

## The Reaction of *cis*-Sulphatoaquotetra-Ammine-Cobalt(III) Ion with Chromium(II) Ion in Aqueous Perchloric Acid

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The reduction of *cis*-sulphatoaquotetra-ammine-cobalt(III) ion by chromium(II) in aqueous perchloric acid proceeds through both single- and double-bridged transition states. The rate constants are  $k_{SB} = 0.49/[H^+] + 3.2 + 7.8[H^+]$  and  $k_{DB} = 0.36/[H^+] + 0.37$  ( $l. mole^{-1}sec.^{-1}$ ; 25°C; 1.0 ionic strength) respectively.

### Introduction

Studies of electron transfer reactions over the past fifteen years<sup>1-5</sup> have shown that there are two mechanisms by which electron transfer may proceed: (1), the inner-sphere process, in which the two metal ions share a common ligand in the transition state; and (2), the outer-sphere process, in which the first coordination shells of both metal ions remain intact. The reduction of a complex  $A_4MXY$  (where X and Y are *cis* to one another, and potential bridging groups) may involve single-bridging through either X or Y, or double bridging through both ligands simultaneously (Figure 1). However, such reactions, in which there is more than one possible path for electron transfer, have not been studied extensively.<sup>6-10</sup>

We wish to report our observations on the chromium(II) reduction of *cis*-sulphatoaquotetra-ammine-cobalt(III) perchlorate, an example of this class, and on the nature of the substitution-inert chromium(III) product.

### Experimental Section

**Materials.** Reagent grade perchloric acid (70%), concentrated sulphuric acid, and the inorganic salts were used without further purification.

*cis*-Sulphatoaquotetra-ammine-cobalt(III) perchlorate containing water labelled with oxygen-18 was prepared in a manner similar to the method of Ephraim and Flügel:<sup>11</sup> carbonatotetra-ammine-cobalt(III) sulphate was dissolved in sulphuric acid, heated, allowed to cool, and diluted with oxygen-18 labelled water (1.5 atom per cent). The solution was worked up and the product isolated in the usual way. Found:  $NH_3$ , 20.0%;  $SO_4^{2-}$ , 25.14% (calculated:  $NH_3$ , 20.0%;  $SO_4^{2-}$ , 25.24%).

**Solutions.** Standard sodium perchlorate solutions were prepared by the neutralisation of electrolytic sodium hydroxide with perchloric acid. Chromium(II) perchlorate, obtained by zinc reduction of a chromium(III) perchlorate solution, was stored under a nitrogen.<sup>12</sup> The chromium(II) content was determined by potentiometric titration with potassium permanganate, and the acidity by elution through a Dowex 50W-X8 ( $H^+$  form) ion exchange resin in a nitrogen atmosphere, followed by titration of the eluate with standard base:

$$[H^+]_{\text{solution}} = [H^+]_{\text{total}} - 2[Cr^{II}]$$

**Kinetic Measurements.** The cobalt(III) complex, aqueous perchloric acid, and sodium perchlorate were introduced into a 10 cm. thermostatted optical cell

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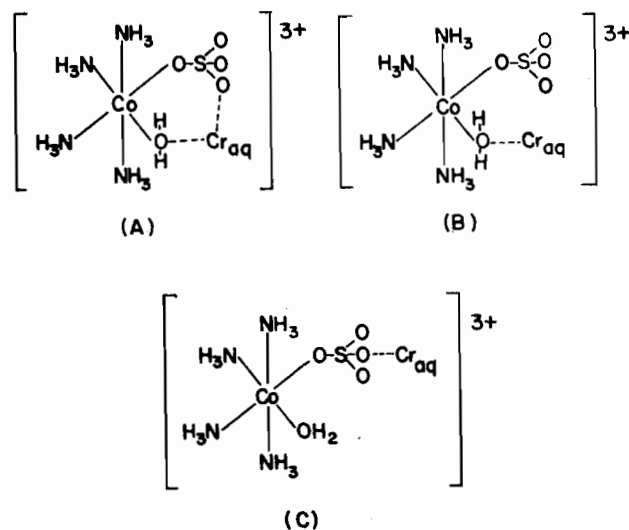


Figure 1. Possible transition states for electron transfer from chromium(II) to *cis*-sulphatoaquotetra-amminecobalt(III) in perchloric acid. (A) Double-bridging; (B) single-bridging through water; (C) single-bridging through sulphate.

and purged with nitrogen for fifteen minutes. A measured amount of chromium(II) solution was injected through a serum cap, the contents of the cell mixed rapidly, and the decrease in optical density followed at 360 nm ( $\epsilon_{\text{complex}}=46$ ) with a Cary 14 spectrophotometer. Solutions of low acidity were degassed before the cobalt(III) complex was added, and nitrogen was continued for a further two minutes.

**Ion Exchange Experiments.** *cis*-Sulphatoaquotetra-amine-cobalt(III) perchlorate ( $5 \times 10^{-5}$  moles) was dissolved in 25 ml. of perchloric acid solution which had been adjusted to an ionic strength of one with sodium perchlorate. The solution was deoxygenated by bubbling nitrogen for twenty minutes, and then a stoichiometric amount of chromium(II) added. After reaction the solution was diluted with ten volumes of water and passed over an ion exchange resin (Dowex 50W-X8 in the hydrogen ion form, in a 1 cm. by 3 cm. column). This was washed with distilled water and then with 0.2 M perchloric acid to remove the +1 charged species (sulphatopenta-aquochromium(III) ion). The eluate was collected in small portions, made alkaline with 25% sodium hydroxide, and oxidised with 30% hydrogen peroxide. The column was considered to be free of the +1 species when the treated eluate was no longer coloured. All the portions were combined, heated to destroy excess peroxide, diluted to 500 ml. with distilled water, and the optical density measured at 372 nm ( $\epsilon=4830$ ). The +3 species, hexa-aquochromium(III) ion, was eluted with 4 M perchloric acid and treated in the same way. Cobalt(II) precipitated as the oxide and was removed by filtration.

**Oxygen-18 Tracer Experiments.** The oxygen-18 reactions were carried out in a manner similar to the ion exchange above. One millimole of the labelled complex was dissolved in 100 ml. of the perchloric acid solution, degassed, and treated with the stoichiometric amount of chromium(II) iron. The reaction mixture was diluted with one volume of water and passed through a 1 cm. by 8 cm. column of Dowex resin. Ten ml. of perchloric acid (0.2 M) was used to wash the column. The eluate was reduced to a volume of 5 ml. by an alcohol-ether azeotrope method.<sup>13</sup> Tetraphenylarsonium chloride was added to precipitate remaining perchlorate ion (most of the perchloric acid having been extracted into the ether), and after filtering the solution was evaporated to dryness under vacuum in a rotary evaporator. The solid resulting was sulphatopenta-aquochromium(III) chloride, and its identity was confirmed by infrared comparison with an authenticated sample of  $(\text{HO}_2)_5\text{CrSO}_4 \cdot \text{Cl}$ , prepared from thionyl chloride and chromium(VI) oxide. The spectra contain peaks at 3400 (s), 1625 (m), 1115 (s), 1045 (s), and 990 (m)  $\text{cm}^{-1}$ . The first two peaks arise from the coordinated water, the latter three from the monodentate sulphate. The material is very hygroscopic and must be stored in a desiccator.

The oxygen of the chromium(III) product was converted to carbon dioxide by the method of Anbar

and Guttman.<sup>14</sup> The relative intensities of the mass 44 and 46 peaks in the mass spectrum of the gas were measured on a Nuclide Model 12-90 Gl. 2 mass spectrometer and compared with those from an unenriched sample of carbon dioxide. The percentage transfer was obtained from the ratio

$$\frac{\% \text{ }^{18}\text{O} (\text{labelled ligand}) - 0.191 \times 100}{0.686 - 0.191}$$

where %  $^{18}\text{O}$  (labelled ligand) is given by the difference

$$(4x + y + 4z + 1)\% \text{ }^{18}\text{O} (\text{gas sample}) - (4x + y + 4z)\% \text{ }^{18}\text{O} (\text{natural})$$

$x$  = number of sulphate groups in molecule

$y$  = number of water molecules from solvent (=4)

$z$  = number of perchlorate groups (reference sample only)

(see Table III).

## Results and Discussion

The reduction of *cis*-sulphatoaquotetra-amine-cobalt(III) by chromium(II) ion is first order in both oxidant and reductant, and in addition shows an acid dependence of the form

$$k_{\text{obs.}} = 0.85 / [\text{H}^+] + 3.6 + 7.8[\text{H}^+] \quad (1)$$

The specific rates observed are listed in Table I. The form of this acid dependence finds some support from those for the reduction of related complexes. Thus

**Table I.** Observed Specific Rates for the Chromium(II) Ion Reduction of *cis*-Sulphatoaquotetra-aminocobalt(III) in Perchloric Acid at 25°C

$[\text{H}^+]$ $M$	$k_{\text{obs.}}$ , $M^{-1} \text{sec.}^{-1}$	$[\text{H}^+]$ $M$	$k_{\text{obs.}}$ , $M^{-1} \text{sec.}^{-1}$
0.05	22.8	0.40	9.2 <sub>7</sub>
0.10	13.6	0.60	9.1 <sub>8</sub>
0.15	9.6 <sub>5</sub>	0.70	10.5
0.20	9.2 <sub>8</sub>	1.00	11.5

$$[\text{Co}^{\text{III}}]_0 = 0.5 - 1.5 \times 10^{-3} M; \quad [\text{Cr}^{\text{II}}]_0 = 0.02 - 0.24 M; \quad \mu = 1.0.$$

the observed specific rate for the chromium(II) reduction of sulphatobis(ethylenediamine)cobalt(III) is similar<sup>15</sup> to the last two terms of (1),

$$k_{\text{obs.}} = 35 + 56[\text{H}^+]$$

suggesting that the first order dependence is due to the sulphate ligand. The observed specific rate for the reduction of aquopentaaminocobalt(III) by chromium(II) is similar<sup>16</sup> to the first two terms of (1),

$$k_{\text{obs.}} = 1.5 / [\text{H}^+] + 0.5$$

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(15) R. T. M. Fraser, *Inorg. Chem.*, 2, 954 (1963).

(16) H. Taube, *Can. J. Chem.*, 37, 129 (1959).

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which suggests in turn that the water ligand is reactive at lower acidities. A comparison of the rate of reduction of the sulphatopenta-amminecobalt(III) ion ( $k = 18.9 M^{-1} \text{ sec.}^{-1}$ ),<sup>17</sup> which it should be pointed out does not show acid dependence, with that for the acid-independent path of the *cis*-sulphatoaquotetra-amminecobalt(III) ion shows that the latter is six times slower. By contrast, *cis* substitution of a water molecule in azidopenta-amminecobalt(III) ion enhances its rate of reduction by iron(II) by a factor of thirty.<sup>6</sup> Again, the acetatopenta-amminecobalt(III) complex is reduced ( $k = 0.32 M^{-1} \text{ sec.}^{-1}$ )<sup>18</sup> about one hundred times slower by chromium(II) than is *cis*-acetatoaquotetra-amminecobalt(III).

At present there is no explanation for the behaviour of the *cis* sulphatoaquo complex, since little is known about the effects of a second ligand which can also act as a bridging group. It has been suggested that the relative reactivities (towards a particular reductant) of two ligands, X and Y, in penta-ammine complexes gives a measure of their effectiveness as bridges in their tetra-ammine complex  $A_4MYX$ . Thus the azide ligand probably provides the electron transfer path in the chromium(II) reduction of *cis*-azido-aquotetra-amminecobalt(III),<sup>6</sup> since (i) the reaction is acid-independent, and (ii) the rate of reduction of the azido penta-ammine is  $10^6$  times faster than that of the aquo complex. Where the rates are quite similar, as they are for the reduction by chromium(II) ion of acetato- and aquopenta-amminecobalt(III) perchlorates, the reduction of the tetra-ammine may well involve double-bridging. *cis*-Acetatoaquotetra-amminecobalt(III) with chromium(II) shows an acid-inverse path,<sup>7</sup> and ion exchange experiments have shown that over a wide range of acidity, acetate is transferred to reductant.

The results of similar ion exchange experiments with the products of the chromium(II)—*cis*-sulphato-aquotetra-amminecobalt(III) reaction are listed in Table II: over the range of acid concentration studied,

Table II. Results of Ion Exchange Experiments<sup>a</sup>

$[H^+]$ , M	(Cr <sup>III</sup> ) <sup>+</sup> %	(Cr <sup>III</sup> ) <sup>3+</sup> %
0.05	73.5	—
0.10	75.5	—
0.50	74.5	1

<sup>a</sup>  $5 \times 10^{-5}$  equivalents of cobalt(III) complex added to  $5 \times 10^{-5}$  equivalents of chromium(II).

Table III. Results of the Labelling Experiments

Complex	$[H^+]$	% <sup>18</sup> O in gas sample	% <sup>18</sup> O labelled ligand	% <sup>18</sup> O transferred
<i>cis</i> -Co(NH <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O*)(SO <sub>4</sub> ) <sub>2</sub> · ClO <sub>4</sub>		0.246	0.686	
Cr(H <sub>2</sub> O) <sub>5</sub> SO <sub>4</sub> · Cl		0.191 <sup>a</sup>		
Cr(H <sub>2</sub> O) <sub>4</sub> (H <sub>2</sub> O*)SO <sub>4</sub> · Cl	1.00	0.1944	0.221	6.02
»	0.50	0.2000	0.263	14.6
»	0.08	0.2105	0.366	33.0

<sup>a</sup> No enrichment: reference compound.

the only chromium(III) product recovered is the sulphatopenta-aquochromium(III) ion. (Previous workers have obtained<sup>20</sup> only 80% recovery of the lower charged species of a number of chromium-carboxylic acid complexes, attributing the loss of the chromium(III) species to destabilization on the resin itself.)

The strong inverse acid-dependence of the reaction suggests that coordinated water participates in the reaction, and that double bridging becomes possible. The water participation was investigated by incorporating oxygen-18 into the cobalt(III) complex. The amounts of labelled water associated with the chromium ion after reaction are listed in Table III: they increase as the hydrogen ion concentration of the reaction mixture is decreased. Because chromium(III) ion is substitution-inert, labelled water can only be transferred from cobalt to chromium during the electron transfer process itself. Since sulphate is transferred to chromium in all the reactions, and water only part of the time, it must be concluded that both single- and double-bridging (the latter involving sulphate and either water or hydroxide, depending on the hydrogen ion concentration; there is no evidence for single-bridging involving water or hydroxide at any stage) can take place.

If this is so, the rate constant for the single-bridged (SB) reduction and that for the double-bridged (DB) reduction can be derived from the isotope data. For any particular reaction,  $x$ ,

$$k_x = \text{percent product by path } x$$

or

$$\frac{k_{DB, \text{ obs.}}}{k_{SB, \text{ obs.}}} = \frac{\text{percent Cr}^{III} \text{ containing } ^{18}\text{O}}{\text{percent Cr}^{III} \text{ containing } ^{16}\text{O}}$$

The relation between the component constants for each path and the overall observed rate law is

$$(\text{acid-inverse}) \quad \frac{0.85}{[H^+]} = \frac{k_{DB}'}{[H^+]} + \frac{k_{SB}'}{[H^+]}$$

$$3.5 = k_{DB} + k_{SB}$$

and

$$(\text{acid-dependent}) \quad 7.8[H^+] = k_{SB}''[H^+]$$

Protonation of the coordinated water would restrict electron transfer to that through the sulphate ligand, so that it may be assumed that the double-bridged

(17) This work.

(18) R. T. M. Fraser, in «Mechanisms of Inorganic Reactions», *Adv. Chem. Ser.*, 49, 121 (1965).

path does not show a third order term ( $k_{DB}''=0$ );

$$k_{DB \text{ obs.}} = k_{DB}'/[H^+] + k_{DB}$$

$$k_{SB \text{ obs.}} = k_{SB}'/[H^+] + k_{SB} + k_{SB}''[H^+]$$

Using the isotope labelling results from any two different hydrogen ion concentrations, the five specific rates can be evaluated. They are:

$$k_{DB}' = 0.36 \text{ sec.}^{-1}, k_{DB} = 0.37 M^{-1} \text{ sec.}^{-1}$$

and

$$k_{SB}' = 0.49 \text{ sec.}^{-1}, k_{SB} = 3.23 M^{-1} \text{ sec.}^{-1}$$

$$k_{SB}'' = 7.8 M^{-2} \text{ sec.}^{-1}$$

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## Conclusion

This reaction is the fourth example of an authenticated double-bridging: the others are the chromium(II) reductions of the *cis*-diazido complexes of tetra-aquochromium(III),<sup>9</sup> tetra-amminecobalt(III),<sup>19</sup> and bis(ethylenediamine)cobalt(III)<sup>19</sup> ions. In the present case, 41 percent of the reaction proceeds through the double-bridged complex at 0.01 *M*  $H^+$ , but this decreases to 31 percent at 0.1 *M* and to 6 percent at 1.0 *M*. Double-bridging is thus not the major path for the reaction, but the results show that even in those cases where a ligand X (here sulphate) is a much better electron mediator than ligand Y, double-bridging can still be important.

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