)_4(H_2O)_2]^{3+}$ with L-ascorbic acid indicate that the reaction occurs in a 1 : 2 ratio of ascorbate and complex.

The variation of k_{obs} with $[A]_T$ at pH 5.6 and 25 °C for the three complexes is shown in Table 1, showing that the reactions are first order with respect to $[A]_T$.

At $pH \leqslant 2$ the rate of the reactions was very slow, hence it was followed over the range pH 3.7–6 where it could be conveniently measured. The variation of k_{obs} with pH and temperature is shown in Tables 2, 3 and 4 for the ammine, en and tren complexes, respectively. The results indicate that k_{obs} increases with pH and temperature. Table 5 shows the variation of k_{obs} with pH for the oxidation of L-ascorbic acid by $[Co(NH_3)_4(H_2O)_2]^{3+}$ over the range pH 7.1–9.0. This shows that the rate of the reaction decreases with increasing pH over this range.

Mechanism

The pH dependence of the reactions can be attributed to the protonation equilibria of the L-ascorbic acid and the cobalt(III) complexes. Oxidation of L-ascorbic acid can occur by either a one- or two-electron process, eventually forming dehydroascorbic acid (A) as the first isolable product.[5] The mechanism for the reaction is illustrated in Scheme 1.

$$H_2A \overset{K_{a1}}{\rightleftharpoons} HA^- + H^+$$

$$HA^- \overset{K_{a2}}{\rightleftharpoons} A^{2-} + H^+$$

$$[CoL_4(H_2O)_2]^{3+} \overset{K_1}{\rightleftharpoons} [CoL_4(H_2O)(OH)]^{2+} + H^+$$

$$[CoL_4(H_2O)(OH)]^{2+} \overset{K_2}{\rightleftharpoons} [CoL_4(OH)_2]^+ + H^+$$

$$[CoL_4(H_2O)_2]^{3+} + H_2A \xrightarrow{k_1} Co^{II} + H_2A^{\bullet -}$$

$$[CoL_4(H_2O)_2]^{3+} + HA^- \xrightarrow{k_2} Co^{II} + HA^{\bullet}$$

$$[CoL_4(H_2O)_2]^{3+} + A^{2-} \xrightarrow{k_3} Co^{II} + A^{\bullet -}$$

$$[CoL_4(H_2O)(OH)]^{2+} + H_2A \xrightarrow{k_4} Co^{II} + H_2A^{\bullet -}$$

$$[CoL_4(H_2O)(OH)]^{2+} + HA^- \xrightarrow{k_5} Co^{II} + HA^{\bullet}$$

$$[CoL_4(H_2O)(OH)]^{2+} + A^{2-} \xrightarrow{k_6} Co^{II} + A^{\bullet -}$$

$$[CoL_4(OH)_2]^+ + H_2A \xrightarrow{k_7} Co^{II} + H_2A^{\bullet +}$$

$$[CoL_4(OH)_2]^+ + HA^- \xrightarrow{k_8} Co^{II} + HA^{\bullet}$$

$$[CoL_4(OH)_2]^+ + A^{2-} \xrightarrow{k_9} Co^{II} + A^{\bullet -}$$

$$[CoL_4(H_2O)_2]^{3+} + \text{radical} \xrightarrow{\text{fast}} Co^{II} + A + nH^+$$

$$[CoL_4(H_2O)(OH)]^{2+} + \text{radical} \xrightarrow{\text{fast}} Co^{II} + A + nH^+$$

$$[CoL_4(OH)_2]^+ + \text{radical} \xrightarrow{\text{fast}} Co^{II} + A + nH^+$$

Scheme 1

Our investigations in highly acidic media (pH < 2) indicate that the reactions are extremely slow, indicating negligible contribution from the undissociated ascorbic acid, H_2A. Hence, we can neglect the k_1, k_4 and k_7 terms in Scheme 1. At pH > 7

Table 1 Pseudo-first-order rate constants as a function of $[A]_T$ for the reaction of L-ascorbic acid with *cis*-diaquacobalt(III) complexes at pH 5.6 ± 0.1, 25.1 °C, initial [complex] = 1×10^{-3} mol dm^{-3} and $I = 0.3$ mol dm^{-3} ($LiClO_4$)

$[Co(NH_3)_4(H_2O)_2]^{3+}$ *		$[Co(en)_2(H_2O)_2]^{3+}$		$[Co(tren)(H_2O)_2]^{3+}$	
$10^2\ [A]_T$/ mol dm^{-3}	$10^2\ k_{obs}$/ s^{-1}	$10^2\ [A]_T$/ mol dm^{-3}	$10^2\ k_{obs}$/ s^{-1}	$10^2\ [A]_T$/ mol dm^{-3}	$10^2\ k_{obs}$/ s^{-1}
1.0	2.96	1.0	0.56	1.0	0.33
1.5	4.61	1.5	0.76	1.5	0.49
2.0	6.11	2.0	0.94	2.0	0.59
2.5	7.58	2.5	1.10	2.5	0.77
3.0	8.99	3.0	1.18	3.0	0.89
3.5	10.33	3.5	1.35	3.5	0.99
4.0	12.06	4.0	1.49	4.0	1.15
4.5	13.54	4.5	1.69	4.5	1.31
5.0	15.05	5.0	1.79	5.0	1.41

* $I = 0.5$ mol dm^{-3}.

Table 2 Pseudo-first-order rate constants as a function of temperature and pH for the reaction of L-ascorbic acid with $[Co(NH_3)_4(H_2O)_2]^{3+}$ at $[A]_T = 2.5 \times 10^{-2}$ mol dm^{-3}, initial [complex] = 1×10^{-3} mol dm^{-3} and $I = 0.5$ mol dm^{-3} ($LiClO_4$)

25.1 °C*		30.1 °C		35.0 °C		40.0 °C	
pH	$10^2\ k_{obs}$/s^{-1}	pH	$10^2\ k_{obs}$/s^{-1}	pH	$10^2\ k_{obs}$/s^{-1}	pH	$10^2\ k_{obs}$/s^{-1}
3.90	0.30	3.90	0.55	3.91	0.96	3.88	1.94
4.07	0.48	4.07	0.81	4.06	1.55	4.05	2.88
4.25	0.65	4.25	1.12	4.25	2.27	4.22	4.44
4.42	1.04	4.45	1.82	4.45	3.58	4.41	6.97
4.63	1.32	4.63	2.64	4.62	5.11	4.60	9.85
4.84	2.41	4.85	4.05	4.84	7.75	4.81	14.87
5.05	3.63	5.08	6.34	5.07	11.95	5.05	22.23
5.30	5.78	5.31	9.35	5.30	17.79	5.28	33.21
5.55	8.94	5.57	14.15	5.55	25.68	5.54	45.58

* $[A]_T = 3.0 \times 10^{-2}$ mol dm^{-3}.

Table 3 Pseudo-first-order rate constants as a function of temperature and pH for the reaction of L-ascorbic acid with $[Co(en)_2(H_2O)_2]^{3+}$ at $[A]_T = 5.0 \times 10^{-2}$ mol dm^{-3}, initial [complex] = 1.5×10^{-3} mol dm^{-3} and $I = 0.3$ mol dm^{-3} ($LiClO_4$)

20.1 °C*		25.1 °C		30.2 °C		35.0 °C	
pH	$10^3\ k_{obs}$/s^{-1}	pH	$10^3\ k_{obs}$/s^{-1}	pH	$10^3\ k_{obs}$/s^{-1}	pH	$10^3\ k_{obs}$/s^{-1}
4.26	1.32	4.13	0.61	4.10	2.40	4.09	4.29
4.43	1.54	4.32	0.69	4.23	2.95	4.23	5.75
4.62	1.92	4.53	1.10	4.39	4.10	4.38	7.26
4.80	2.34	4.72	1.44	4.59	5.68	4.58	10.25
5.02	3.33	4.95	2.12	4.78	7.64	4.76	14.48
5.25	4.46	5.19	3.13	5.00	10.66	4.98	21.28
5.50	6.71	5.43	4.48	5.23	15.90	5.21	28.27
5.77	10.32	5.69	7.99	5.47	24.06	5.46	42.47
				5.74	34.63	5.72	56.52

* $[A]_T = 3.0 \times 10^{-2}$ mol dm^{-3}.

Table 4 Pseudo-first-order rate constants as a function of temperature and pH for the reaction of L-ascorbic acid with $[Co(tren)(H_2O)_2]^{3+}$ at $[A]_T = 5.0 \times 10^{-2}$ mol dm^{-3}, initial [complex] = 1×10^{-3} mol dm^{-3} and $I = 0.3$ mol dm^{-3} ($LiClO_4$)

25.1 °C*		30.0 °C		35.0 °C		40.0 °C	
pH	$10^3\ k_{obs}$/s^{-1}	pH	$10^3\ k_{obs}$/s^{-1}	pH	$10^3\ k_{obs}$/s^{-1}	pH	$10^3\ k_{obs}$/s^{-1}
4.21	0.82	4.23	1.82	4.19	3.73	4.16	7.41
4.31	1.08	4.34	2.31	4.30	4.46	4.29	9.64
4.45	1.47	4.48	3.10	4.45	6.95	4.43	13.27
4.61	2.22	4.65	4.68	4.62	9.63	4.60	20.17
4.70	2.58	4.71	5.67	4.67	11.28	4.66	22.06
4.97	4.30	4.98	9.96	4.95	20.15	4.94	37.71
5.17	7.07	5.18	15.19	5.16	28.08	5.15	53.66
5.38	10.44	5.42	21.48	5.40	39.78	5.38	71.28
5.65	13.51	5.70	29.32	5.69	53.80	5.68	94.98

* $[A]_T = 3.0 \times 10^{-2}$ mol dm^{-3}.

Table 5 Pseudo-first-order rate constants for the reaction of L-ascorbic acid with $[Co(NH_3)_4(H_2O)_2]^{3+}$ at pH > 7, 25.1 °C, initial [complex] = 1×10^{-3} mol dm^{-3} and $[A]_T = 2.5 \times 10^{-2}$ mol dm^{-3}

pH	k_{obs}	pH	k_{obs}
7.26	0.62	8.26	0.28
7.42	0.58	8.45	0.23
7.62	0.52	8.66	0.18
7.82	0.45	8.86	0.14
7.99	0.40		

the data in Table 5 show that the rate of the reaction decreases with increasing pH, indicating that the contribution involving the A^{2-} species is negligible even at this relatively high pH. Hence, over the pH range of our investigation there would be no contribution from the k_3, k_6 and k_9 terms. At 25 °C the acid-dissociation constants for the ammine, en and tren complexes are 1.02×10^{-8}, 6.46×10^{-9} and 1.26×10^{-8} mol dm^{-3}, respectively. It can therefore be assumed that under our experimental conditions there would be no contributions from the terms involving the $[CoL_4(OH)_2]^+$ species. Based on these assumptions and deductions it can be concluded that the rates of the reactions are given by equation (1). Substituting for

$$\text{rate} = k_2[HA^-][CoL_4(H_2O)_2{}^{3+}] + k_5[HA^-][CoL_4(H_2O)(OH)^{2+}] \quad (1)$$

$[HA^-]$ and the cobalt(III) species based on the total ascorbate and complex concentrations and assuming that $[A^{2-}]$ and $[CoL_4(OH)_2{}^+]$ are negligible, expression (2) is derived. The

$$k_{obs} = \frac{k_2K_{a1}[H^+] + k_5K_{a1}K_1}{(K_{a1} + [H^+])(K_1 + [H^+])}[A]_T \quad (2)$$

stoichiometry of the reaction indicates that an overall two-electron transfer per ascorbate species occurs, indicating that reactions of ascorbate radicals are possibly involved. Equation (2) implies that the rate of the reaction is first order with respect to $[A]_T$ and should increase with an increase in pH,

Table 6 Summary of rate ($dm^3\ mol^{-1}\ s^{-1}$) and activation parameters for the oxidation of L-ascorbic acid by *cis*-diaqua- and aquahydroxo-cobalt(III) species

Complex	T/°C	$10\,k_2$	k_5	$\Delta H_2^{\ddagger}$/kJ mol^{-1}	$\Delta S_2^{\ddagger}$/J K^{-1} mol^{-1}	$\Delta H_5^{\ddagger}$/kJ mol^{-1}	$\Delta S_5^{\ddagger}$/J K^{-1} mol^{-1}
$L_4 = (NH_3)_4$	25	—	5.99 ± 0.16	—	—	82 ± 1	46 ± 2
	30	—	10.3 ± 0.2				
	35	—	18.1 ± 0.4				
	40	33 ± 19	30.7 ± 0.4				
$L_4 = (en)_2$	20	2.97 ± 0.16	0.61 ± 0.01	74 ± 14	−22 ± 47	80 ± 10	25 ± 34
	25	—	0.83 ± 0.03				
	30	6.73 ± 0.42	1.88 ± 0.02				
	35	14.5 ± 1.8	2.91 ± 0.08				
L_4 = tren	25	1.45 ± 0.63	0.68 ± 0.02	124 ± 9	137 ± 30	82 ± 2	26 ± 6
	30	2.62 ± 0.91	1.25 ± 0.03				
	35	7.08 ± 1.61	2.11 ± 0.05				
	40	16.0 ± 3.2	3.45 ± 0.09				

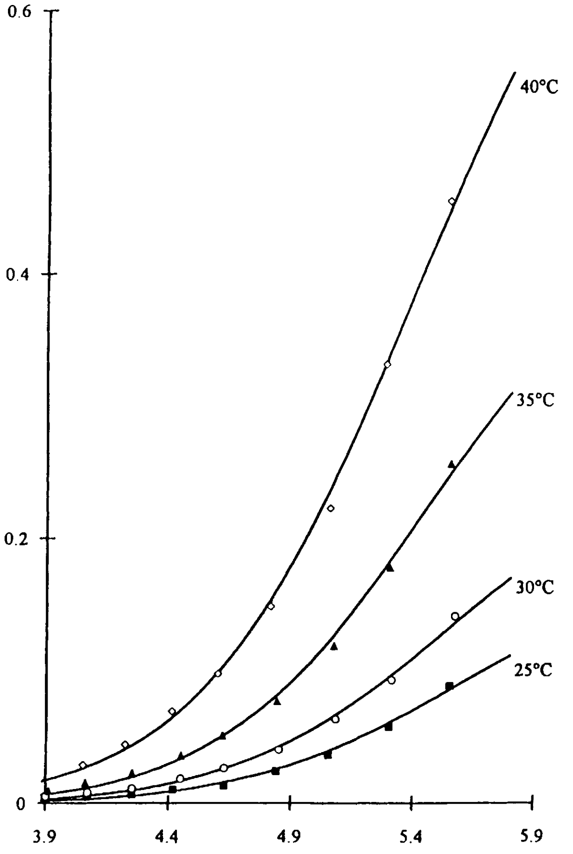

Fig. 1 Variation of k_{obs} with pH for the reaction of L-ascorbic acid with *cis*-$[Co(NH_3)_4(H_2O)_2]^{3+}$

Table 7 Acid dissociation constants for L-ascorbic acid in methanol–water mixtures at I = 0.5 mol dm^{-3} and 25 °C

Vol. % MeOH	pK_{a1}
5	4.00 ± 0.02
10	4.03 ± 0.02
15	4.04 ± 0.02
20	4.06 ± 0.02
30	4.21 ± 0.02
40	4.39 ± 0.02
80	5.7*

* At 20 °C, ref. 30.

reaching a maximum when the concentrations of both HA^- and $[CoL_4(H_2O)(OH)]^{2+}$ are highest. This is observed in Fig. 1. Beyond pH 7 a decrease in k_{obs} values has been observed (Table 5).

A non-linear regression analysis of the data in Tables 2–4 yields the values for k_2 and k_5 summarised in Table 6 for the three complexes. The rate parameters decrease in the order ammine > en > tren. This is a reflection of the steric contribution to the electron-transfer process, indicative of an outer-sphere mechanism, supported by the fact that the reactions occur on the stopped-flow time-scale and, hence, there should be no ligand substitution of the cobalt(III) complexes prior to electron transfer.[11] The rate parameter, k_8, for the reaction of $[Co(NH_3)_4(OH)_2]^+$ with HA^- was determined from a non-linear regression of the data in Table 5, using equation (2). The value is 1.99 ± 0.21 $dm^3\ mol^{-1}\ s^{-1}$. Comparing this value with those for $[Co(NH_3)_4(H_2O)_2]^{3+}$ and $[Co(NH_3)_4(H_2O)(OH)]^{2+}$, ≈0.29 and 5.99 $dm^3\ mol^{-1}\ s^{-1}$ respectively, reveals that the order of reactivity of the species is $[Co(NH_3)_4(H_2O)(OH)]^{2+}$ > $[Co(NH_3)_4(OH)_2]^+$ > $[Co(NH_3)_4(H_2O)_2]^{3+}$.

The increase in the rate constants with temperature can be quantified by using Eyring's absolute-rate expression[6] to calculate the activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. These are also listed in Table 6. The order of reactivity of the $[CoL_4(H_2O)_2]^{3+}$ species is related to the relative order of $\Delta H^{\ddagger}$, which increases with an increasing ligand bulk. The higher reactivity of $[CoL_4(H_2O)(OH)]^{2+}$ relative to the diaqua congeners is consistent with a lower $\Delta H^{\ddagger}$. There is no consistency with the $\Delta S^{\ddagger}$ values for both sets of species. However, for the $[Co(NH_3)_4(H_2O)(OH)]^{2+}$ ion, $\Delta S^{\ddagger}$ seems to determine the higher reactivity relative to the en and tren analogues.

Application of the Marcus cross-relationship

The self-exchange rate constant for the $[Co(NH_3)_4(H_2O)(OH)]^{2+/+}$ couple is not available in the literature but it can be calculated using Marcus theory,[29] which is useful for examining the free energy of activation for adiabatic outer-sphere electron-transfer reactions. According to Marcus theory, the excess free energy of activation for a cross-reaction (ΔG^*_{12}) varies with the standard free-energy change (ΔG°_{12}) for the reactions. The functional form of the Marcus cross-relationship is (3); ΔG^*_{12} can be calculated from

$$\Delta G^*_{12} = w_{12} + \{\lambda_{12}[1 + (\Delta G^{\circ\prime}_{12}/\lambda_{12})]^2\}/4 \qquad (3)$$

the rate constant of the reaction, k_{12}, using equation (4) where

$$k_{12} = Z\exp(-\Delta G^*_{12}/RT) \qquad (4)$$

Z is the collision frequency in solution and has a value of *ca.*

Table 8 Pseudo-first-order rate constants for the oxidation of L-ascorbic acid by *cis*-$[Co(NH_3)_4(H_2O)_2]^{3+}$ as a function of $[A]_T$ and methanol content at pH 5.6 ± 0.2, 25.1 °C, initial [complex] = 1×10^{-3} mol dm^{-3} and $I = 0.5$ mol dm^{-3} ($LiClO_4$)

10^2 $[A]_T$/mol dm^{-3}	10^2 k_{obs}/s^{-1} 10% MeOH	 20% MeOH	 30% MeOH	 40% MeOH
1.0	4.1	6.4	9.1	12.6
2.0	8.4	12.4	17.9	23.5
3.0	12.6	17.4	24.4	34.5
4.0	16.4	23.6	33.7	46.4
5.0	20.4	28.6	40.4	57.3

Table 9 Pseudo-first-order rate constants for the oxidation of L-ascorbic acid by $[Co(NH_3)(H_2O)_2]^{3+}$ as a function pH and methanol content at $[A]_T = 3.0 \times 10^{-2}$ mol dm^{-3}, initial [complex] = 1×10^{-3} mol dm^{-3} and $I = 0.5$ mol dm^{-3} ($LiClO_4$)

10% MeOH pH	 10^2 k_{obs}/s^{-1}	20% MeOH pH	 10^2 k_{obs}/s^{-1}	30% MeOH pH	 10^2 k_{obs}/s^{-1}
3.99	0.39	4.08	0.55	4.27	0.91
4.18	0.66	4.24	0.84	4.42	1.51
4.35	0.98	4.44	1.33	4.61	2.11
4.55	1.52	4.65	2.26	4.82	3.40
4.73	2.17	4.84	2.73	5.00	4.34
4.96	3.32	5.04	4.92	5.22	6.07
5.17	5.18	5.29	7.31	5.45	10.61
5.42	8.04	5.51	11.26	5.71	16.53
5.66	12.07	5.76	16.69	5.97	24.01

10^{11} dm^3 mol^{-1} s^{-1}. The reorientation parameter, λ_{12}, is defined by equation (5) where ΔG^*_{11} and ΔG^*_{22} refer to the self-

$$\lambda_{12} = 2(\Delta G^*_{11} - w_{11} + \Delta G^*_{22} - w_{22}) \qquad (5)$$

exchange reactions of the reagents and w_{11} and w_{22} represent the work terms involved in the reactions. The term $\Delta G^{\circ\prime}_{12}$ [equation (6)] is the free-energy change of the reaction for the

$$\Delta G^{\circ\prime}_{12} = \Delta G^{\circ}_{12} + w_{21} - w_{12} \qquad (6)$$

particular medium and temperature and w_{21} and w_{12} are the work terms required to bring the products or reactants together at the separation distance in the activated complex. The work term, w_{ij}, required to bring reactants to the contact distance σ ($= r_i + r_j$) is calculated from the Debye–Huckel interaction potential, allowing for ionic strength effects.[11] The interionic distance σ was calculated using the published values of 0.34 and 0.32 nm for the ionic radii of HA^- and $[Co(NH_3)_4(H_2O)(OH)]^{2+}$, respectively.[11,19] The value of ΔG°_{12} for the reaction was determined using the published values for the reduction potentials for the couples $HA^{\bullet}$–HA^- and $[Co(NH_3)_4(H_2O)(OH)]^{2+/+}$, 0.71 and 0.33 V respectively.[11] The self-exchange rate constant for the HA^-–$HA^{\bullet}$ couple was previously reported[11] to be 1.6×10^5 dm^3 mol^{-1} s^{-1}. That for the $[Co(NH_3)_4(H_2O)(OH)]^{2+/+}$ couple, using the rate constant determined in this study (k_5), is 170 dm^3 mol^{-1} s^{-1}. The reported value[11] for the $[Co(NH_3)_4(H_2O)_2]^{3+/2+}$ couple is 1.6×10^{-4} dm^3 mol^{-1} s^{-1} which is much less than that for its conjugate base. This could be due to the lower charge of the latter, which would result in lower work and reorientation energy terms which include contributions from solvent reorientation and inner-sphere changes in bond lengths and angles in the activated state.

Martinez *et al.*[11] concluded correctly that the contribution to the redox process from the $[Co(NH_3)_4(H_2O)(OH)]^{2+}$ ion is negligible over the pH range of their study. However, their conclusion that the diaqua species is more reactive than the aquahydroxo species is not in agreement with our work which covers a more extensive $[H^+]$ range, or the work of Tsukahara *et al.*[8] with diaqua tetradentate macrocyclic complexes.

Effect of methanol content of the solvent

The first acid-dissociation constant of L-ascorbic acid as a function of the methanol content of the solvent was determined by the above-mentioned method and is listed in Table 7. This shows a decrease in the dissociation constant with increasing methanol content which is consistent with the change in medium. The previously published[30] value of 5.7 for pK_{a1} in 80% methanol at 20 °C is also included for comparison.

The spectral changes and stoichiometry are similar to those observed for the aqueous medium, implying that the same mechanism is involved. Kinetic studies in mixed solvents were done under similar conditions of ionic strength, pH and $[A]_T$ as those in the purely aqueous medium and the results are shown in Tables 8–13. A plot of k_{obs} *versus* $[A]_T$ for the reaction of the cobalt(III) complexes in methanol–water mixtures shows a slight intercept which increases with increasing methanol content. This is due to a slow reaction of the complexes with acetate ions of the buffer. A detailed study was reported by Bhattacharya *et al.*[31] which focused on the kinetics, mechanism and solvent effects on the reaction of $[Co(NH_3)_4(H_2O)_2]^{3+}$ with acetate. The rate constant for this reaction at 25 °C is 2.0×10^{-5} dm^3 mol^{-1} s^{-1}.

The rate parameters, k_5, for the reduction of the cobalt(III) complexes in methanol–water were obtained from a non-linear regression analysis of the data in Tables 9, 11 and 13 for the NH_3, en and tren complexes, respectively, using equation (2). These are summarised in Table 14 and indicate that the rate constant increases with increasing methanol content of the solvent. This variation can be analysed into initial- and transition-state contributions[32–38] by determining $\delta_m \Delta G^{\ddagger}$ for each solvent composition and combining these values with the transfer chemical potentials of the complexes[39,40] and ascorbate ion so as to determine the transfer parameters of the transition states, using relationship (7), where δ_m is the solvent

$$\delta_m \mu^{\ddagger} = \delta_m \Delta G^{\ddagger} + \delta_m \mu^{\circ}(\text{complex}) + \delta_m \mu^{\circ}(HA^-) \qquad (7)$$

operator, $\delta_m \mu^{\circ}$ represents the transfer chemical potential and $\delta_m \mu^{\ddagger}$ represents the transfer chemical potential of the transition state. The transfer chemical potential of the undissociated L-ascorbic acid was determined from the variation of solubility with methanol content of the solvent[39] and is assumed to be equivalent to the transfer chemical potential of the ascorbate anion, HA^-, since the charge contribution to the transfer chemical potentials of HA^- relative to H_2A is believed to be negligible.

The results are shown in Table 15 for $[CoL_4(H_2O)(OH)]^{2+}$. The increase in rate with increasing methanol content is due to destabilisation of both initial and transition states with the initial state being more destabilised. This can be attributed to a decrease in charge and increase in size of the transition states, thus facilitating greater solubility of the transition states in the methanol–water mixtures relative to the initial states. As the size of the complex increases, a simultaneous increase in the

Table 10 Pseudo-first order rate constants for the oxidation of L-ascorbic acid by *cis*-$[Co(en)_2(H_2O)_2]^{3+}$ as a function of $[A]_T$ and methanol content at pH 5.6 ± 0.2, 25.1 °C, initial [complex] = 1×10^{-3} mol dm^{-3} and I = 0.3 mol dm^{-3} ($LiClO_4$)

10^2 $[A]_T$/ mol dm^{-3}	10^2 k_{obs}/s^{-1}			
	10% MeOH	20% MeOH	30% MeOH	40% MeOH
1.0	0.62	0.99	1.27	2.06
2.0	1.23	1.55	2.14	3.09
3.0	1.57	2.13	2.92	4.27
4.0	1.97	2.72	3.63	5.37
5.0	2.40	3.22	4.32	6.17

Table 11 Pseudo-first-order rate constants for the oxidation of L-ascorbic acid by $[Co(en)_2(H_2O)_2]^{3+}$ as a function of pH and methanol content at $[A]_T$ = 3.0×10^{-2} mol dm^{-3}, initial [complex] = 1×10^{-3} mol dm^{-3} and I = 0.3 mol dm^{-3} ($LiClO_4$)

10% MeOH		20% MeOH		30% MeOH		40% MeOH	
pH	10^3 k_{obs}/s^{-1}	pH	10^3 k_{obs}/s^{-1}	pH	10^3 k_{obs}/s^{-1}	pH	10^3 k_{obs}/s^{-1}
4.48	1.94	4.61	2.05	4.73	3.06	4.93	4.34
4.66	2.34	4.81	2.86	4.95	4.07	5.12	5.87
4.86	3.08	5.01	3.93	5.14	5.50	5.33	7.95
5.09	4.46	5.23	5.75	5.38	8.07	5.51	11.0
5.34	6.63	5.47	8.67	5.62	11.7	5.81	17.1
5.59	10.1	5.73	13.4	5.88	18.0	6.07	26.2
5.87	16.4	6.00	20.9	6.16	29.2	6.34	45.6

Table 12 Pseudo-first-order rate constants for the oxidation of L-ascorbic acid by *cis*-$[Co(tren)(H_2O_2)_2]^{3+}$ as a function of $[A]_T$ and methanol content at pH 5.6 ± 0.2, 25.1 °C, initial [complex] = 1×10^{-3} mol dm^{-3} and I = 0.3 mol dm^{-3} ($LiClO_4$)

10^2 $[A]_T$/ mol dm^{-3}	k_{obs}/s^{-1}		
	10% MeOH	20% MeOH	30% MeOH
1.0	4.26	6.93	10.6
2.0	7.58	11.6	15.9
3.0	12.1	16.1	21.9
4.0	14.4	20.2	27.7
5.0	19.4	24.8	32.3

Table 13 Pseudo-first-order rate constants for the oxidation of L-ascorbic acid by $[Co(tren)(H_2O)_2]^{3+}$ as a function of pH and methanol content at $[A]_T$ = 5.0×10^{-2} mol dm^{-3}, initial [complex] = 1×10^{-3} mol dm^{-3} and I = 0.3 mol dm^{-3} ($LiClO_4$)

10% MeOH		20% MeOH		30% MeOH	
pH	10^2 k_{obs}/s^{-1}	pH	10^2 k_{obs}/s^{-1}	pH	10^2 k_{obs}/s^{-1}
4.33	1.30	4.46	2.27	4.59	3.53
4.45	1.59	4.56	2.65	4.70	4.43
4.52	1.97	4.70	3.31	4.81	5.69
4.76	3.33	4.87	4.93	4.99	8.06
4.91	3.92	5.02	6.80	5.16	10.9
5.12	6.54	5.20	9.57	5.34	16.1
5.28	8.58	5.44	15.5	5.57	22.5
5.58	14.2	5.63	20.5	5.81	27.8
5.76	18.8	5.89	25.2	6.01	34.7

Table 14 Summary of rate parameters for the reaction of the L-ascorbic acid monoanion (HA^-) with $[CoL_4(H_2O)(OH)]^{2+}$ species

	k_5/dm^3 mol^{-1} s^{-1}				
Species	0% MeOH	10% MeOH	20% MeOH	30% MeOH	40% MeOH
$[Co(NH_3)_4(H_2O)(OH)]^{2+}$	5.99 ± 0.16	7.07 ± 0.23	8.83 ± 0.35	10.5 ± 0.6	—
$[Co(en)_2(H_2O)(OH)]^{2+}$	0.61 ± 0.01	1.31 ± 0.03	1.44 ± 0.04	1.65 ± 0.08	5.99 ± 0.02
$[Co(tren)(H_2O)(OH)]^{2+}$	0.68 ± 0.02	0.78 ± 0.01	0.95 ± 0.02	1.11 ± 0.02	—

Table 15 Initial state–transition state analysis of the oxidation of L-ascorbic acid by cobalt(III) species in binary aqueous methanol mixtures at 25 °C; i.s. = inner sphere

Species	Vol. % MeOH	$\delta_m\mu^\theta$ (i.s.)/ kJ mol^{-1}	$\delta_m\Delta G^\ddagger$/ kJ mol^{-1}	$\delta_m\mu^\ddagger$/ kJ mol^{-1}
$[Co(NH_3)_4(H_2O)(OH)]^{2+}$	10	3.9	−0.4	3.5
	20	7.4	−1	6.4
	30	10.8	−1.4	9.4
$[Co(en)_2(H_2O)(OH)]^{2+}$	10	2.4	−1.9	0.5
	20	6.6	−2.1	4.5
	30	8.2	−2.5	5.7
	40	8.8	−3.1	5.7
$[Co(tren)(H_2O)(OH)]^{2+}$	10	0.9	−0.3	0.6
	20	5.3	−0.8	4.5
	30	6.5	−1.2	5.3

stability of the transition state relative to the initial state is expected. However, the effect of size is expected to reach a maximum value since the decrease in charge density of the transition state, which is also a contributing factor to the enhanced reactivity in mixed-solvent media, will not be significant after a certain complex size is reached. This charge–size balance is possibly accounting for the observed maximum changes in reactivity with solvent composition for *cis*-$[Co(en)_2(OH)(H_2O)]^{2+}$ relative to the NH_3 and tren analogues.

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