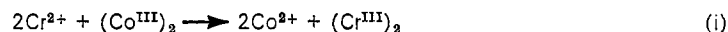


Kinetic Studies on the Reaction of Cr^{2+} with the μ -Amido- μ -sulphato- and μ -Amido- μ -selenato-bis[tetra-amminecobalt(III)] Complexes

By R. S. Taylor, Mark Green, and A. G. Sykes,* Department of Inorganic and Structural Chemistry, The University, Leeds LS2 9JT

The kinetics of the reduction (i) of the μ -amido- μ -sulphato-bis[tetra-amminecobalt(III)] complex with chromium(II) have been studied in perchlorate media, $\mu = 2.0\text{M}$ (LiClO_4). The reaction proceeds in two stages, each involv-



ing the attack of a chromium(II) and reduction of a cobalt(III). Formation of a cobalt(III)-chromium(III) intermediate in the first stage has been studied by the stopped-flow method. The rate law is $-\text{d} \ln [(\text{Co}^{\text{III}})_2]/\text{d}t = k_1[\text{Cr}^{2+}]$, and at 25°C $k_1 = 7.4 \text{ l mol}^{-1} \text{ s}^{-1}$, $\Delta H_1^\ddagger = 8.7 \pm 0.1 \text{ kcal mol}^{-1}$, and $\Delta S_1^\ddagger = -25.3 \pm 0.3 \text{ cal mol}^{-1} \text{ K}^{-1}$. The second stage has been studied by conventional techniques; the rate law is $-\text{d} \ln [\text{Co}^{\text{III}}, \text{Cr}^{\text{III}}]/\text{d}t = (k_2 + k_3[\text{H}^+]^{-1}) [\text{Cr}^{2+}]$. At 25°C $k_2 = 0.256 \text{ l mol}^{-1} \text{ s}^{-1}$, $\Delta H_2^\ddagger = 14.6 \pm 0.7 \text{ kcal mol}^{-1}$ and $\Delta S_2^\ddagger = -12.2 \pm 2.5 \text{ cal mol}^{-1} \text{ K}^{-1}$ and $k_3 = 0.192 \text{ s}^{-1}$, $\Delta H_3^\ddagger = 13.9 \pm 1.0 \text{ kcal mol}^{-1}$, and $\Delta S_3^\ddagger = -15.3 \pm 3.4 \text{ cal mol}^{-1} \text{ K}^{-1}$. Spectra of the intermediate and the final product, believed to be chromium(III) dimer, have been obtained. The first stage of the reaction of the μ -amido- μ -selenato-complex is *ca.* 50 times faster than that of the sulphato-complex $k_1 = 372 \text{ l mol}^{-1} \text{ s}^{-1}$, $\Delta H_1^\ddagger = 7.2 \pm 0.2 \text{ kcal mol}^{-1}$ and $\Delta S_1^\ddagger = -22.6 \pm 0.6 \text{ cal mol}^{-1} \text{ K}^{-1}$. Subsequent reactions could not be studied because of precipitation of selenium.

DETAILS of the preparation of the μ -amido- μ -sulphato-complex, $(\text{NH}_3)_4\text{Co} \cdot \mu(\text{NH}_2\text{SO}_4) \cdot \text{Co}(\text{NH}_3)_4^{3+}$, as the bromide salt were first reported by Werner.¹ I.r. studies

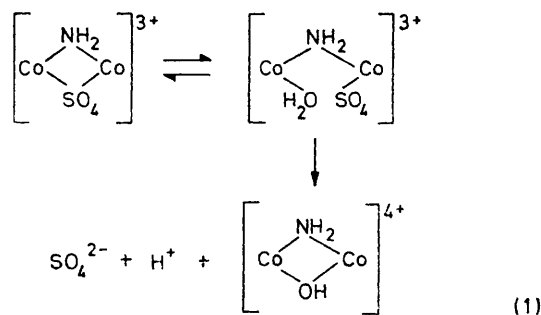
¹ A. Werner, *Annalen*, 1910, **375**, 1.

² (a) K. Nakamoto, J. Fujita, S. Tanaka, and M. Kobayashi, *J. Amer. Chem. Soc.*, 1957, **79**, 4904; (b) N-G. Vannerberg, *Arkiv Kemi*, 1963, **20**, 245; (c) N. Tanaka, H. Sugi, and J. Fujita, *Bull. Chem. Soc. Japan*, 1964, **37**, 640.

have confirmed the presence of a bridging sulphate ion with C_{2v} symmetry.² More recently Thewalt³ has determined the structure of the nitrate salt of the analogous μ -amido- μ -sulphato-bis[bis(ethylenediamine)-cobalt(III)] complex and shown that the sulphate is

³ U. Thewalt, unpublished work, quoted in A. G. Sykes and J. A. Weil, *Progr. Inorg. Chem.*, 1970, **13**, 1.

bonded Co-O-SO₂-O-Co. In solution the μ -amido- μ -sulphato-structure of the ammine complex is retained,⁴ and the complex reacts only slowly to give the μ -amido-aquo-sulphato-complex (which is present in steady-state concentrations) and the μ -amido- μ -hydroxo-complex [reaction (1)].⁴ Since the reaction of the μ -amido-



μ -sulphato-complex with Cr²⁺ is rapid the reactions in (1) do not interfere. The μ -amido- μ -selenato-bis[tetra-amminecobalt(III)] complex has been prepared in a similar way.⁵ Aquation of this complex is about five times faster than that of the μ -amido- μ -sulphato-complex, but is again much too slow for it to interfere with the redox study. Comparisons with related redox reactions have been made.⁶

The First Stage of the Reaction of the μ -Amido- μ -sulphato-complex with Cr²⁺.—This was studied by the stopped-flow method by following the disappearance of the μ -amido- μ -sulphato-complex at the 538 nm peak ($\epsilon = 362 \text{ l mol}^{-1} \text{ cm}^{-1}$). The cobalt(III)–chromium(III) intermediate which is formed has an absorption coefficient $\epsilon = 69 \text{ l mol}^{-1} \text{ cm}^{-1}$ at this wavelength. Pseudo-first-order conditions were used [chromium(II) in large excess], and first-order plots of $\log (\text{OD}'_t - \text{OD}'_\infty)$ against time were linear to 80–90% completion. Absorbance OD'_∞ values were obtained from oscilloscope traces after 6–8 half-lives of the reaction. Rate constants are listed in Table 1, where k_1 is defined by the rate law (2). There was no hydrogen-ion dependence

$$-d \ln[(\text{Co}^{\text{III}})_2]/dt = k_1[\text{Cr}^{2+}] \quad (2)$$

over the range $[\text{H}^+] = 0.06\text{--}1.95\text{M}$. At 25 °C $k_1 = 7.4 \text{ l mol}^{-1} \text{ s}^{-1}$ and from the temperature-dependence ($\log k_1/T$ against $1/T$), $\Delta H_1^\ddagger = 8.7 \pm 0.1 \text{ kcal mol}^{-1}$, and $\Delta S_1^\ddagger = -25.3 \pm 0.3 \text{ cal mol}^{-1} \text{ K}^{-1}$. The activation parameters and errors here and elsewhere have been determined by a least-squares programme, individual rate constants were given equal weighting.

The Second Stage of the Reaction of the μ -Amido- μ -sulphato-complex with Cr²⁺.—The slower second stage of the reduction was followed by conventional spectrophotometric techniques. The most convenient wavelengths were 538 nm (the maximum for the μ -amido- μ -sulphato-complex) and 520 nm (position of maximum absorbance change in this region). At least a ten-fold

excess of chromium(II) was used. About 9–10 half-lives for the first stage of the reaction had elapsed before the first readings were recorded. Plots of $\log (\text{OD}'_t - \text{OD}'_\infty)$ against time were linear to 75–85% completion. An inverse hydrogen-ion dependence was observed over the range $[\text{H}^+] = 0.25\text{--}1.9\text{M}$ (Figure 1). Bimolecular rate constants, k_{obs} , defined by the rate law (3) are in Table 2; k_2 and k_3 values are summarised

$$\frac{-1}{[\text{Cr}^{2+}]} \frac{d \ln [\text{Co}^{\text{III}}_2 \cdot \text{Cr}^{\text{III}}]}{dt} = k_{\text{obs}} = k_2 + k_3[\text{H}^+]^{-1} \quad (3)$$

in Table 3. From the temperature-dependence $\Delta H_3^\ddagger = 14.6 \pm 0.7 \text{ kcal mol}^{-1}$, $\Delta S = -12.2 \pm 2.5 \text{ cal mol}^{-1}$

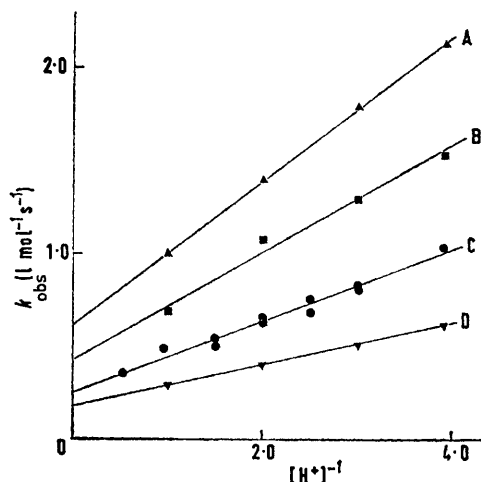


FIGURE 1 The hydrogen-ion dependence for the second stage of the reaction of the μ -amido- μ -sulphato-bis[tetra-amminecobalt(III)] with Cr²⁺, $\mu = 2.0\text{M}$ (LiClO₄); the intercept corresponds to k_2 and the gradient to k_3 ; temperatures: A, 35; B, 30; C, 25; and D, 20 °C

TABLE 1

Rate constants k_1 for the first stage of the reaction of Cr²⁺ with the μ -amido- μ -sulphato-bis[tetra-amminecobalt(III)] complex, $\mu = 2.0\text{M}$ (LiClO₄); the number of runs which have been averaged are indicated in parentheses

Temp. (°C)	$[\text{H}^+](\text{M})$	$10^3[\text{Cr}^{2+}](\text{M})$	$10^4[(\text{Co}^{\text{III}})_2](\text{M})$	$k_1 (\text{l mol}^{-1} \text{s}^{-1})$
25	1.91	27.5	4.52	7.45 (2)
	1.05	27.5	4.68	7.24 (2)
	1.05	28.2	4.68	7.37 (2)
	1.96	14.4	4.52	7.23 (2)
	1.91	27.5	1.51	7.59 (2)
	0.67	28.0	3.14	7.30 (2)
	0.67	28.0	3.14	7.43 (3)
30	1.25	6.9	5.00	9.73 (3)
35	0.5	6.9	4.70	12.0 (3)
40	0.5	6.9	4.70	15.3 (2)
45	0.4	6.9	4.13	20.3 (3)
50	0.4	6.9	4.13	25.1 (3)

K^{-1} , $\Delta H_3^\ddagger = 13.9 \pm 1.0 \text{ kcal mol}^{-1}$, and $\Delta S_3^\ddagger = -15.3 \pm 3.4 \text{ cal mol}^{-1} \text{ K}^{-1}$.

Spectra of the Binuclear Intermediate and Product in the

⁴ M. B. Stevenson, A. G. Sykes, and R. S. Taylor, *J. Chem. Soc. (A)*, 1970, 3214.

⁵ S. W. Foong and A. G. Sykes, to be published.

⁶ A. G. Sykes, Mark Green, and R. S. Taylor, to be published.

Reaction of the Sulphato-complex.—The spectrum of the intermediate was obtained by recording scan spectra (scan time over the range 320–600 nm *ca.* 1 min) during the second stage of the reaction. Kinetic plots at each wavelength were extrapolated back to the time of mixing. An allowance was made for the contributions

allowance was again made for contribution from excess of chromium(II) and the cobalt(II) product. Because a two-term rate law is effective for the second stage the hydrogen-ion concentration was expected to have an influence on the product spectrum. No significant variation was observed over the range $[H^+] = 0.3$ –

TABLE 2

Rate constants k_{obs} for the second stage of the reaction of Cr^{2+} with the μ -amido- μ -sulphato-bis[tetra-amminecobalt(III)] complex

Temp. (°C)	$[H^+](M)$	$10^3[Cr^{2+}](M)$	$10^4[(Co^{III})_2](M)$	$k_{obs} (l\ mol^{-1}\ s^{-1})$
20	1.00	9.08	6.15	0.294
	0.50	9.30	3.97	0.413
	0.33	9.25	4.51	0.516
	0.255	9.19	5.09	0.627
25	1.91	27.0	4.52	0.354
	1.05	27.0	4.68	0.488
	0.67	27.7	3.14	0.54
	0.67	6.59	3.14	0.51
	0.50	27.5	4.70	0.65
	0.50	6.43	4.70	0.64
	0.40	27.6	4.13	0.68
	0.40	6.49	4.13	0.75
	0.33	27.5	4.67	0.83
	0.33	6.43	4.67	0.82
30	0.26	6.40	5.03	1.05
	1.00	6.93	6.15	0.67
	0.50	7.15	3.97	1.08
	0.33	7.10	4.51	1.30
35	0.26	7.04	5.09	1.54
	1.00	6.93	6.15	1.00
	0.50	7.15	3.97	1.40
	0.33	7.10	4.51	1.79
	0.26	7.04	5.09	2.13

TABLE 3

A summary of k_2 and k_3 values for the second-stage in the reaction of Cr^{2+} with the μ -amido- μ -sulphato-bis[tetra-amminecobalt(III)] complex, $\mu = 2.0M$ ($LiClO_4$)

Temp. (°C)	20	25	30	35
$k_2 (l\ mol^{-1}\ s^{-1})$	0.183 ± 0.006	0.256 ± 0.023	0.425 ± 0.080	0.619 ± 0.013
$k_3 (s^{-1})$	0.113 ± 0.002	0.192 ± 0.010	0.291 ± 0.030	0.387 ± 0.05

from excess of chromium(II) [and any chromium(III) impurity], and for the cobalt(II) product from the first stage ($\epsilon_{max} = 4.8$ at 509 nm). The spectrum obtained is believed to be that of the cobalt(III)–chromium(III) binuclear complex $(NH_3)_5Co \cdot SO_4 \cdot Cr(H_2O)_5^{4+}$. A comparison with the spectrum which would be observed for a solution containing equivalent amounts of $Co(NH_3)_5SO_4^{7+}$ and $Cr(H_2O)_5SO_4^{8+}$ is given in Figure 2. While the two spectra are of the same general shape, the mononuclear complexes, and indeed other related mononuclear complexes which might be relevant, are less strongly absorbing. This greater absorption is consistent with the formation of a binuclear complex.

Spectra of the final chromium(III) product were measured on completion of the second stage. An

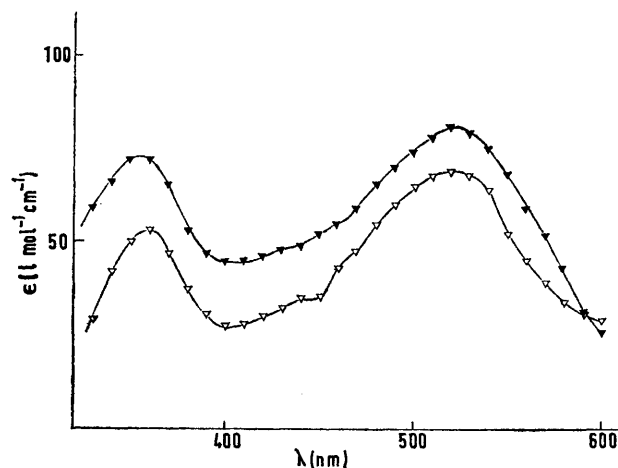


FIGURE 2 The spectrum of the product of the first stage of the reaction of the μ -amido- μ -sulphato-complex believed to be $(NH_3)_5Co \cdot SO_4 \cdot Cr(H_2O)_5^{4+}$ (upper curve), and the spectrum which would be observed for a solution containing equivalent amounts of $Co(NH_3)_5SO_4^{7+}$ and $Cr(H_2O)_5SO_4^{8+}$

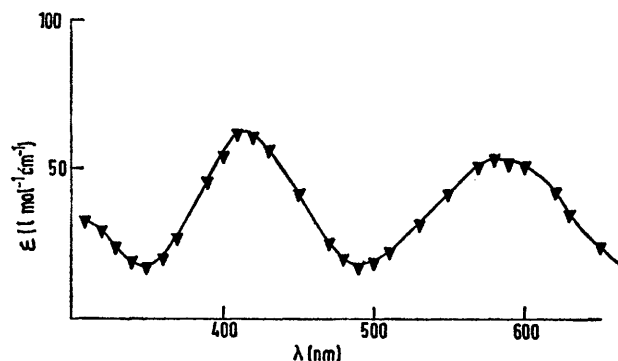


FIGURE 3 The spectrum of the dichromium(III) product of the second stage of the reaction; a possible formula is indicated in (III)

1.75M, and isosbestic points for the second stage of the redox reaction at 392, 433, and 575 nm remained essentially unchanged. Details of spectra (Table 4 and Figure 3), indicate the formation of a binuclear chromium(III) product rather than mononuclear chromium(III) products, which would necessarily be $Cr(H_2O)_5SO_4^{9+}$ and/or $Cr(H_2O)_6^{3+}$. Information regarding spectra^{9–12} of binuclear chromium(III) complexes (Table

⁸ K. M. Jones and J. Bjerrum, *Acta Chem. Scand.*, 1965, 19, 974.

⁹ J. E. Finholt, K. Caulton, K. Kimball, and E. Uhlenhopp, *Inorg. Chem.*, 1968, 7, 610.

¹⁰ M. G. Thompson, Thesis, University of California, Berkeley, 1964, UCRC 11410.

¹¹ J. E. Finholt, Lawrence Radiation Laboratory Report, UCRC, 8879, 1960.

¹² J. E. Finholt and S. N. Deming, *Inorg. Chem.*, 1967, 6, 1533.

⁷ A sample of $[Co(NH_3)_5SO_4]Br$ prepared from carbonato penta-amine-cobalt(III) gave good agreement with existing data, *e.g.*, J. Candlin, J. Halpern, and D. L. Trimm, *J. Amer. Chem. Soc.*, 1964, 86, 1019; L. L. Po and R. B. Jordan, *Inorg. Chem.*, 1968, 7, 526.

5) do not allow a definite assignment of formula to the product to be made. Small changes in absorption were observed during a further 15 h.

Aquation of the Binuclear Intermediate formed in the Reaction of the Sulphato-complex.—Attempts to isolate

TABLE 4

Details of spectra ^a of the binuclear chromium(III) products following the second stage of the reaction of Cr²⁺ with (NH₃)₄Co·μ(NH₂,SO₄)·Co(NH₃)₄³⁺ at 25 °C, μ = 2.0M (LiClO₄)

[H ⁺](M)	λ (nm)	ε (l mol ⁻¹ cm ⁻¹)	λ (nm)	ε (l mol ⁻¹ cm ⁻¹)
0.19	417	66	582	54
0.31	419	56	582	48
1.68	416	76	580	58
1.75	418	62	584	52

^a Absorption coefficients are quoted per mole of complex and not per chromium(III).

the cobalt(III)–chromium(III) intermediate (NH₃)₅Co·SO₄·Cr(H₂O)₅⁴⁺ were unsuccessful (see Experimental section). A solution of the binuclear intermediate

TABLE 5

Details of spectra ^a of known binuclear chromium(III) complexes, and of Cr(H₂O)₅SO₄⁺

Complex	λ (nm)	ε (l mol ⁻¹ cm ⁻¹)	λ (nm)	ε (l mol ⁻¹ cm ⁻¹)	Ref.
(H ₂ O) ₄ Cr·μ(OH,SO ₄)Cr(H ₂ O) ₄ ³⁺	422	42.0	585	39.0	9
(H ₂ O) ₅ Cr·OH·Cr(H ₂ O) ₅ ⁵⁺	420	42.0	598	32.2	10
(H ₂ O) ₄ Cr·μ(OH,OH)Cr(H ₂ O) ₄ ⁴⁺	416	40.6	580	34.6	10
	416	40.2	580	34.4	11
Cr(H ₂ O) ₅ SO ₄ ⁺	417	37.6	587	38.0	12
	418	38.0	588	37.4	8

^a Absorption coefficients are quoted per mole of complex and not per chromium(III) as in refs. 8–12.

was prepared by the reaction of the μ-amido-μ-sulphato-bis[tetra-amminecobalt(III)] complex with chromium(II) in *ca.* 10% excess of the 1:1 stoichiometric amount. The aquation of the intermediate to mononuclear complexes is slow and could be studied by following the decrease in absorption at the 520 nm maximum. The absence of a marked shift from the 520 nm peak suggests that Co(NH₃)₅SO₄⁺ (ε_{max} = 64 ± 2 at 515 nm) and not Co(NH₃)₅H₂O³⁺ (ε_{max} = 47.3 at 490 nm) is the predominant cobalt(III) product.¹³ At 25 °C the rate of aquation of Co(NH₃)₅SO₄⁺ (*ca.* 11 × 10⁻⁷ s⁻¹)¹⁴ and Cr(H₂O)₅SO₄⁺ (8.4 × 10⁻⁷ s⁻¹ in 1M-HClO₄, μ = 1.00M)¹² are of the same order of magnitude and both complexes would be expected to form. The latter has absorption peaks at 417 and 587 nm (Table 5). Rate constants for the aquation of the intermediate at 25 °C and μ = 2.0M (LiClO₄) are in the region 10⁻⁴–10⁻⁵ s⁻¹. The kinetics are complex in that there is at least one subsequent aquation reaction, and some dichromium(III) product is also present. There was no indication of a significant hydrogen-ion dependence over the range [H⁺] = 0.3–1.75M.

¹³ See, *e.g.*, values quoted in R. Davies, A. K. E. Hagopian, and A. G. Sykes, *J. Chem. Soc. (A)*, 1969, 623.

¹⁴ H. Taube and F. A. Posey, *J. Amer. Chem. Soc.*, 1953, **75**, 1463.

The Reaction of the μ-Amido-μ-selenato-complex with Cr²⁺.—It was possible to study only the first stage of the reaction because a precipitate of selenium forms subsequently. The first stage is rapid and was studied by the stopped-flow method. There is a decrease in absorption at the 542 nm peak of the μ-amido-μ-selenato-complex (ε = 315), and this is consistent with the reduction of cobalt(III). Pseudo-first-order plots were generally linear to >75% completion; OD'_∞ values were as observed after 8–10 half-lives (*t*_{1/2} *ca.* 80 ms at 25 °C). Precipitation of selenium occurred after a few seconds. The OD'_∞ values for runs at 542 nm corresponded to ε = 100 ± 10 l mol⁻¹ cm⁻¹. By analogy with the previous reaction an ε value >60 would be expected at this wavelength if a binuclear intermediate is formed. Since however we do not have details of the spectra of the complexes Co(NH₃)₅SeO₄⁺ and Cr(H₂O)₅SeO₄⁺ a firm assignment is not possible. No attempt was made to determine the full spectrum. Rate constants *k*₁ as defined in equation (2) are shown in Table 6. The reaction is significantly faster than that of the sulphato-complex. At 25 °C *k*₁ = 372 l mol⁻¹ s⁻¹,

Δ*H*₁[‡] = 7.2 ± 0.2 kcal mol⁻¹, and Δ*S*[‡] = -22.6 ± 0.6 cal mol⁻¹ K⁻¹.

TABLE 6

Rate constants *k*₁ for the first stage of the reaction of Cr²⁺ with the μ-amido-μ-selenato-bis[tetra-amminecobalt(III)] complex, μ = 2.0M (LiClO₄); numbers of runs indicated in parentheses

Temp.(°C)	[H ⁺](M)	10 ³ [Cr ²⁺](M)	10 ⁴ [(Co ^{III}) ₂](M)	<i>k</i> ₁ (l mol ⁻¹ s ⁻¹)
35	0.50	9.75	4.90	569 (3)
30	0.50	9.75	4.90	460 (2)
25	1.05	27.9	3.90	360 (3)
	0.96	37.9	3.90	371 (3)
	0.76	91.5	3.90	363 (2)
	0.50	9.75	4.90	387 (3)
20	0.50	9.75	4.90	279 (3)
15	0.50	9.75	1.56	237 (4)
	0.50	9.75	4.90	239 (3)

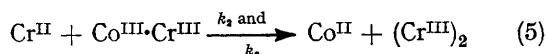
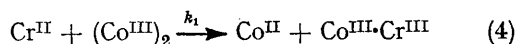
DISCUSSION

Although a full account of their work has not appeared, Miller *et al.*¹⁵ have reported a rate constant 360 l mol⁻¹ s⁻¹ for the reaction of Cr²⁺ with selenato-penta-amminecobalt(III) at 25 °C. This is about 20 times faster than the rate constant for the corresponding

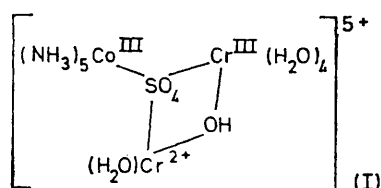
¹⁵ R. G. Miller, D. E. Peters, and R. T. M. Fraser, 'Exchange Reactions,' IAEA, Vienna, 1965, p. 203.

reaction of the sulphato-complex (both at $\mu = 1.0\text{M}$).^{15,16} The reduction of the μ -amido- μ -selenato-complex with Cr^{2+} is similarly faster than the reaction of the μ -amido- μ -sulphato-complex (factor of 50). It has been shown that uncomplexed selenate is rapidly reduced by the Cr^{2+} to elemental selenium, and in the present study we conclude that Cr^{2+} reduces either free selenate or the selenate ligand in a mononuclear or binuclear chromium(III) complex. The faster Cr^{2+} reduction of the selenato-cobalt(III) complexes compared to the sulphato-cobalt(III) complexes can be explained in terms of the ease with which these oxyanions are themselves reduced. The reaction sequence which is observed for the sulphato-complex is probably effective also for the selenato-complex.

The mechanism of the reaction of the μ -amido- μ -sulphato-complex can be written as reactions (4) and (5).

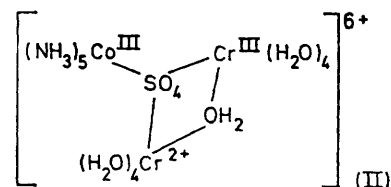


As already indicated the cobalt(III)-chromium(III) complex in (4) is in all probability the μ -sulphato-[penta-amminecobalt(III)][penta-aquochromium(III)] complex, $(\text{NH}_3)_5\text{Co}\cdot\text{SO}_4\cdot\text{Cr}(\text{H}_2\text{O})_5^{4+}$. Details of the mechanisms for k_2 and k_3 in the second stage (5), although not as certain, are of no less interest. If k_2 and k_3 are both inner-sphere, which is generally the preferred route for reactions of Cr^{2+} , then two products $(\text{H}_2\text{O})_5\text{Cr}\cdot\text{SO}_4\cdot\text{Cr}(\text{H}_2\text{O})_5^{4+}$ and $(\text{H}_2\text{O})_5\text{Cr}\cdot\text{OH}\cdot\text{Cr}(\text{SO}_4)(\text{H}_2\text{O})_4^{3+}$ respectively would be expected. The fact that product spectra are independent of hydrogen-ion concentration may not in itself be important, since no significant spectral shift would be expected for chromium(III) complexes which differ only slightly in composition. However we also note the high enthalpy of activation for k_2 , $\Delta H^\ddagger = 14.6 \text{ kcal mol}^{-1}$, which suggests that the mechanism is different from that for k_1 . The inverse hydrogen-ion dependence for k_3 is consistent with hydroxy-bridging, but whether it is reasonable to invoke remote attack of the Cr^{2+} , when the electron has subsequently to be transferred to the cobalt(III) centre, is not clear. As a possible alternative we suggest for k_3 an activated complex as in (I) in which the Cr^{2+} makes use of two bridging ligands. Similarly (II) may

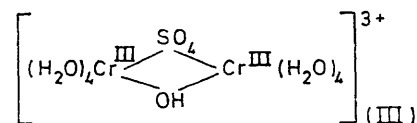


be effective for the k_2 path. Both (I) and (II) would be expected to give the same product (III) following

¹⁶ J. Candlin *et al.*, ref. 7. Activation parameters obtained by these workers for the reaction of Cr^{2+} with $\text{Co}(\text{NH}_3)_5\text{SO}_4^{4+}$ were $\Delta H^\ddagger = 6.2 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -32 \text{ cal mol}^{-1} \text{ K}^{-1}$; R. T. M. Fraser, *Inorg. Chem.*, 1963, 2, 954 has reported values $\Delta H^\ddagger = 8.3 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -25 \text{ cal mol}^{-1} \text{ K}^{-1}$.



electron transfer, loss of a labile cobalt(II), and in the case of (II) loss of a proton. Finholt *et al.* have pre-



pared (III) by refluxing a concentrated solution of chromium(III) sulphate in alkaline solution, and then separating (III) by an ion-exchange procedure. Details of the spectrum which they obtained are given in Table 5. There is good agreement in ϵ values. Although we consider formation of (III) to be a strong possibility, other products clearly cannot be excluded. Strong supporting evidence for a double-bridged activated complex has been obtained in the study of the Cr^{2+} reduction of the μ -amido- μ -phosphato complex.⁶ It is not clear to us however why a singly-bridged activated complex should provide a favourable reaction pathway for k_1 , while a double-bridged activated complex should be required for k_2 and k_3 . The tendency of one co-ordination sphere of the cobalt(III)-chromium(III) intermediate to rotate relative to the other may be important. A further factor, about which we have no information but which may nevertheless influence the mechanism of the reaction is the relative stabilities of the complexes $(\text{H}_2\text{O})_4\text{Cr}\cdot\mu(\text{OH},\text{SO}_4)\cdot\text{Cr}(\text{H}_2\text{O})_4^{3+}$ and $(\text{H}_2\text{O})_5\text{Cr}\cdot\text{SO}_4\cdot\text{Cr}(\text{H}_2\text{O})_5^{4+}$. The latter has not as yet been isolated (or identified). The rate constant k_3 and activation parameters ΔH_3^\ddagger and ΔS_3^\ddagger are composite terms since they include the step in which the chromium(III) conjugate-base form is produced.

EXPERIMENTAL

Samples of the complexes $[(\text{NH}_3)_4\text{Co}\cdot\mu(\text{NH}_2,\text{SO}_4)\cdot\text{Co}(\text{NH}_3)_4]\text{Br}_3\cdot\text{H}_2\text{O}$ ^{1,17} and $[(\text{NH}_3)_4\text{Co}\cdot\mu(\text{NH}_2,\text{SeO}_4)\cdot\text{Co}(\text{NH}_3)_4](\text{ClO}_4)_3\cdot 1.5\text{H}_2\text{O}$ ⁵ were prepared as described elsewhere. Stock solutions of chromium(II) perchlorate (0.25M in 0.6M-HClO₄) were prepared by electrolytic reduction of chromium(III) perchlorate at a mercury-pool cathode. The chromium(II) was determined spectroscopically ($\epsilon = 4.82$ at 715 nm). Techniques used for storing and transferring the chromium(II) under air-free conditions were as used in previous work in these laboratories. A Durrum-Gibson stopped-flow spectrophotometer and Unicam SP 500 and 800 (recording) spectrophotometers were used. The selenium which was precipitated following the first stage of the reaction of the μ -amido- μ -selenato-complex was identified (a) by its brick-red colour, (b) its

¹⁷ M. B. Stevenson and A. G. Sykes, *J. Chem. Soc. (A)*, 1969, 2979.

insolubility in dilute mineral acid, and (c) its solubility in hot 9M-H₂SO₄.

Details of the procedure used in attempting to isolate the cobalt(III)–chromium(III) intermediate were as follows. To an almost saturated solution of the μ -amido- μ -sulphato-complex (bromide salt) in 2M-HClO₄ at 35–40 °C, a 5–10% excess of Cr²⁺ in 2M-HClO₄ was added. After sufficient time had elapsed for the completion of the first stage the vessel was opened to the atmosphere to remove excess of Cr²⁺ by reaction with oxygen. On cooling the solution we were unable to isolate any solid, and even when the technique of freezing in an ice–salt mixture and slowly warming to room temperature was used, no solid was

obtained. The solution was then divided into two. To one half concentrated HBr was added to *ca.* 1M, and to the other half sulphuric acid was added to *ca.* 1M. In neither case was any solid obtained even on repeated cooling (ice–salt) and warming. It is concluded that the intermediate is very much more soluble than the original μ -amido- μ -sulphato-dicobalt complex. No attempt was made to isolate the final chromium(III) product.

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