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# Kinetics and mechanism of the reduction of the molybdatopentaamminecobalt(III) ion by aqueous sulfite and aqueous potassium hexacyanoferrate(II)

Alvin A. Holder<sup>a</sup>, Tara P. Dasgupta<sup>b,\*</sup>

<sup>a</sup> Department of Biological and Chemical Sciences, University of the West Indies, Cave Hill Campus, PO Box 64, Bridgetown, St. Michael, Barbados

<sup>b</sup> Department of Chemistry, University of the West Indies, Mona Campus, Mona, Kingston 7, Jamaica

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Dedicated to Professor A.G. Sykes

## Abstract

A detailed investigation on the oxidation of aqueous sulfite and aqueous potassium hexacyanoferrate(II) by the title complex ion has been carried out using the stopped-flow technique over the ranges,  $0.01 \leq [\text{S(IV)}]_{\text{T}} \leq 0.05 \text{ mol dm}^{-3}$ ,  $4.47 \leq \text{pH} \leq 5.12$ , and  $24.9 \leq \theta \leq 37.6 \text{ }^{\circ}\text{C}$  and at ionic strength  $1.0 \text{ mol dm}^{-3}$  ( $\text{NaNO}_3$ ) for aqueous sulfite and  $0.01 \leq [\text{Fe(CN)}_6^{4-}] \leq 0.11 \text{ mol dm}^{-3}$ ,  $4.54 \leq \text{pH} \leq 5.63$ , and  $25.0 \leq \theta \leq 35.3 \text{ }^{\circ}\text{C}$  and at ionic strength  $1.0$  or  $3.0 \text{ mol dm}^{-3}$  ( $\text{NaNO}_3$ ) for the hexacyanoferrate(II) ion. Both redox processes are dependent on pH and reductant concentration in a complex manner, that is, for the reaction with aqueous sulfite,  $k_{\text{obs}} = \{(k_1 K_1 K_2 K_3 + k_2 K_1 K_4 [\text{H}^+]) [\text{S(IV)}]_{\text{T}} / ([\text{H}^+]^2 + K_1 [\text{H}^+] + K_1 K_2)\}$  and for the hexacyanoferrate(II) ion,  $k_{\text{obs}} = \{(k_1 K_3 K_4 K_5 + k_2 K_3 K_6 [\text{H}^+]) [\text{Fe(CN)}_6^{4-}]_{\text{T}} / ([\text{H}^+]^2 + K_3 [\text{H}^+] + K_3 K_4)\}$ . At  $25.0 \text{ }^{\circ}\text{C}$ , the value of  $k'_1$  (the composite of  $k_1 K_3$ ) is  $0.77 \pm 0.07 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ , while the value of  $k'_2$  (the composite of  $k_2 K_4$ ) is  $(3.78 \pm 0.17) \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  for aqueous sulfite. For the hexacyanoferrate(II) ion,  $k'_1$  (the composite of  $k_1 K_5$ ) is  $1.13 \pm 0.01 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ , while the value of  $k'_2$  (the composite of  $k_2 K_6$ ) is  $2.36 \pm 0.05 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  at  $25.0 \text{ }^{\circ}\text{C}$ . In both cases there was reduction of the cobalt(III) centre to cobalt(II), but there was no reduction of the molybdenum(VI) centre.  $k_{22}$ , the self-exchange rate constant, for aqueous sulfite (as  $\text{SO}_3^{2-}$ ) was calculated to be  $5.37 \times 10^{-12} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ , while for  $\text{Fe(CN)}_6^{4-}$ , it was calculated to be  $1.10 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  from the Marcus equations. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Redox; Ferrocyanide; Molybdenum(VI); Aqueous sulfite; Cobalt(III)

## 1. Introduction

Over the past 2 decades a number of systems have been studied in our laboratory and by collaborators elsewhere that involve the reactions of various aqua transition metal complex ions with ‘free’ sulfite in aqueous solution. The studies reported include the reactions of the aquapentaammine complexes of cobalt(III) [1–3], rhodium(III) [4], platinum(IV) [5], and chromium(III) [4], along with  $(\text{tren})\text{Co}(\text{OH}_2)_2^{3+}$  ( $\text{tren} = 2, 2', 2''\text{-triaminotriethylamine}$ ) [3]. The kinetic data show that in each instance the most significant first step in the overall process is very rapid nucleophilic attack by

ligand hydroxide on dissolved  $\text{SO}_2$  to form an O-bonded sulfito complex, a reaction which is readily reversed by immediate acidification [1–5]. Metal-to-oxygen bonding is not involved in this reversible process as confirmed by NMR measurements [6]. Subsequent reactions in the cobalt(III) systems comprise O-bonded to S-bonded isomerisation, internal redox, sulfite ion addition, or a combination of these processes depending on the pH and the nature of the  $\text{N}_4$  or  $\text{N}_5$  ligand grouping [1].

The hexacyanoferrate(II) anion on the other hand can reduce some pentaamminecobalt(III) complexes to Co(II) via an outer-sphere electron transfer step [7]. In the past, the reductions of a series of substituted (pyridine)pentaamminecobalt(III) complexes by hexacyanoferrate(II) proceed via the formation of an ion-pair,

\* Corresponding author. Fax: +1-876-977 1835.

E-mail address: tara@uwimona.edu.jm (T.P. Dasgupta).

followed by internal electron transfer within the ion-pair [8]. It is postulated that the ion-pairs feature approach by  $\text{Fe}(\text{CN})_6^{4-}$  on the ammonia side of the cobalt(III) complexes [8]. The electron transfer process is assumed to be adiabatic and the variations in rate are associated with changes in the reduction potentials and/or rate constants for self-exchange of the cobalt(III) complexes [8].

The title complex  $\{[(\text{H}_3\text{N})_5\text{CoOMoO}_3]^+\}$  is binuclear with a cobalt(III) centre and a molybdenum(VI) centre, so it is possible that one or both metal centres can be reduced by both reductants, that is, Co(III) to Co(II), Mo(VI) to Mo(V) (or even lower oxidation states). Also it is possible that there could be anation by the aqueous sulfite followed by internal redox depending on the pH. Clearly both reactions with aqueous sulfite and the hexacyanoferrate(II) (ferrocyanide) anion are of vital importance.

## 2. Experimental

### 2.1. Materials

All reagents were of analytical grade (BDH). Ultra-pure water, obtained by deionising distilled water using a Milli-Q Reagent Grade water system, was used for preparative work and to make up solutions for all physical measurements. Solid  $\text{Na}_2\text{S}_2\text{O}_5$  (BDH) was the source of aqueous sulfite; this salt is very stable in the solid form but hydrates rapidly and completely when dissolved in water to yield aqueous sulfite [1].

### 2.2. Preparation of the complex

$[(\text{H}_3\text{N})_5\text{CoOMoO}_3]\text{ClO}_4$  was prepared by the method outlined previously [9]. Visible spectrum:  $\lambda_{\text{max}}$  (nm (0.1 mol dm<sup>-3</sup>  $\text{Na}_2\text{MoO}_4$ ) 360 and 526 ( $\epsilon$  (dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) 61 and 92). Lit. [9]:  $\lambda_{\text{max}}$  (nm (0.1 mol dm<sup>-3</sup>  $\text{Na}_2\text{MoO}_4$ ) 360 and 526 ( $\epsilon$  (dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) 61.3 and 91.7).

### 2.3. Kinetic measurements

All visible and ultraviolet spectra were recorded with either a Pye Unicam Model PU 8800 or a Hewlett–Packard 8452A diode array spectrophotometer. All kinetic measurements were made using a Hi-Tech SF-51 stopped-flow spectrophotometer interfaced with a computer. The spectrophotometer syringes were immersed in a water-bath linked to a thermostat system (Haake D8) capable of maintaining temperatures within  $\pm 0.02$  °C.

For the electron transfer reactions involving aqueous sulfite solution or  $\text{K}_4\text{Fe}(\text{CN})_6$  (potassium hexacyanoferrate(II)) the following was carried out: Stock solutions

of the complex of known concentration were prepared in volumetric flasks (10 cm<sup>3</sup>). The ionic strength of each solution was adjusted to the required value with appropriate amounts of  $\text{NaNO}_3$  and the flasks were thermostatted for 10 min before introducing the solutions into the syringes of the stopped-flow apparatus. The apparatus was equilibrated at the reaction temperature for at least 0.5 h prior to use and the solutions were kept in one of the thermostatted drive syringes for 5 min before each experiment.

The other syringe contained the respective reducing agent, buffer (potassium hydrogen phthalate–NaOH or  $\text{CH}_3\text{CO}_2\text{Na}$ – $\text{CH}_3\text{CO}_2\text{H}$ ), and supporting electrolyte ( $\text{NaNO}_3$ ). This syringe with its contents was also pre-thermostatted at the desired temperature. Both reactants were then mixed in the stopped-flow spectrophotometer after triggering.  $\text{Na}_2\text{H}_2\text{EDTA}$  (with the reductant, supporting electrolyte, and buffer) was used in the reaction involving  $\text{Fe}(\text{CN})_6^{4-}$  so as to sequester the  $\text{Co}_{(\text{aq})}^{2+}$  formed [7]. Constant ionic strength was maintained at 1.0 mol dm<sup>-3</sup> ( $\text{NaNO}_3$ ) in all cases (or 3.0 mol dm<sup>-3</sup> in one case for the reaction with the ferrocyanide anion). The  $\text{NaNO}_3$  solution was standardised by an ion-exchange method using Dowex 50 W-X8 (50 mesh, H<sup>+</sup> form) resin. The redox processes were followed at 524 nm, where the largest absorbance change occurred. An excess of reductant was used in all cases to ensure pseudo-first order conditions.

The kinetic data were collected and processed with a Hi-Tech Scientific IS-1 software suite V 1.0a. The pseudo-first order rate constants ( $k_{\text{obs}}$ ) were determined by a non-linear least squares regression to fit the curve of the photomultiplier voltage versus time. The reported rate constants are an average of at least three kinetic runs. The standard deviation for each  $k_{\text{obs}}$  is  $\pm 5\%$ . The pH of each solution was measured on an Orion Research EA 920 Expandable Ion Analyser, fitted with a Cole Partner combination electrode.

### 2.4. Stoichiometry

The redox stoichiometry [reductant: complex] was determined by measuring the absorbance at 416 nm (for  $\text{Fe}(\text{CN})_6^{4-}$ ) and 524 nm (for aqueous sulfite) of buffered solutions containing the complex at a fixed concentration while varying added reductant, then determining the break in the plot of absorbance versus the ratio, [complex]: [reductant].

## 3. Results and discussions

### 3.1. Reduction with aqueous sulfite

#### 3.1.1. Nature of the reaction

On reacting  $[(\text{H}_3\text{N})_5\text{CoOMoO}_3]^+$  in aqueous sulfite solutions at pH 5.29 (potassium hydrogen phthalate–

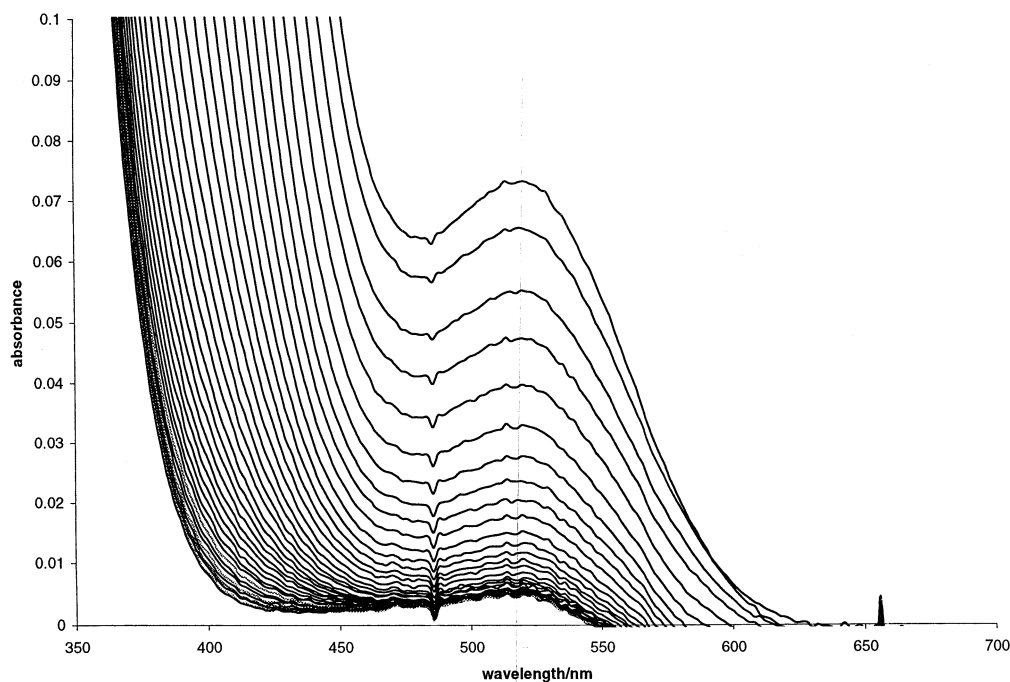
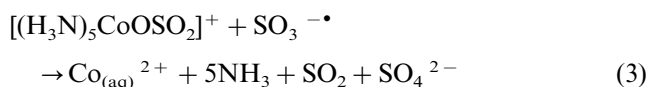
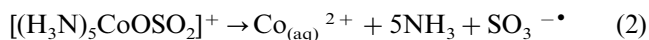
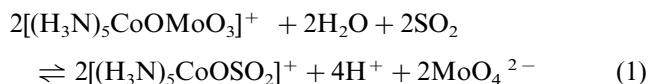


Fig. 1. Repetitive scan for the reduction of  $[(\text{H}_3\text{N})_5\text{CoOMoO}_3]^+$  by aqueous sulfite at  $23.8^\circ\text{C}$ .  $[\text{complex}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{S(IV)}] = 0.05 \text{ mol dm}^{-3}$ ,  $I = 1.0 \text{ mol dm}^{-3}$  ( $\text{NaNO}_3$ ), pH 5.66 (buffer =  $\text{CH}_3\text{CO}_2\text{H}-\text{CH}_3\text{CO}_2\text{Na}$ ), cycle time = 25 s.

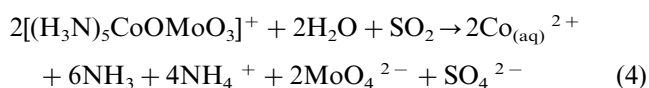
sodium hydroxide buffer) there was an immediate yellow coloration, which slowly got paler with time. At the end of the reaction a pale pink solution left behind. The pale pink solution was due to the formation of  $\text{Co}_{(\text{aq})}^{2+}$ , which was identified by the thiocyanate–acetone test [10]. Molybdate(VI) was tested in the solution by using the molybdyl ‘oxinate’ method [11]; this proved positive for molybdate(VI). Fig. 1 shows a repetitive scan of the reaction over the wavelength range. Preliminary studies of the reaction of aqueous sulfite with the title complex ion indicate that there is a uniphase reaction at 524 nm, resulting in the reduction of  $[(\text{H}_3\text{N})_5\text{CoOMoO}_3]^+$  to  $\text{Co}_{(\text{aq})}^{2+}$ .

### 3.2. Stoichiometry of the reaction

The stoichiometric data in Table 1 are consistent with the reaction summarised in the following equations:



Overall:



We favour direct reduction by the  $\text{SO}_3^{2-}$  ligand (Eq. (2)), with the formation of the radical anion [13],  $\text{SO}_3^{\bullet-}$  and  $\text{Co}_{(\text{aq})}^{2+}$ . The  $\text{SO}_3^{\bullet-}$  radical anion is then scavenged by the  $[(\text{H}_3\text{N})_5\text{CoOSO}_2]^+$  ion. Analyses of the final reaction mixture confirmed the presence [10] of  $\text{Co}_{(\text{aq})}^{2+}$  at concentrations exactly equal to the initial concentrations of the Co(III) complex, and this finding was independent of reaction conditions. The identity of the sulfur-containing reaction product with aqueous  $\text{BaCl}_2$

Table 1

Stoichiometry of the reaction between  $[(\text{H}_3\text{N})_5\text{CoOMoO}_3]^+$  and aqueous sulphite at  $25.0^\circ\text{C}$ , pH 5.64 ( $\text{CH}_3\text{CO}_2\text{Na}-\text{CH}_3\text{CO}_2\text{H}$  buffer),  $I = 1.0 \text{ mol dm}^{-3}$  ( $\text{NaNO}_3$ ),  $[\text{complex}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $\lambda = 524 \text{ nm}$ , cell path length = 1.00 cm

$[\text{S(IV)}]_{\text{T}}/[\text{complex}]$	Absorbance
0.0625	0.148
0.125	0.123
0.250	0.100
0.375	0.065
0.500 <sup>a</sup>	0.025
1.000	0.024
1.500	0.025
2.000	0.023
2.500	0.024
3.000	0.023
3.500	0.028
4.000	0.026
4.500	0.026
5.000	0.024
5.500	0.030

<sup>a</sup> Break point occurs at  $[\text{S(IV)}]_{\text{T}}/[\text{complex}] = 0.50$ .



sulfite species are the  $\text{HSO}_3^-$  and  $\text{SO}_3^{2-}$  ions, while  $[(\text{H}_3\text{N})_5\text{CoOMoO}_3]^+$  and  $[(\text{H}_3\text{N})_5\text{CoOMoO}_2(\text{OH})]^{2+}$ , exist in equilibrium [9], but since the  $\text{p}K_1$  of  $[(\text{H}_3\text{N})_5\text{CoOMoO}_2(\text{OH})]^{2+}$  is 2.09; the deprotonated species,  $[(\text{H}_3\text{N})_5\text{CoOMoO}_3]^+$ , is the reactive species in the reaction as over the pH range and it exists in > 99% as the predominant cobalt(III) species. The observed pseudo-first order rate constants,  $k_{\text{obs}}$ , increase with an increase in pH (Table 3), and this observation may be interpreted in terms of the reactive species via the proposed mechanism in Scheme 1 where  $K_1 = 1.26 \times 10^{-2} \text{ mol dm}^{-3}$  and  $K_2 = 5.01 \times 10^{-7} \text{ mol dm}^{-3}$  at 25 °C [2]. Based on the increase of  $k_{\text{obs}}$  with pH it can be deduced that  $\text{SO}_3^{2-}$  is the more reactive species in the electron transfer reaction; so the  $k_1$  path is the main contributing path over the pH range.

The proposed mechanism given in Scheme 1 leads to the expression:

$$k_{\text{obs}} = \{(k_1 K_1 K_2 K_3 + k_2 K_1 K_4 [\text{H}^+]) [\text{S(IV)}]_{\text{T}}\} / ([\text{H}^+]^2 + K_1 [\text{H}^+] + K_1 K_2) \quad (6)$$

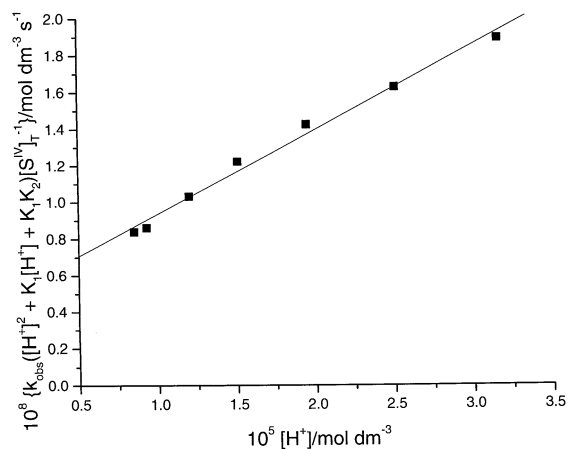


Fig. 3. A plot of  $[k_{\text{obs}}([\text{H}^+]^2 + K_1[\text{H}^+] + K_1 K_2) [\text{S(IV)}]_{\text{T}}^{-1}]$  vs.  $[\text{H}^+]$  for the reduction of  $[(\text{H}_3\text{N})_5\text{CoOMoO}_3]^+$  by aqueous sulfite at 25.0 °C.

Table 4

Rate parameters and  $\text{p}K$  values<sup>a</sup> for the reaction between  $[(\text{H}_3\text{N})_5\text{CoOMoO}_3]^+$  and aqueous sulfite

$\theta$ (°C)	$k'_1$ ( $\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ )	$10^2 k'_2$ ( $\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ )	$\text{p}K_1$	$\text{p}K_2$
25.0	$0.77 \pm 0.07$	$3.60 \pm 0.18$	1.90	6.30
31.2	$2.63 \pm 0.10$	$6.85 \pm 0.33$	1.98	6.30
36.4	$5.85 \pm 0.52$	$21.54 \pm 1.28$	2.03	6.30

$\Delta H^\ddagger = 134 \pm 8 \text{ kJ mol}^{-1}$ ;  $\Delta H_2^\ddagger = 116 \pm 27 \text{ kJ mol}^{-1}$ ;  $\Delta S_1^\ddagger = 204 \pm 27 \text{ J mol}^{-1} \text{ K}^{-1}$ ;  $\Delta S_2^\ddagger = 116 \pm 88 \text{ J mol}^{-1} \text{ K}^{-1}$ .

<sup>a</sup> Ref. [2].

where  $[\text{S(IV)}]_{\text{T}}$  represents the total sulfite concentration. The expression can be rearranged to give:

$$\{k_{\text{obs}}([\text{H}^+]^2 + K_1[\text{H}^+] + K_1 K_2) [\text{S(IV)}]_{\text{T}}^{-1}\} = k_1 K_1 K_2 K_3 + k_2 K_1 K_4 [\text{H}^+] \quad (7)$$

A plot of the left hand side of Eq. (7) versus  $[\text{H}^+]$  is linear in the pH range  $4.47 \leq \text{pH} \leq 5.12$ , the slope being  $k_2 K_1 K_4$  and intercept being  $k_1 K_1 K_2 K_3$ . A plot at 25.0 °C shown in Fig. 3 is linear over the pH range. A linear regression analysis was carried out and due to the inability to separate  $k_1$  from  $K_3$  and  $k_2$  from  $K_4$ , it was necessary to combine  $k_1$  and  $K_3$  to give  $k'_1$ , and to combine  $k_2$  and  $K_4$  to give  $k'_2$ . The rate and activation parameters, along with the  $\text{p}K_1$  and  $\text{p}K_2$  values are [2] shown in Table 4.

In our work the separation of the equilibrium constant and the rate constant for the electron transfer has proven to be difficult. This is due to the equilibrium of the two reactive species, namely,  $\text{HSO}_3^-$  and  $\text{SO}_3^{2-}$ . It would not be correct to neglect the contribution from  $\text{HSO}_3^-$  in the  $k_2$  path (see Scheme 1).

At 25.0 °C the value of  $k'_1$  is  $0.77 \pm 0.07 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ , while the value of  $k'_2$  is  $(3.60 \pm 0.18) \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ ; so one can see that  $\text{SO}_3^{2-}$  reacts about 21 times faster than  $\text{HSO}_3^-$ . The transition state involving  $\text{HSO}_3^-$  is more ordered than that involving  $\text{SO}_3^{2-}$  as can be seen from the respective values for entropy of activation, the values being  $\Delta S_2^\ddagger = 116 \pm 88 \text{ J mol}^{-1} \text{ K}^{-1}$  and  $\Delta S_1^\ddagger = 204 \pm 27 \text{ J mol}^{-1} \text{ K}^{-1}$ , respectively.

We can compare our studies with electron transfer reactions involving sulfite and other Co(III) complexes. What is noticeable is that after the formation of the ion-pair in Scheme 1 there is intermolecular electron transfer. The rate constant for the intramolecular electron transfer [1] of the complex,  $[(\text{H}_3\text{N})_5\text{CoOSO}_2]^+$ , after  $\text{SO}_2$  addition to  $[(\text{H}_3\text{N})_5\text{CoOH}_2]^{3+}$ , within the pH range 3–7, is  $1.4 \times 10^{-2} \text{ s}^{-1}$ . The activation parameters are  $\Delta H^\ddagger = 112.5 \text{ kJ mol}^{-1}$  and  $\Delta S^\ddagger$  is  $96.7 \text{ J mol}^{-1} \text{ K}^{-1}$  at 25 °C. For  $[(\text{H}_3\text{N})_5\text{CoSO}_3]^+$ , the rate [5] constant is  $\sim 1 \times 10^{-4} \text{ s}^{-1}$ . Our rate of electron transfer by  $\text{SO}_3^{2-}$  occurs at a rate of  $0.77 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  at 25.0 °C, which is faster than either of the electron transfer reaction involving either Co(III) complex. The activation parameters ( $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ ) for the  $\text{SO}_3^{2-}$ , term ( $k'_1$ ) during the electron transfer process is comparable with those for the  $[(\text{H}_3\text{N})_5\text{CoSO}_3]^+$  system.

The  $[(\text{tren})\text{Co}(\text{OH}_2)(\text{OSO}_2)]^+$  complex undergoes [2,5,13] only a redox reaction for  $\text{pH} < 5$  but at higher pH values shows evidence for the disappearance of the redox reaction, while addition of a second sulfite anion yields a stable complex of stoichiometry  $[(\text{tren})\text{Co}(\text{SO}_3)_2]^-$ , which predominates at a pH of 7.2 or higher [13]. Similarly, the bis(ethylenediamine) species,  $\text{cis}-(\text{en})_2\text{Co}(\text{OSO}_2)^+$  exhibits [14] redox over the pH ranges 3–7 as the only observable secondary process.

Table 5

Summary of the activation parameters for various redox reactions involving some cobalt(III) complexes and sulfite ('free' and co-ordinated) in aqueous solution

Complex <sup>a</sup>	$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> )	$\Delta S^\ddagger$ (J mol <sup>-1</sup> K <sup>-1</sup> )	Reference
[(H <sub>3</sub> N) <sub>5</sub> CoOSO <sub>2</sub> ] <sup>+</sup> (1)	112.5 ± 0.8	96.7 ± 117.6	[2]
[(tren)Co(OH <sub>2</sub> )(OSO <sub>2</sub> )] <sup>+</sup> (2)	101.3 ± 34.3	34.3 ± 27.6	[5]
[(phen) <sub>2</sub> Co(SO <sub>3</sub> H)SO <sub>3</sub> ] <sup>+</sup> (3)	104.6 ± 9.6	4.6 ± 29.3	[16]
[(bpy) <sub>2</sub> Co(SO <sub>3</sub> H)SO <sub>3</sub> ] <sup>+</sup> (4)	132.6 ± 2.1	91.6 ± 6.7	[16]
[(phen) <sub>2</sub> Co(SO <sub>3</sub> H)- (OH <sub>2</sub> )] <sup>2+</sup> (5)	118.4 ± 7.9	51.5 ± 24.3	[16]
[(H <sub>3</sub> N) <sub>5</sub> CoOMoO <sub>3</sub> ] <sup>+</sup> (6)	134 ± 8	204 ± 27	this work
[(H <sub>3</sub> N) <sub>5</sub> CoOMoO <sub>3</sub> ] <sup>+</sup> (6)	116 ± 27	116 ± 88	this work
A (7)	117.6 ± 5.9	117.6 ± 0.4	[17]

A, [(H<sub>3</sub>N)<sub>3</sub>Co(μ-OH)<sub>2</sub>(μ-SO<sub>3</sub>)Co(NH<sub>3</sub>)<sub>3</sub>]<sup>2+</sup>.

<sup>a</sup> Each complex is numbered in Fig. 4.

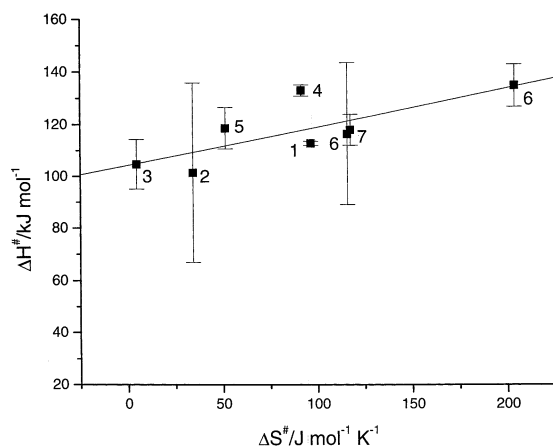


Fig. 4. An isokinetic plot of the activation parameters for various redox reactions involving some cobalt(III) complexes and sulfite ('free' and co-ordinated) in aqueous solution.

Meanwhile, the long chain tetraethylenepentaammine (tetren) analogue of  $\alpha\beta$  S-[(tetren)Co(OSO<sub>2</sub>)]<sup>+</sup>, undergoes a slow internal rearrangement to the S-bonded form with no evidence for redox even at elevated temperatures [3]. There is evidence of a complex anation reaction by aqueous sulfite at much higher pH with the title complex ion, with the production of yellow cobalt(III) complex [15].

A summary of data concerning the redox reactions of a selection of sulfito cobalt(III) complexes is shown in Table 5. As depicted in Table 5 the activation parameters found for the  $\mu$ -sulfito species compares reasonably well with those of the mononuclear systems implying a similarity in nature of the mechanisms. However, it is believed that the  $\mu$ -sulfito species undergoes a two electron transfer process with the reduction of the two cobalt(III) centres and the simultaneous oxidation of S(IV) to S(VI). This contrasts with the mononuclear cobalt(III) sulfite species which involves one-electron

transfer between the cobalt(III) centre and the sulfito ligand.

The activation parameters in Table 5 are very similar and can be used in an isokinetic plot of  $\Delta H^\ddagger$  versus  $\Delta S^\ddagger$  since

$$\Delta H^\ddagger = \Delta G_o^\ddagger + \beta_o \Delta S^\ddagger \quad (8)$$

where  $\beta_o$  is the isokinetic temperature and  $\Delta G_o^\ddagger$  is the intrinsic free energy of activation. Fig. 4 shows such a plot where the linearity proves that a common mechanism exists for the sulfite cobalt(III) complexes and the reaction involving aqueous sulfite and the title complex ion, with  $\Delta G_o^\ddagger = 104 \pm 5$  kJ mol<sup>-1</sup> and  $\beta_o = 144 \pm 51$  K.

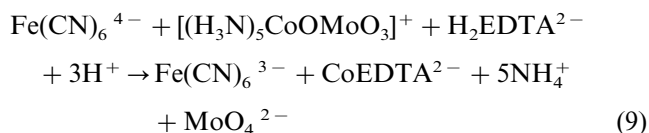
### 3.4. Reduction with hexacyanoferrate(II)

#### 3.4.1. Nature of the reaction

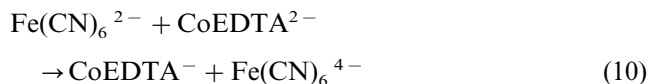
On mixing  $\text{Fe(CN)}_6^{4-}$  and  $[(\text{H}_3\text{N})_5\text{CoOMoO}_3]^+$  in aqueous solution a precipitate (presumably cobalt(II) hexacyanoferrate(II) and/or cobalt(II) hexacyanoferrate(III)) was formed, and, therefore, homogeneous kinetic measurements were precluded. However, when disodium dihydrogen ethylenediaminetetraacetate ( $\text{Na}_2\text{H}_2\text{EDTA}$ ) was added to the solution to complex the cobalt(II) formed, no precipitate was produced [7]. A repetitive scan for the reaction at 25.0 °C is shown in Fig. 5, where an increase in absorbance is observed.

### 3.5. Stoichiometry of the reaction

The stoichiometric data in Table 6 are consistent with the reaction summarised in the following equation:



Eventually a reddish purple colour is produced over a period of hours. The formation of the reddish purple colour is straightforward. The  $\text{Fe(CN)}_6^{3-}$  and  $\text{CoEDTA}^{2-}$  produced in Eq. (9) undergo an electron transfer reaction [8] that produces purple  $\text{CoEDTA}^-$ . This reaction is very slow and does not interfere with the reaction of interest, Eq. (9).



The purple product of  $\text{CoEDTA}^-$  was identified spectrophotometrically.

### 3.6. Aqueous potassium hexacyanoferrate, temperature and pH dependence of the reaction

Kinetic runs were carried out over the ranges,  $0.01 \leq [\text{Fe(CN)}_6^{4-}] \leq 0.11$  mol dm<sup>-3</sup>,  $4.54 \leq \text{pH} \leq 5.63$ , and

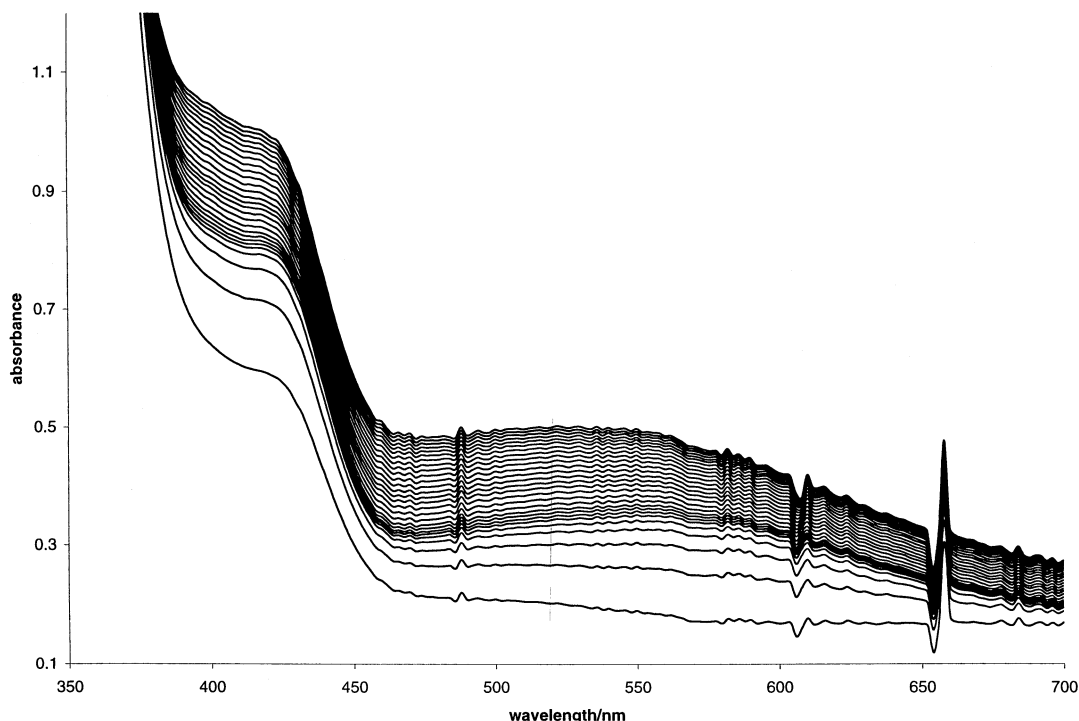


Fig. 5. Repetitive scan for the reduction of  $[(\text{H}_3\text{N})_5\text{CoOMoO}_3]^+$  by  $\text{Fe}(\text{CN})_6^{4-}$  at  $25.0\text{ }^\circ\text{C}$ .  $[\text{complex}] = 0.5 \times 10^{-3}\text{ mol dm}^{-3}$ ,  $[\text{Fe}(\text{CN})_6^{4-}] = 0.025\text{ mol dm}^{-3}$ ,  $I = 1.40\text{ mol dm}^{-3}$  ( $\text{NaNO}_3$ ), pH 5.51 (buffer =  $\text{CH}_3\text{CO}_2\text{H}-\text{CH}_3\text{CO}_2\text{Na}$ ), cycle time, 25 s.

$25.0 \leq \theta \leq 35.3\text{ }^\circ\text{C}$  and at ionic strength 1.0 or  $3.0\text{ mol dm}^{-3}$  ( $\text{NaNO}_3$ ). Tables 7 and 8 summarise the results obtained for  $k_{\text{obs}}$  at the various pH values,  $[\text{Fe}(\text{CN})_6^{4-}]$ , and temperatures. From the tables one can see that  $k_{\text{obs}}$  is dependent on both pH and  $[\text{Fe}(\text{CN})_6^{4-}]$ .  $k_{\text{obs}}$  increases with increasing  $[\text{Fe}(\text{CN})_6^{4-}]$  and tends to reach a saturation point at high  $[\text{Fe}(\text{CN})_6^{4-}]$ . This implies that there is ion-pair formation (as shown in Scheme 2) from which Eq. (11) is derived:

$$k_{\text{obs}} = k_1 K_5 [\text{Fe}(\text{CN})_6^{4-}] / (1 + K_5 [\text{Fe}(\text{CN})_6^{4-}]) \quad (11)$$

Eq. (11) can be rearranged to form

$$1/k_{\text{obs}} = 1/k_1 + (k_1 K_5 [\text{Fe}(\text{CN})_6^{4-}]) \quad (12)$$

A plot of the left hand side of Eq. (12) versus  $1/[\text{Fe}(\text{CN})_6^{4-}]$  is shown in Fig. 6, from which  $k_1 = (2.52 \pm 0.54) \times 10^{-1}\text{ s}^{-1}$  and  $K = 5.15 \pm 1.26\text{ mol}^{-1}\text{ dm}^3\text{ s}^{-1}$  at  $35.3\text{ }^\circ\text{C}$ , after carrying out linear regression on Eq. (12).

There is evidence [18] that the ferrocyanide anion may exhibit, in principle, the behaviour of a quadrivalent Brønsted base. The corresponding base strengths can be expressed conveniently in terms of the successive ionisation constants of the respective conjugate acids [19], viz. by Scheme 3. At  $25\text{ }^\circ\text{C}$  [19],  $K_1 > K_2 > 0.1\text{ mol dm}^{-3}$ ,  $K_3 = (6.0 \pm 2.0) \times 10^{-3}\text{ mol dm}^{-3}$ , and  $K_4 = (6.7 \pm 0.3) \times 10^{-5}\text{ mol dm}^{-3}$ . Fig. 7 shows the variation of the ferrocyanide species with pH. Over the pH range of the reaction, the main species in aqueous

solution are  $\text{H}_2\text{Fe}(\text{CN})_6^{2-}$ ,  $\text{HFe}(\text{CN})_6^{3-}$ ,  $\text{Fe}(\text{CN})_6^{4-}$ , and  $[(\text{H}_3\text{N})_5\text{CoOMoO}_3]^+$ .

The  $k_{\text{obs}}$  values decrease with an increase in pH (Table 8); so based the trend the mechanism in Scheme 2 is proposed, where  $K_3 = 6.0 \times 10^{-3}\text{ mol dm}^{-3}$  and  $K_4 = 6.7 \times 10^{-5}\text{ mol dm}^{-3}$  at  $25\text{ }^\circ\text{C}$  [19].

Based on the decrease of  $k_{\text{obs}}$  with pH it can be deduced that  $\text{HFe}(\text{CN})_6^{3-}$  is the more reactive ferrocyanide species in the electron transfer reaction; so  $k_2$  is the main contributing path over the pH range.

Table 6

Stoichiometry of the reaction between  $[(\text{H}_3\text{N})_5\text{CoOMoO}_3]^+$  and  $\text{Fe}(\text{CN})_6^{4-}$  at  $25.0\text{ }^\circ\text{C}$ , pH 5.56 ( $\text{CH}_3\text{CO}_2\text{Na}-\text{CH}_3\text{CO}_2\text{H}$  buffer),  $[\text{complex}] = 1 \times 10^{-3}\text{ mol dm}^{-3}$ ,  $I = 1.0\text{ mol dm}^{-3}$  ( $\text{Na}_2\text{NO}_3$ ),  $[\text{Na}_2\text{H}_2\text{EDTA}] = 3 \times 10^{-3}\text{ mol dm}^{-3}$ ,  $\lambda = 416\text{ nm}$ , cell path length =  $1.00\text{ cm}$

$[\text{Fe}(\text{CN})_6^{4-}]/[\text{complex}]$	Absorbance
0.125	0.126
0.250	0.150
0.500	0.192
0.750	0.223
1.000 <sup>a</sup>	0.251
2.000	0.343
3.000	0.409
4.000	0.477
5.000	0.536
6.000	0.600

<sup>a</sup> Break point occurs at  $[\text{Fe}(\text{CN})_6^{4-}]/[\text{complex}] = 1.00$ .



Table 7

Pseudo-first order rate constants for the reaction between  $[(\text{H}_3\text{N})_5\text{CoOMoO}_3]^+$  and  $\text{Fe}(\text{CN})_6^{4-}$

$[\text{Fe}(\text{CN})_6^{4-}]$ (mol dm <sup>-3</sup> )	$10^2 k_{\text{obs}}$ (s <sup>-1</sup> )
0.01	1.27
0.02	2.10
0.03	3.30
0.04	4.31
0.05	5.17
0.06	6.08
0.07	6.98
0.08	7.60
0.09	8.32
0.10	9.07
0.11	9.57

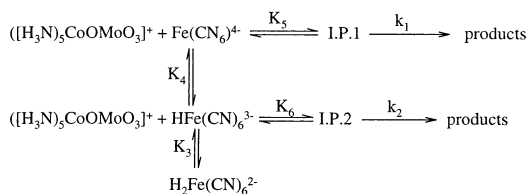
Variation in  $[\text{Fe}(\text{CN})_6^{4-}]$ ,  $[\text{complex}] = 0.5 \times 10^{-3}$  mol dm<sup>-3</sup>,  $[\text{Na}_2\text{H}_2\text{EDTA}] = 1.5 \times 10^{-3}$  mol dm<sup>-3</sup>,  $\lambda = 524$  nm,  $I = 3.0$  mol dm<sup>-3</sup> ( $\text{NaNO}_3$ ), pH 5.59 ( $\text{CH}_3\text{CO}_2\text{Na}-\text{CH}_3\text{CO}_2\text{H}$  buffer),  $\theta = 35.3$  °C.

Table 8

Pseudo-first order rate constants for the reaction between  $[(\text{H}_3\text{N})_5\text{CoOMoO}_3]^+$  and  $\text{Fe}(\text{CN})_6^{4-}$

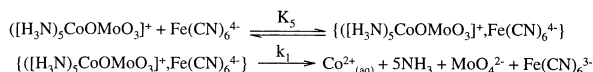
pH	$\theta = 25.0$ °C	pH	$\theta = 30.4$ °C	pH	$\theta = 35.3$ °C
	$10^2 k_{\text{obs}}$ (s <sup>-1</sup> )		$10^2 k_{\text{obs}}$ (s <sup>-1</sup> )		$10^1 k_{\text{obs}}$ (s <sup>-1</sup> )
4.54	3.79	4.54	8.73	4.53	1.59
4.62	3.61	4.63	8.47	4.63	1.54
4.72	3.46	4.73	8.29	4.72	1.47
4.82	3.36	4.83	7.93	4.83	1.44
5.04	3.13	4.94	7.71	4.94	1.38
5.16	3.10	5.05	7.55	5.05	1.33
5.27	3.06	5.16	7.35	5.17	1.30
5.38	3.01	5.27	7.16	5.27	1.24
5.62	2.98	5.40	6.96	5.41	1.21
—	—	5.63	6.86	—	—

Variation in pH and temperature,  $\lambda = 524$  nm,  $[\text{complex}] = 0.5 \times 10^{-3}$  mol dm<sup>-3</sup>,  $I = 1.0$  mol dm<sup>-3</sup> ( $\text{NaNO}_3$ ),  $[\text{Fe}(\text{CN})_6^{4-}] = 0.025$  mol dm<sup>-3</sup>, Buffer =  $\text{CH}_3\text{CO}_2\text{Na}-\text{CH}_3\text{CO}_2\text{H}$ ,  $[\text{Na}_2\text{H}_2\text{EDTA}] = 1.5 \times 10^{-3}$  mol dm<sup>-3</sup>.



I.P. = ion-pair

Ion-pairing due to  $\text{Fe}(\text{CN})_6^{4-}$ :



Scheme 2.

The proposed mechanism given in Scheme 2 leads to the expression:

$$k_{\text{obs}} = \{(k_1 K_3 K_4 K_5 + k_2 K_3 K_6 [\text{H}^+]) [\text{Fe}(\text{CN})_6^{4-}]_{\text{T}}\} / ([\text{H}^+]^2 + K_3 [\text{H}^+] + K_3 K_4) \quad (13)$$

where  $[\text{Fe}(\text{CN})_6^{4-}]_{\text{T}}$  represents the total ferrocyanide concentration.

The expression can be rearranged to give:

$$\begin{aligned}
 \{k_{\text{obs}} ([\text{H}^+]^2 + K_3 [\text{H}^+] + K_3 K_4 [\text{Fe}(\text{CN})_6^{4-}]_{\text{T}}^{-1})\} \\
 = k_1 K_3 K_4 K_5 + k_2 K_3 K_6 [\text{H}^+] \quad (14)
 \end{aligned}$$

A plot of the left hand side of Eq. (14) versus  $[\text{H}^+]$  is linear in the range  $4.53 \leq \text{pH} \leq 5.63$ , the slope being  $k_2 K_3 K_6$  and the intercept being  $k_1 K_3 K_4 K_5$ . A plot at 25.0 °C shown in Fig. 8 is linear over the pH range. A linear regression analysis was carried out and due to the inability to separate  $k_1$  from  $K_5$  and  $k_2$  from  $K_6$ , it was necessary to combine  $k_1$  and  $K_5$  to give  $k'_1$ , and to combine  $k_2$  and  $K_6$  to give  $k'_2$ .  $K_3$  and  $K_4$  are independent of temperature as deduced from literature [19]. The rate and activation parameters are shown in Table 9.

At 25.0 °C the value of  $k'_1$  is  $1.13 \pm 0.01$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>, while the value of  $k'_2$  is  $2.36 \pm 0.05$  mol<sup>-1</sup> dm<sup>3</sup>; so one can see that  $\text{HFe}(\text{CN})_6^{3-}$  reacts with

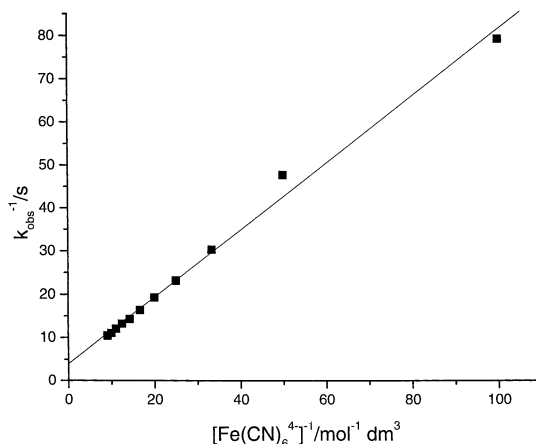
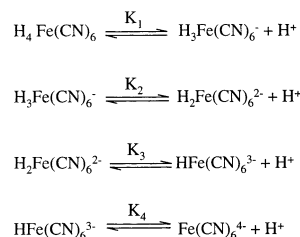
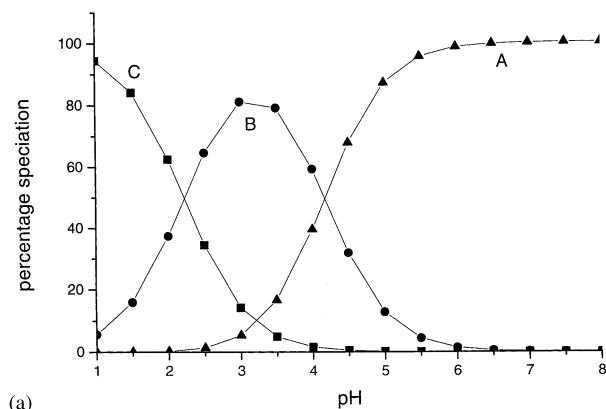


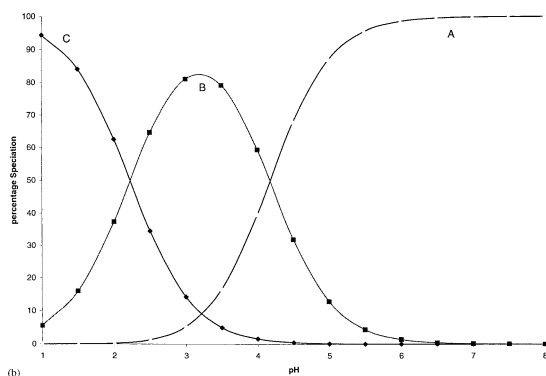
Fig. 6. A plot of  $k_{\text{obs}}^{-1}$  vs.  $[\text{Fe}(\text{CN})_6^{4-}]^{-1}$  for the reduction of  $[(\text{H}_3\text{N})_5\text{CoOMoO}_3]^+$  by  $\text{Fe}(\text{CN})_6^{4-}$  at 35.3 °C.



Scheme 3.



(a)



(b)

Fig. 7. A plot showing the percent speciation of  $\text{Fe}(\text{CN})_6^{4-}$  (A),  $\text{HFe}(\text{CN})_6^{3-}$  (B), and  $\text{H}_2\text{Fe}(\text{CN})_6^{2-}$  (C), with variation in pH.

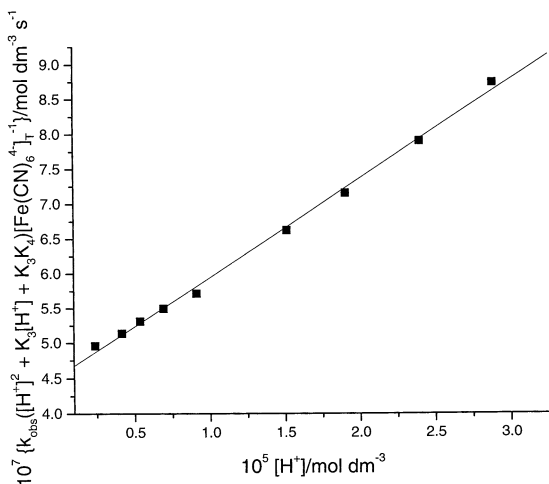


Fig. 8. A plot of  $\{k_{\text{obs}}([\text{H}^+]^2 + K_3[\text{H}^+] + K_3K_4)[\text{Fe}(\text{CN})_6^{4-}]^{-1}\}$  vs.  $[\text{H}^+]$  for the reduction of  $[(\text{H}_3\text{N})_5\text{CoOMoO}_3]^+$  by  $\text{Fe}(\text{CN})_6^{4-}$  at 25.0 °C.

$[(\text{H}_3\text{N})_5\text{CoOMoO}_3]^+$  about two times faster than  $\text{Fe}(\text{CN})_6^{4-}$ . The transition state involving  $\text{Fe}(\text{CN})_6^{4-}$  is more ordered than that involving  $\text{HFe}(\text{CN})_6^{3-}$  as can be seen from the respective values for the entropy of activation, the values being  $\Delta S_1^\ddagger = 99 \pm 31 \text{ J mol}^{-1} \text{ K}^{-1}$  and  $\Delta S_2^\ddagger = 126 \pm 17 \text{ J mol}^{-1} \text{ K}^{-1}$ , respectively.

$k_1' = 4.60 \pm 0.06 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  at 35.3 °C from Table 9 and given the fact that  $k_1' = k_1 K_5$  and that

$k_1 = (2.52 \pm 0.54) \times 10^{-1} \text{ s}^{-1}$  and that  $K_5 = 5.15 \pm 1.26 \text{ mol}^{-1} \text{ dm}^3$  at 35.3 °C,  $I = 3.0 \text{ mol dm}^{-3}$  ( $\text{NaNO}_3$ ), and pH 5.59; from Eq. (12),  $k_1' = 1.30 \pm 0.60 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ . This value of  $k_1' = 1.30 \pm 0.60 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  is less than the value  $k_1' = 4.60 \pm 0.06 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  at 35.3 °C and  $I = 1.0 \text{ mol dm}^{-3}$  ( $\text{NaNO}_3$ ) from Table 9. This shows that  $k_1'$  decreases with an increase in ionic strength, a clear indication that the effect of ionic strength on rates of ionic reactions is well established [20]. For species of like charges, the rate increases with an increase in ionic strength, while for species of opposite charges, the rate decreases as the ionic strength increases. The rate is unaffected by ionic strength for uncharged species. From our decrease in  $k_1'$  with an increase in ionic strength from 1.0 to 3.0  $\text{mol dm}^{-3}$ , it shows that species of unlike charges due to  $[(\text{H}_3\text{N})_5\text{CoOMoO}_3]^+$  and  $\text{Fe}(\text{CN})_6^{4-}$  reacting to form the ion-pair in Scheme 2.

We now compare our reaction between  $[(\text{H}_3\text{N})_5\text{CoOMoO}_3]^+$  and  $\text{Fe}(\text{CN})_6^{4-}$  with other reactions involving  $\text{Fe}(\text{CN})_6^{4-}$  and other cobalt(III) complexes. Our value of  $K_5 = 5.15 \pm 1.26 \text{ mol}^{-1} \text{ dm}^3$  is less ( $1/55$  of the value) than that of  $3.0 \times 10^2 \text{ mol}^{-1} \text{ dm}^3$  from the reaction [21] of  $[(\text{H}_3\text{N})_5\text{Co}(\text{OAc})]^{2+}$  and  $\text{Fe}(\text{CN})_6^{4-}$ , while  $k_1$  for the acetate complex is  $3.7 \times 10^{-4} \text{ s}^{-1}$ . For the reaction involving  $[(\text{H}_3\text{N})_5\text{CoOH}_2]^{3+}$  and  $\text{Fe}(\text{CN})_6^{4-}$  [7],  $K = 1500 \pm 100 \text{ mol}^{-1} \text{ dm}^3$  and  $k_1 = (1.9 \pm 0.1) \times 10^{-1} \text{ s}^{-1}$ , which shows that the two values of  $k_1$  are very similar under experimental errors. The value of  $K_5$  for our system is much lower than for  $[(\text{H}_3\text{N})_5\text{Co}(\text{OAc})]^{2+}$  and  $[(\text{H}_3\text{N})_5\text{CoOH}_2]^{3+}$ .

The value of  $k_1$  for our system is slightly higher than the system reported by Miralles et al. [8] for reductions of various substituted (pyridine)pentaamminecobalt(III) complexes by  $\text{Fe}(\text{CN})_6^{4-}$ . Their  $k_1$  values ranged from  $1.51 \times 10^{-2}$  to  $76 \times 10^{-2} \text{ s}^{-1}$ , while their  $K_5$  values were much higher than ours, clearly due to the +3 charge on the cobalt(III) complexes. Miralles et al. [8] concluded that internal, outer-sphere electron transfer process occur within the ion-pair containing a pyridine bound to the cobalt(III) centre. Based on this fact, we can conclude that an internal, outer-sphere electron transfer process has occurred within the ion-

Table 9

Rate parameters for the reduction of  $[(\text{H}_3\text{N})_5\text{CoOMoO}_3]^+$  by  $\text{Fe}(\text{CN})_6^{4-}$

$\theta$ (°C)	$k_1'$ ( $\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ )	$k_2'$ ( $\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ )
25.0	$1.13 \pm 0.01$	$2.36 \pm 0.05$
30.4	$2.66 \pm 0.01$	$5.55 \pm 0.07$
35.3	$4.60 \pm 0.06$	$10.5 \pm 0.2$

$\Delta H_1^\ddagger = 102 \pm 8 \text{ kJ mol}^{-1}$ ;  $\Delta H_2^\ddagger = 108 \pm 4 \text{ kJ mol}^{-1}$ ;  $\Delta S_1^\ddagger = 99 \pm 31 \text{ J mol}^{-1} \text{ K}^{-1}$ ;  $\Delta S_2^\ddagger = 126 \pm 17 \text{ J mol}^{-1} \text{ K}^{-1}$ .

Table 10

Summary of the activation parameters for the reduction of  $[(\text{H}_3\text{N})_5\text{CoOMoO}_3]^+$  by some reducing agents

Reductant <sup>a</sup>	$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> )	$\Delta S^\ddagger$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> )	$\Delta S^\ddagger$ (J mol <sup>-1</sup> K <sup>-1</sup> )
Ascorbate (1) <sup>b</sup>	29 ± 7	-124 ± 30	99 ± 9	67 ± 35
Fe(CN) <sub>6</sub> <sup>4-</sup> (2) <sup>c</sup>	102 ± 8	99 ± 31	108 ± 4	126 ± 17
Aqueous sulfite (3) <sup>c</sup>	134 ± 8	204 ± 27	116 ± 27	116 ± 88

<sup>a</sup> Each reductant is numbered in Fig. 9.<sup>b</sup> [22].<sup>c</sup> This work.

pair formed between  $[(\text{H}_3\text{N})_5\text{CoOMoO}_3]^+$  and  $\text{Fe(CN)}_6^{4-}$ .

The rate constants and thermodynamic parameters for the reduction of  $[(\text{H}_3\text{N})_5\text{CoOMoO}_3]^+$  by some reductants, viz. L-ascorbic acid [22],  $\text{Fe(CN)}_6^{4-}$ , and aqueous sulfite, are summarised in Table 10. The activation parameters for the reactions are very similar and can be used in an isokinetic plot of  $\Delta H^\ddagger$  versus  $\Delta S^\ddagger$ . The isokinetic plot is shown in Fig. 9. It is concluded that a common mechanism exists, with  $\Delta G^\ddagger = 72 \pm 3$  kJ mol<sup>-1</sup> and  $\beta_0 = 324 \pm 22$  K. Below this temperature the reactions are controlled by  $\Delta H^\ddagger$ , that is, the lower the  $\Delta H^\ddagger$  value, the higher the rate constant; and above this temperature by  $\Delta S^\ddagger$  values. It was evident that from the studies carried out on this work, that an outer-sphere electron transfer took place with the reduction of the Co(III) centre to  $\text{Co}_{(\text{aq})}^{2+}$  when reductants such as L-ascorbic acid [22],  $\text{Fe(CN)}_6^{4-}$ , and aqueous sulfite are used. The molybdenum(VI) centre, however, remains unaffected.

### 3.7. Calculation of self-exchange rate constants for both aqueous sulfite (as $\text{SO}_3^{2-}$ ) and $\text{Fe(CN)}_6^{4-}$

Redox reactions involving cobalt(III) complexes are often viewed as outer-sphere electron transfer reactions [22]. The equations from the Marcus theory [23–25] are used in predicting rate constants for heteronuclear outer-sphere redox reactions from the self-exchange rate constants for each partner and the overall equilibrium constant:

$$k_{12} = (k_{11}k_{22}k_{12}f_{12})^{1/2} \quad (15)$$

$$\log f_{12} = \frac{(\log K_{12})^2}{4 \log \left( \frac{k_{11}k_{22}}{10^{22}} \right)} \quad (16)$$

$$\ln K_{12} = \frac{nF(E_{11}^\circ - E_{22}^\circ)}{RT} \quad (17)$$

where  $k_{22}$ , the self-exchange rate constant for either reductant,  $k_{11}$ , the self-exchange rate constant for the oxidant,  $E_{11}^\circ$ , redox potential for the oxidant  $\{[(\text{H}_3\text{N})_5\text{CoOMoO}_3]^+\}$ ,  $E_{22}^\circ$ , redox potential for the reductant,  $K_{12}$ , the equilibrium constant for the cross reaction, and  $k_{12}$ , the second order rate constant for the cross reaction. Normally one would use the Marcus

equations [23–25] on knowing the self-exchange rates of both reductants and oxidants, in order to calculate  $k_{12}$  and compare it with the observed  $k_{12}$ , but in our case,  $k_{22}$  for aqueous sulfite (as  $\text{SO}_3^{2-}$ ) is not known so we need to calculate it. The self-exchange rate constant,  $k_{22}$ , for  $\text{Fe(CN)}_6^{4-}$  has been reported as  $(0.1\text{--}9) \times 10^4$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup> in water at various ionic strengths [26,27]. The self-exchange rate constant,  $k_{11}$ , for  $[(\text{H}_3\text{N})_5\text{CoOMoO}_3]^+$ , is  $2.32 \times 10^{-5}$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup> [22],  $k_{12}$  ( $k'_1$ ) ( $0.77$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup> at 25.0 °C for the cross reaction involving  $\text{SO}_3^{2-}$ ) is the cross-reaction rate constant,  $E_{22}^\circ$ , -0.93 V [28] for the  $\text{SO}_4^{2-}$ ,  $\text{H}_2\text{O}/\text{SO}_3^{2-}$ ,  $\text{OH}^-$  couple, while  $E_{11}^\circ$  for  $[(\text{H}_3\text{N})_5\text{CoOMoO}_3]^+$ , +0.12 V [22].  $K_{12}$  is the equilibrium constant ( $5.67 \times 10^{17}$ ), and  $k_{22}$  is the self-exchange rate constant for aqueous sulfite as  $\text{SO}_3^{2-}$ , which is unknown. From the rate constant for the aqueous sulfite (as  $\text{SO}_3^{2-}$ ) reduction of  $[(\text{H}_3\text{N})_5\text{CoOMoO}_3]^+$  ( $k_{12} = 0.77$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>), the self-exchange rate constant,  $k_{22}$ , for aqueous sulfite (as  $\text{SO}_3^{2-}$ ) was calculated to be  $5.37 \times 10^{-12}$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>.

For the reaction involving  $\text{Fe(CN)}_6^{4-}$ , where  $k_{12}$  ( $k'_1$ ) ( $1.13$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup> at 25.0 °C) is the cross-reaction rate constant,  $k_{11}$ , the self-exchange rate constant for  $[(\text{H}_3\text{N})_5\text{CoOMoO}_3]^+$ , is  $2.32 \times 10^{-5}$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup> [22],  $k_{22}$  is the self-exchange rate constant for

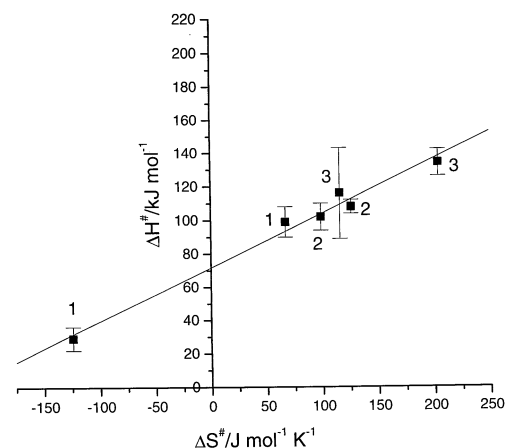


Fig. 9. An isokinetic plot of the activation parameters for the reduction of  $[(\text{H}_3\text{N})_5\text{CoOMoO}_3]^+$  by some reducing agents.

$\text{Fe}(\text{CN})_6^{4-}$ ,  $E_{22}^\circ$ , + 0.36 V at zero ionic strength [29] for the  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  couple, while  $E_{11}^\circ$  for  $[(\text{H}_3\text{N})_5\text{CoOMoO}_3]^+$ , + 0.12 V [22]. We calculated  $k_{22}$  for  $\text{Fe}(\text{CN})_6^{4-}$  as  $1.10 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  from the Marcus equations [23–25], which is much higher than the reported value of  $(0.1\text{--}9) \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  in water at various ionic strengths [26]. This discrepancy probably is due to the method carried out and the approximations used in the calculations by the authors [27] in determining  $k_{22}$  for  $\text{Fe}(\text{CN})_6^{4-}$ . We believe that our  $k_{22}$  value is correct under the controlled conditions carried out for the cross reaction.

In summary,  $k_{22}$ , the self-exchange rate constant, for aqueous sulfite (as  $\text{SO}_3^{2-}$ ) was calculated to be  $5.37 \times 10^{-12} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ , while for  $\text{Fe}(\text{CN})_6^{4-}$ , it was calculated to be  $1.10 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  from the Marcus equations [23–25].

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