

Inter- and Intramolecular Reactions of Binuclear Chromium(III) Amine Complexes with Bridging and Terminally Coordinated Carboxylate

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Springborg, J., 1992. Inter- and Intramolecular Reactions of Binuclear Chromium(III) Amine Complexes with Bridging and Terminally Coordinated Carboxylate. – Acta Chem. Scand. 46: 1047–1054.

It is shown that, in aqueous, acidic solution, the cation $\Delta, \Lambda\text{-(en)}_2\text{Cr(OH)(CF}_3\text{COO)-Cr(en)}_2^{4+}$ (I) enters into a rapidly established equilibrium with the monohydroxo-bridged species $\Delta, \Lambda\text{-(H}_2\text{O)(en)}_2\text{Cr(OH)Cr(en)}_2\text{(OCOCF}_3\text{)}^{4+}$ (III). The equilibrium has been studied spectrophotometrically [all constants mentioned in the following are for $I = 1.0 \text{ M (NaClO}_4\text{)}$ and 25°C]: $K_1 = k_1/k_{-1} = [\text{III}]/[\text{I}] = 0.39(2)$; $\Delta H^\circ = -1(2) \text{ kJ mol}^{-1}$; $\Delta S^\circ = -10(8) \text{ J mol}^{-1} \text{ K}^{-1}$. $k_1 = 5.4(5) \times 10^{-3} \text{ s}^{-1}$; $\Delta H^\ddagger = 68(3) \text{ kJ mol}^{-1}$; $\Delta S^\ddagger = -61(10) \text{ J mol}^{-1} \text{ K}^{-1}$; $k_{-1} = 1.37(11) \times 10^{-2} \text{ s}^{-1}$; $\Delta H^\ddagger = 69(3) \text{ kJ mol}^{-1}$; $\Delta S^\ddagger = -51(9) \text{ J mol}^{-1} \text{ K}^{-1}$. The monohydroxo-bridged species III deprotonates to $\Delta, \Lambda\text{-(HO)(en)}_2\text{Cr(OH)Cr(en)}_2\text{(OCOCF}_3\text{)}^{3+}$ (IV), and the acid-dissociation constant was determined potentiometrically, $\text{p}K_a = 3.4(2)$; $\Delta H^\circ = 42(10) \text{ kJ mol}^{-1}$; $\Delta S^\circ = 75(36) \text{ J mol}^{-1} \text{ K}^{-1}$. The two new monohydroxo-bridged species, III and IV, were characterized in solution only.

In basic solution I deprotonates, $\text{p}K_a = 9.4(1)$, forming the oxo-bridged species $\Delta, \Lambda\text{-(en)}_2\text{Cr(O)(CF}_3\text{COO)Cr(en)}_2^{3+}$ (II), which undergoes an extremely fast carboxylato bridge cleavage giving IV. The reaction of II is first-order in hydroxide and may involve C–O rather than Cr–O bond cleavage. The second-order rate constant, possibly a composite term, is $k_2 = 4.8(2) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$; $\Delta H^\ddagger = 32(3) \text{ kJ mol}^{-1}$; $\Delta S^\ddagger = -66(11) \text{ J mol}^{-1} \text{ K}^{-1}$.

The monohydroxo-bridged species (III and its basic form IV) are unstable in acidic and basic solutions. In acidic and weakly basic solutions the dominant reaction (in addition to the equilibration reaction with I) is an intramolecular reaction of IV to give the dihydro-bridged species $\Delta, \Lambda\text{-(en)}_2\text{Cr(OH)}_2\text{Cr(en)}_2^{4+}$ (V): $k_3 = 4.8(1) \times 10^{-2} \text{ s}^{-1}$; $\Delta H^\ddagger = 78(1) \text{ kJ mol}^{-1}$; $\Delta S^\ddagger = -9(3) \text{ J mol}^{-1} \text{ K}^{-1}$. In more basic solutions, competition was observed between the intramolecular reaction (k_3) and an intermolecular base-catalyzed hydrolysis of the carboxylato ligand (k_4) to give the monohydroxo-bridged species $\Delta, \Lambda\text{-(HO)(en)}_2\text{Cr(OH)Cr(en)}_2\text{(OH)}^{3+}$ (VIII). The latter reaction is first-order in hydroxide, and it dominates completely at pH 13. The second-order rate constant was determined to be $k_4 = 4.8(1) \text{ M}^{-1} \text{ s}^{-1}$; $\Delta H^\ddagger = 88(2) \text{ kJ mol}^{-1}$; $\Delta S^\ddagger = 63(6) \text{ J mol}^{-1} \text{ K}^{-1}$. The acid-dissociation constants of NH_4^+ and of $(\text{HOCH}_2)_3\text{CNH}_3^+$ (trisH⁺) were determined in 0.1 M NH_4^+ (or trisH⁺), 0.9 M NaClO_4 by glass-electrode measurements: $\text{p}K_a(\text{NH}_4^+) = 9.465(5)$; $\Delta H^\circ = 59.6(6) \text{ kJ mol}^{-1}$; $\Delta S^\circ = 18.8(21) \text{ J mol}^{-1} \text{ K}^{-1}$; $\text{p}K_a(\text{trisH}^+) = 8.231(6)$; $\Delta H^\circ = 53.4(11) \text{ kJ mol}^{-1}$; $\Delta S^\circ = 21.6(38) \text{ J mol}^{-1} \text{ K}^{-1}$.

Hydroxo-bridged polynuclear chromium(III) complexes have been studied intensively during the last two decades, and a general understanding of the mechanistic, thermodynamic, spectroscopic and structural aspects has been achieved.^{1–5} The study of these species has relation to soil chemistry, solid state physics, and to bioinorganic chemistry.^{1,2} The relation to bioinorganic chemistry arises from the fact that many metalloproteins or metalloenzymes contain metal clusters held together by hydroxo bridges. Many of these biological systems, however, contain additional bridges, and hemerythrin may be mentioned as one well known example.^{6,7} This is a binuclear iron(II) oxygen carrier, which has two carboxylato bridges and one hydroxo bridge. Similar hetero-bridged complexes are known for chromium(III), but the properties of these complexes have

been studied far less than those containing only hydroxo bridges.^{8–10} We recently described the synthesis and crystal structure of the hetero-bridged complex $\Delta, \Lambda\text{-(en)}_2\text{Cr(OH)(CF}_3\text{COO)Cr(en)}_2^{4+}$ (I).^{10,*} In the present work we report a kinetic and thermodynamic investigation of a series of inter- and intramolecular reactions of this complex in acidic and basic solutions.

Experimental

Materials and instrumentation. $\Delta, \Lambda\text{-[(en)}_2\text{Cr(OH)(CF}_3\text{COO)Cr(en)}_2\text{]Br}_4 \cdot 4\text{H}_2\text{O}$ was prepared as described

* Structures I–VIII are shown later in Scheme 1.

Table 1. Acid-dissociation constants of NH_4^+ and trisH^+ in 0.1 M $\text{NH}_4\text{ClO}_4/0.1$ M trisHClO_4 , 0.9 M NaClO_4 .

Acid	T / °C	$K_a(\text{obs})$ / 10^{-10} M	$K_a(\text{calc})^a$ / 10^{-10} M
NH_4^+	25.0	3.42	3.44 ^b
NH_4^+	15.0	1.51	1.49
NH_4^+	9.9	0.944	0.952
trisH^+	25.0	58.9	59.7
trisH^+	15.0	29.0	28.1
trisH^+	8.1	15.9	16.1

^aCalculated using $\Delta H^\circ = 59.6(6)$ kJ mol⁻¹ and $\Delta S^\circ = 18.8(21)$ J mol⁻¹ K⁻¹ for NH_4^+ and $\Delta H^\circ = 53.4(11)$ kJ mol⁻¹ and $\Delta S^\circ = 21.6(38)$ J mol⁻¹ K⁻¹ for trisH^+ . ^bThis value is identical to the value $\text{p}K_a = 9.463$ ($K_a = 3.44 \times 10^{-10}$ M) reported for the same conditions.¹⁵

previously.¹⁰ All other chemicals were of analytical grade. Kinetic data for the slow reactions were obtained using a Perkin-Elmer Lambda diode array spectrophotometer. The fast reactions were monitored using stopped-flow apparatus, either Dionex or Hi-Tech PQ/SF-53. Visible absorption spectra were measured using the diode array spectrophotometer (resolution 1.5 nm and scan time 0.1 s per spectrum or resolution 0.25 nm and scan time 0.1 s per 100 nm). Potentiometric measurements were made with Radiometer PHM 52 potentiometer using a GK 2301 C combined glass and calomel electrode. The calomel electrode was modified to contain 1 M NaCl.

Measurements and calculations. Pseudo-first-order rate constants, $k_{\text{obs}}(i)$, and spectra of the pure species were calculated from the absorbance, A , as a function of time, t , by means of regression analysis using eqn. (1) or (2).

$$A = A_1 + A_2 \exp(-k_{\text{obs}} t) \quad (1)$$

$$A = A_1 + A_2 \exp[-k_{\text{obs}}(1)t] + A_3 \exp[-k_{\text{obs}}(2)t] \quad (2)$$

For stopped-flow measurements the calculations were based upon absorbances measured at a single wavelength. For diode array measurements the calculations were based upon absorbances measured at 200–300 different wavelengths. The values of k_{obs} given in the following are in each case the average of at least two determinations. The calculations of k_{obs} were based upon the method of successive integration,¹¹ whereas for the diode array measurements, calculations were modified to include, in one calculation, absorbances versus time for many wavelengths.

The hydrolysis of **I** in base was studied using the stopped-flow method. However, since solutions of **I** are unstable and rapidly form an equilibrium mixture of **I** and **III** ($t_{1/2} = 36$ s at 25 °C), it was not possible to conduct the experiments using reactant solutions with pure **I**. As reactant solutions were therefore used, solutions containing **I** and **III** in equilibrium (72% **I** and 28% **III** as calculated from the thermodynamic constants given later in Table 6). Such solutions are unstable (see Results) and were always pre-

pared within minutes before the experiment. When the equilibrium solutions are mixed with the basic buffer solutions, two fast reactions occur. The first is deprotonation of **III** ($\text{p}K_a = 4$ at 0 °C) to form **IV** and the second reaction is hydrolysis of **I** (and its deprotonated form **II**), forming **IV**. The latter reaction was monitored at 485 nm. The change of absorbance followed a first-order expression, and the pseudo-first-order rate constants were independent of the wavelength, as shown by a few additional measurements at 550, 450 and 400 nm.

The kinetics of the base hydrolysis of **IV** (steps 2 and 3, see Results) were studied as described above (stopped-flow) or by dissolving the bromide salt of **I** directly in the basic solvent (diode array, $\lambda = 300$ –600 nm). The latter method was also applied to the study of the acid hydrolysis of **I** ($\lambda = 300$ –600 nm).

The kinetic and thermodynamic studies of the equilibrium between **I** and **III** were performed using diode array measurements ($\lambda = 350$ –550 nm). Solutions of **III** were prepared *in situ* by base hydrolysis of **I**, as discussed under Results.

Activation parameters were estimated by non-linear least-squares calculations using eqn. (3).

$$k_r = (k_B T/h) \exp(-\Delta H^\ddagger/RT + \Delta S^\ddagger/R) \quad (3)$$

The acid-dissociation constant of **III** was determined by glass electrode measurements by adding base to an acidic equilibrium solution of **I** and **III**. Since all species (**I**, **III** and **IV**) are unstable, the pH had to be measured as quickly as possible (20–40 s) after addition of the base, and the pH value at the time of mixing was obtained by linear extrapolation. Since **I** does not exhibit acid–base properties in this pH region (3–4), the concentration of **III** and **IV** could be calculated from the solution stoichiometry. The concentration equilibrium constants were then calculated using the definition $\text{pH} = -\log([\text{H}^+]/M)$. Concentration pH standards were made in the actual salt medium. The acid-dissociation constants of NH_4^+ were determined by measuring the pH of a 0.1 M NH_4ClO_4 , 0.1 M NH_3 , 0.9 M NaClO_4 solution at three different temperatures also using concentration pH standards. The same procedure was used for $(\text{HOCH}_2)_3\text{CNH}_2(\text{tris})$. The concentration of hydroxide ions in buffer solutions was calculated using the parameters given in Table 1, together with the parameters $\text{p}K_w = 13.80$ (25 °C, 1 M NaClO_4) and $\Delta H^\circ(K_w) = 57.86$ kJ mol⁻¹.^{12–14}

Isolation of V from base hydrolysis of IV. The bromide salt of **I** (0.177 g, 0.200 mmol) was dissolved at 25.0 °C in 1.0 M NH_3 , 0.01 M NH_4ClO_4 and 0.99 M NaClO_4 (1.0 ml), and after 58 s a saturated aqueous solution of NH_4Br (1.0 ml) was added and the mixture was cooled in an ice bath. After 2 min the purple precipitate was filtered off and washed with 50% ethanol, 96% ethanol and diethyl ether, and then dried in the air. Yield 0.119 g (81%). The product was identified by its visible absorption spectrum¹⁶ as Δ, Λ -[(en)₂Cr(OH)₂Cr(en)₂]Br₄ · 2H₂O.

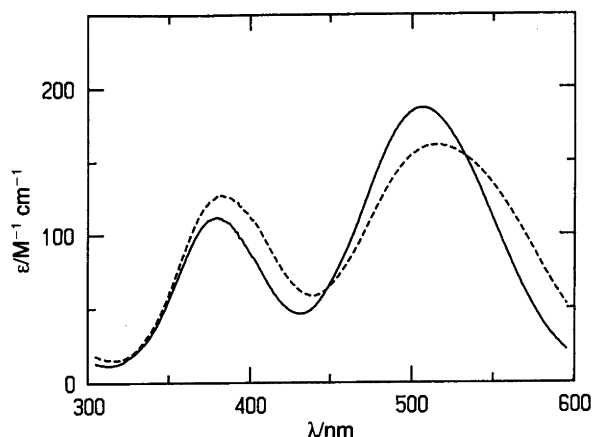


Fig. 1. Absorption spectra of III (—) and its deprotonated form IV (---) measured at 0.8°C as described in the text.

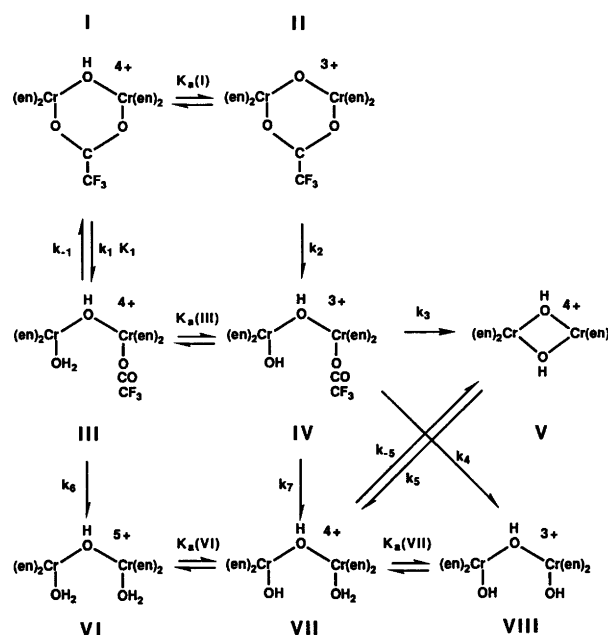
Results and discussion

Base hydrolysis of Δ, Λ -(en)₂Cr(OH)(CF₃COO)Cr(en)₂³⁺ (I). The carboxylato-bridged species I undergoes a series of parallel and consecutive reactions in basic solution: the first step is carboxylato bridge cleavage, the second step involves hydrolysis of the trifluoroacetate ligand by inter- and intramolecular reactions and the last step is an equilibration between monohydroxo- and dihydroxo-bridged species without coordinated trifluoroacetate. The reactions were studied for [OH⁻] = 10⁻⁶–10⁻¹ M at several temperatures in the region 0.8–25.0°C. In all experiments the ionic strength was kept constant using NaClO₄ (I = 1.0 M). In most cases, the three reaction phases were kinetically well separated and could be studied independently. Well defined rate constants were then obtained using the eqn. (1). In some cases, however, the rate constants were separated only by a factor of ten, and reliable constants were then obtained by using eqn. (2), sometimes in combination with monitoring at a wavelength at which the remaining step does not contribute significantly to the change of absorbance. The three steps are discussed separately in the following paragraphs.

Step 1: base catalyzed carboxylato bridge cleavage. The carboxylato-bridged species I undergoes an extremely fast bridge cleavage in basic solution (*t*_{1/2} = 1.6 ms in 0.1 M NaOH at 25°C). The product was not isolated as a salt, but was characterized in solution as described in the following. The colour of freshly prepared basic solutions of the bromide salt of I is reddish-purple compared to the red colour of I in acidic solution. The spectra of these basic solutions, measured at 0.8°C, changed with time and extrapolations back to the time of dissolution gave identical spectra for pH 8–11.6 (0.8°C), respectively. This is interpreted as a very fast base-catalyzed cleavage of a carboxylate bond in I, giving the hydroxo-bridged species Δ, Λ -(HO)(en)₂Cr(OH)Cr(en)₂(CF₃COO)³⁺, IV (Scheme 1). This is strongly supported by the following observations.

Addition of excess acid to the reddish-purple basic solutions of IV resulted in an instantaneous colour shift into red, owing to protonation of the terminally coordinated hydroxo ligand forming Δ, Λ -(H₂O)(en)₂Cr(OH)Cr(en)₂(CF₃COO)³⁺, III. The spectra of the acidic solutions of III changed with time (see later), and extrapolations back to the time when acid had been added gave the same spectrum for any combination of the following conditions [0°C, p*K*_a(NH₄⁺) = 10.4, C_{NH₃} = 0.1 M, C_{dimer} = 2 × 10⁻³ M]: Base hydrolysis at pH 9.4, 10.4 or 11.4 (ammonia buffer) was followed by addition of excess perchloric acid to give [H⁺] = 0.1 or 0.01 M for the acidified solutions. Since the basic solutions are unstable, the addition of acid was made as quickly as possible and the same result was obtained when acid was added 5 or 10 s after the complex had been dissolved in the base. This shows that the initial fast reaction in base must have *t*_{1/2} < 1 s, and also that the subsequent reactions in base must have *t*_{1/2} ≫ 10 s (0°C), as confirmed by the kinetic studies described in the following.

The spectra of III and IV are shown in Fig. 1. The first ligand-field band of the hydroxo species IV (516 nm) is red-shifted 10 nm relative to that of the aqua species I (506 nm), which is close to the value 10–11 nm predicted on the basis of spectral data reported¹⁶ for the analogous binuclear species VI–VIII (Scheme 1). The observation that identical spectra for the acid form (III) were obtained at pH 1–2 and that identical spectra for the deprotonated form (IV) were obtained at pH 8–11.6 (tris and ammonia buffers) shows that p*K*_a for this species lies in the region 4–6. This was confirmed by potentiometric pH measurements which gave p*K*_a = 4.02 at 0°C (see Experimental, Tables 2 and 6). The spectral data in the base also show that deprotonation of the hydroxo bridge in IV must be negligible for pH < 12, and it is therefore estimated that p*K*_a must be greater than



Scheme 1.

Table 2. Determination of the acid-dissociation constant of III in 1 M NaClO₄.

T/°C	[IV]/[III]	K _a (obs)/M	K _a (calc) ^a /M
11.0	0.76	1.73 × 10 ⁻⁴	1.92 × 10 ⁻⁴
11.0	1.54	2.07 × 10 ⁻⁴	—
0.0	0.35	8.6 × 10 ⁻⁵	9.46 × 10 ⁻⁵
0.0	0.76	8.2 × 10 ⁻⁵	—
0.0	1.54	11.6 × 10 ⁻⁵	—

^aCalculated from the thermodynamic parameters in Table 6.

13. This is in agreement with the pK_a values of similar monohydroxo-bridged +4 charged ions; e.g. VIII has pK_a > 14.¹⁶

The notion that the reaction (I → IV) could be an acid-base reaction (such as deprotonation of the hydroxo-bridge in I) can be ignored, since in that case the subsequent addition of excess acid would have resulted in quantitative reformation of the starting species. Also note that the thermodynamic and kinetic data for the equilibrium between I and III (see later) strongly support the assignment presented here. The notion that the reaction is hydroxo-bridge cleavage leading to the carboxylato-bridged species (H₂O)(en)₂Cr(CF₃COO)Cr(en)₂(OH)⁴⁺ can be excluded. In that case its equilibrium with I should show a dependence on the hydrogen ion concentration, owing to the acid-base properties of terminally coordinated hydroxide, which clearly is not the case (see later). It is also noted that the reactions of IV to give monohydroxo- and dihydroxo-bridged species (see later) support this assignment.

A kinetic study of the bridge cleavage reaction of I was made by spectrophotometry using the stopped-flow

Table 3. Observed and calculated rate constants for the base hydrolysis of I.

[OH ⁻]/M	k _{obs} /s ⁻¹	k _{calc} /s ⁻¹
T = 25.0 °C		
0.091 80	400	438
0.041 80	185	200
0.016 80	86	80
0.006 84	36.4	32.7
0.001 84	8.1	8.8
T = 15.4 °C		
0.091 80	250	275
0.041 80	123	125
0.016 80	54.5	50.2
0.006 84	24.4	20.5
T = 7.4 °C		
0.091 80	154	182
0.041 80	79.0	82.7
0.016 80	35.0	33.2
0.006 84	16.7	13.5
0.001 84	3.19	3.64

^ak_{calc} = k₂[OH⁻]. Activation parameters for k₂ are given in Table 6.

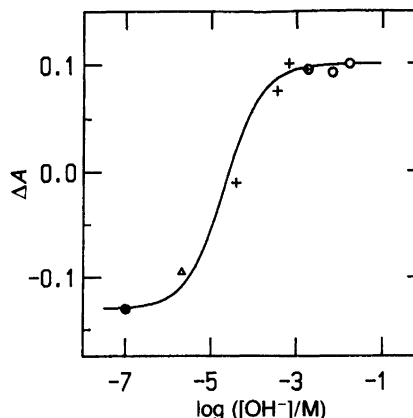


Fig. 2. The observed changes in absorbances ($A_{\text{prod}} - A_{\text{react}}$) as a function of [OH⁻] for stopped-flow measurement of the reaction of I in base (485 nm, 10 mm cell, 25 °C, [dimer] = 3.4 × 10⁻³ M). The hydroxide concentrations were obtained using NaOH (○), ammonia buffer (+) or tris buffer (△). The change in absorbance for the reaction at low pH was calculated from the known absorbances of I and IV and is shown by ●. The solid line is the calculated change.

method. The reaction was studied using NaOH, NH₃/NH₄⁺ buffers, tris/trisH⁺ buffers and mixtures of NaOH and NH₃. In all experiments the change of absorbance followed first-order kinetics.

The change of absorbance varied with the hydroxide ion concentration, but was independent of the base, as seen in Fig. 2. At high [OH⁻] the reaction is followed by an increase in absorbance, while a decrease is observed at low [OH⁻] (λ = 485 nm). This is interpreted as the involvement of an acid-base reaction. Since the product IV does not exhibit acid-base properties in this region (see above) it seems likely that the reaction is a deprotonation of I to form an oxo-bridged species, II. The theoretical change in absorbance for the conversion of I into IV may be calculated from the known molar absorbances of I and IV and is also shown in Fig. 2. Using the latter value, together with the observed absorbance changes, the acid dissociation

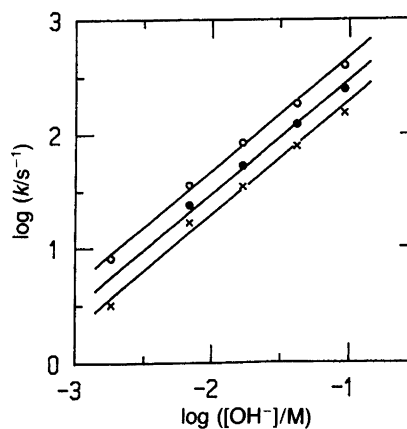


Fig. 3. Calculated (solid line) and observed rate constants for the reaction of I in basic solutions at 7.4 (×), 15.4 (●) and 25 (○) °C.

Table 4. Observed and calculated rate constants for the base hydrolysis of IV.

$[\text{OH}^-]/\text{M}$	$k_{\text{obs}}/\text{s}^{-1}$	$k_{\text{calc}}/\text{s}^{-1}$
$T = 25.0^\circ\text{C}$		
0.000 002	0.049 8	0.047 9
0.000 038	0.044 4	0.048 1
0.000 304	0.047 1	0.049 4
0.000 650	0.050 9	0.051 0
0.001 410	0.056 7	0.054 6
0.001 700	0.058 7	0.056 0
0.006 290	0.080 7	0.077 8
0.015 900	0.120	0.123
0.040 600	0.244	0.241
0.093 400	0.500	0.492
$T = 15.4^\circ\text{C}$		
0.000 039	0.015 7	0.016 4
0.000 310	0.016 5	0.016 8
0.003 210	0.022 0	0.020 8
0.006 290	0.024 9	0.025 2
0.015 900	0.037 7	0.038 8
0.040 600	0.071 3	0.073 6
0.093 400	0.142	0.148
$T = 7.4^\circ\text{C}$		
0.000 040	0.006 47	0.006 31
0.000 320	0.006 57	0.006 44
0.003 210	0.008 10	0.007 84
0.006 290	0.009 78	0.009 32
0.015 900	0.013 4	0.014 0
0.040 600	0.025 5	0.025 9
0.093 400	0.054 4	0.051 3
$T = 0.8^\circ\text{C}$		
0.000 039	0.002 85	0.002 76
0.000 436	0.002 61	0.002 83

^aCalculated using eqn. (4) and the parameters in Table 6.

constant of I can be estimated by the method of non-linear least-squares. This gave $\text{p}K_a = 9.4(0.1)$ at 25°C .

In those experiments where the base was hydroxide, the observed pseudo-first-order rate constant, k_{obs} , showed an almost linear dependence of $[\text{OH}^-]$, as shown in Fig. 3. It follows from the discussion above that the double bridged complex is completely deprotonated in this pH region, and that the reaction therefore corresponds to the conversion of II into IV. Least-squares calculations using the expression $k_{\text{calc}} = k_2[\text{OH}^-]$ gave the kinetic parameters shown in Table 6. The agreement between calculated and observed rate constants (Table 3) is not too good, and may indicate that the dependence on the hydroxide ion concentration is more complex than has been assumed, as discussed further in the following section.

Kinetic studies using ammonia and tris buffers were made at 25°C . At $[\text{OH}^-] = 0.0018 \text{ M}$ (25°C), the observed rate constant is 8.1 s^{-1} , when the base is pure hydroxide, but it is 62 s^{-1} for an ammonia buffer ($[\text{NH}_3] = 0.05 \text{ M}$). Also, it was found that the rate constants increase when the buffer concentration is increased: Ammonia buffers with $[\text{OH}^-] = 0.000 35 \text{ M}$ gave $k_{\text{obs}} = 24$ and 42 s^{-1} , respec-

tively, for $[\text{NH}_3] = 0.09 \text{ M}$ and 0.27 M . Several other experiments confirmed these trends, which unambiguously show that the hydrolysis is subject to general base catalysis. A similar result was obtained using tris buffers ($k_{\text{obs}} = 0.22 \text{ s}^{-1}$ for $[\text{OH}^-] = 2 \times 10^{-6} \text{ M}$). Finally, it was found that the accelerating influence by ammonia vanished at very high pH: In 0.05 M NaOH , 0.1 M NH_3 , the rate constant (87 s^{-1}) is nearly identical to the value for 0.05 M NaOH (86 s^{-1}). No attempt was made to study this issue in further detail.

Step 2: base-catalyzed cleavage of the carboxylate bond in IV. The reaction of IV in basic solutions was monitored by the stopped-flow method as described above (7.4 – 25.0°C) and by diode-array spectrophotometry (0.8°C). This gave well defined pseudo-first-order rate constants. The hydroxide ion concentration was varied from 10^{-6} to 10^{-1} M using NaOH and buffer solutions as described above. In this case no general base catalysis was observed. The variation of k_{obs} could be expressed as shown in eqn. (4), and the

$$k_{\text{obs}} = k_3 + k_4[\text{OH}^-] \quad (4)$$

activation parameters for k_3 and k_4 were obtained by a non-linear least-squares calculation. It is seen that all parameters are well defined and that there is good agreement between the calculated and observed rate constants (Tables 4 and 6 and Fig. 4). We interpret k_3 as an intramolecular attack by coordinated hydroxide to give V and k_4 as an intermolecular reaction with hydroxide to give VIII (Scheme 1). This is in agreement with the dependence of the product distribution on the hydroxide ion concentration. The ligand field spectra of the product solutions [calculated using eqn. (2)] varied with the concentration of hydroxide. In 1 M NaOH the spectrum is identical to that of $\Delta, \Lambda\text{-(HO)(en)}_2\text{Cr(OH)Cr(en)}_2\text{(OH)}^{3+}$, VIII. For solutions with $\text{pH} < 11$ the spectra were nearly identical to that $\Delta, \Lambda\text{-(en)}_2\text{Cr(OH)}_2\text{Cr(en)}_2\text{(OH)}^{4+}$, V. At $\text{pH } 10.4$ the kinetic experiment gave $(\epsilon, \lambda)_{\text{max}} = (198, 541)$ for the first ligand-field band, which is close to the values $[(\epsilon, \lambda)_{\text{max}} = (199, 540)]$ reported¹⁶ for V. These observations are in

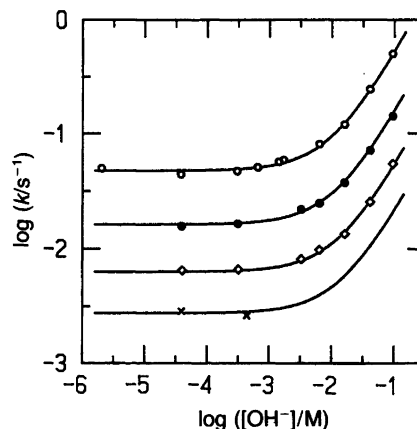


Fig. 4. Calculated (solid line) and observed rate constants for the reaction of IV in basic solutions at 0.8 (\times), 7.4 (\diamond), 15.4 (\bullet) and 25 (\circ) $^\circ\text{C}$.

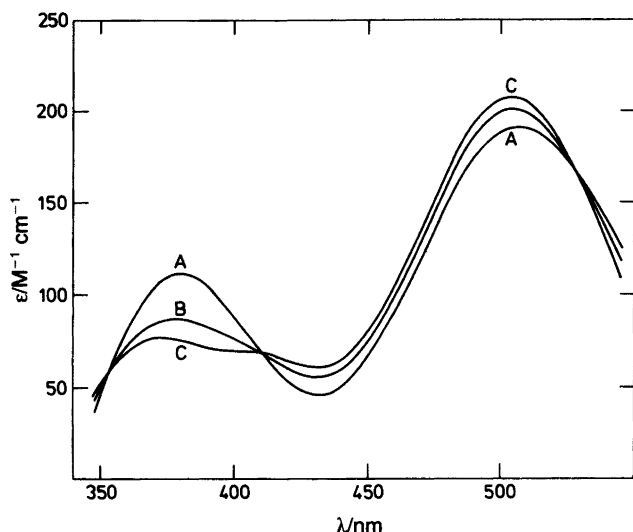


Fig. 5. Absorption spectra of I (C), III (A) and their equilibrium solution (B) measured in 0.01 M HClO₄ and 0.99 M NaClO₄ at 0.8°C.

agreement with the product distribution calculated from eqn. (4). The (intermediate and nearly quantitative) formation of V at low [OH⁻] was further substantiated by the isolation of its sparingly soluble bromide salt in a yield of 81% {within 58 s at [OH⁻] = (1.55 ± 0.19) × 10⁻⁴ M at 25°C, see Experimental}. Note that the formation of this ion and the isolation of the bromide salt occur within a timescale which does not allow the ion's formation via the monohydroxo-bridged species VII, and at a pH at which its equilibrium concentration is very small (calculated from data in Ref. 16). It is therefore certain that the dihydroxo-bridged species is formed directly from IV and not via, for example, VI or VII. Finally, from the rate constants k_3 , k_4 and k_5 (from Ref. 16) it is calculated that the maximum concentration of V under these conditions is obtained after 58 s, at which time the distribution of the species is calculated to be: 6% IV, 80.6% V and 13.4% VIII (1.4% VIII from direct hydrolysis of IV and 12% VIII via hydrolysis of V). The agreement between the observed and calculated values for V is excellent.

Step 3: equilibration between monohydroxo- and dihydroxo-bridged species V–VIII. The last step is an equilibration between the hydroxobridged species (V–VIII) formed in step 2. Kinetic and thermodynamic data for these reactions have been published,¹⁶ although kinetic data were limited to neutral and acidic conditions. This step was therefore studied only briefly in the present work, and primarily in order to establish further the stoichiometry proposed for step 2. It follows from the published¹⁶ thermodynamic parameters that the final equilibrium solution will contain 100% monohydroxo-bridged species for pH above 10, but even at pH 7.5 the amount of monohydroxo-bridged species is significant (ca. 60%). It is therefore expected that the change in absorbance for step 3 will decrease with increasing [OH⁻] and that it will be negligible

at pH 14. Our observations were all in agreement with these predictions. Kinetic data for step 3 were likewise in agreement with the published data. For pH 10.3 we obtained $k_{\text{obs}} = 4.4 \times 10^{-4} \text{ s}^{-1}$ (0.8°C), which is close to the value $3.7 \times 10^{-4} \text{ s}^{-1}$ calculated from the published¹⁶ data, assuming that there is no base-catalyzed contribution to the bridge-cleavage reactions. The minor deviation between the observed and calculated rate constants could be due to the presence of bromide in the present experiment or to a minor contribution from a base-catalyzed path. With these reservations in mind the result is in keeping with the observation that no base-catalyzed bridge cleavage was observed in the corresponding $\Delta, \Delta/\Delta, \Delta$ system for pH < 9.¹⁷

Formation and cleavage of the carboxylato bridge in acidic solution. The equilibrium between the doubly bridged species I and its parent monohydroxo-bridged species III was studied spectrophotometrically. The spectra of acidic solutions initially containing I (made from the bromide salt) or III (made *in situ* as described above) were recorded at 0.8°C. In each case the spectra changed with time and then became constant after ca. 40 min. The change of the absorbance with time followed first-order kinetics. The final spectra and the observed rate constants were independent of the hydrogen-ion concentration, which was varied from 0.01 to 1.0 M, and were identical for solution initially containing either I or III. These observations are interpreted in terms of an equilibrium between I and III, as shown in Scheme 1. Additional measurements at 8.0 and 18.0°C gave a similar result. The spectra of the pure species I and III and of the equilibrium solution are shown in Fig. 5 and were used to determine the equilibrium constant K_1 (Table 5). The kinetic parameters for k_1 and k_{-1} were

Table 5. Determination of the equilibrium constant $K_1 = [\text{III}]/[\text{I}]$ and the rate constants k_1 and k_{-1} .

[H ⁺]/M	$K_1(\text{obs})$	$K_1(\text{calc})^a$	$k_{\text{obs}}/\text{s}^{-1}$	$k_{\text{calc}}^b/\text{s}^{-1}$
<i>T</i> = 18.0°C				
0.10	0.40	0.393	0.008 7	0.009 6
0.01	0.41	—	0.009 8	—
<i>T</i> = 8.0°C				
0.10	0.36	0.397	0.003 97	0.003 39
0.01	0.38	—	0.003 47	—
<i>T</i> = 0.8°C				
1.0	0.38	0.400	0.001 57	0.001 53
0.1	0.40	—	0.001 56	—
0.05	0.45 ^c	—	0.001 54	—
0.02	0.40	—	0.001 36	—
0.01	0.40	—	0.001 49	—

^aCalculated from the values of ΔH° and ΔS° given in Table 6.

^bCalculated using eqn. (5) and the parameters given in Table 6.

^cIn this experiment the kinetic data and the spectrum of the equilibrium solution were obtained using a solution initially composed by the monohydroxo-bridged species III; all the other experiments were made starting with the doubly bridged species I.

Table 6. Thermodynamic and kinetic parameters at 25 °C and $I = 1.0$ M (NaClO₄) for the reactions shown in Scheme 1.

Constant	Value ^a	ΔH° or ΔH^\ddagger /kJ mol ⁻¹	ΔS° or ΔS^\ddagger /J mol ⁻¹ K ⁻¹
K_1	0.39(2)	-0.7(21)	-10(8)
k_1/s^{-1}	$5.38(45) \times 10^{-3}$	67.9(27)	-61(9)
k_{-1}/s^{-1}	$1.37(11) \times 10^{-2}$	68.6(27)	-51(9)
$k_2/M^{-1} s^{-1}$	$4.8(2) \times 10^3$	32.4(30)	-66(11)
k_3/s^{-1}	$4.80(8) \times 10^{-2}$	77.8(9)	-9(3)
$k_4/M^{-1} s^{-1}$	4.75(14)	88.0(18)	63(6)
$k_5/s^{-1,b}$	$6.9(5) \times 10^{-3}$	80(2)	-18(7)
$k_{-5}/s^{-1,b}$	$9.3(7) \times 10^{-3}$	84(2)	-1(7)
K_5^b	0.75(2)	-3(1)	-13(3)
$pK_a(\text{I})^d$	9.4(1)	-	-
$pK_a(\text{III})^d$	3.36(15)	42(10)	75(36)
$pK_a(\text{VI})^{b,d}$	0.48(3)	12(3)	30(9)
$pK_a(\text{VII})^{c,d}$	7.513(7)	26.3(12)	-56(4)

^aStandard deviations are given in parenthesis in units of the last decimal. ^bFrom Ref. 16. ^cThe value for pK_a at 25 °C has been determined in this work, and the values for ΔH° and ΔS° were calculated using this value and the value $pK_a = 7.935(20)$ at 0.0 °C taken from data given in Ref. 16. ^d $pK_a = -\log(K_a/M)$.

obtained by non-linear least-squares calculations using

$$k_{\text{calc}} = k_1 + k_{-1} = k_1(1 + K_1)/K_1 \quad (5)$$

eqn. (5), and the result is shown in Tables 5 and 6.

Acid hydrolysis of terminally coordinated carboxylate. The acidic equilibrium solution containing **I** and **III** in equilibrium is unstable and slowly forms an equilibrium solution containing the monohydroxo- and dihydroxo-bridged species **V–VII**, shown spectrophotometrically and by isolation of the bromide salt of **V**. The change of the absorbance with time followed first-order kinetics, and at 25 °C the value $k_{\text{obs}} = 9.1(4) \times 10^{-5} \text{ s}^{-1}$ was found for 0.05 M HClO₄, 0.95 M NaClO₄. The reaction is 180 times and 210 times slower than the equilibration reactions between **I** and **III** and between **V** and **VII**, respectively. The rate-determining step must therefore be loss of trifluoroacetate, which may occur either via the intramolecular reaction of **IV** (k_3) or by intermolecular reactions of **III** or **IV** with water (k_6 or k_7). An intramolecular reaction alone leads to expression (6),

$$k_{\text{calc}} = \frac{K_1 K_a k_3}{(1 + K_1)[\text{H}^+]} \quad (6)$$

which contains only known parameters and gives $k_{\text{calc}} = 12(4) \times 10^{-5} \text{ s}^{-1}$ at $[\text{H}^+] = 0.05$ M. The calculated value is within error identical to k_{obs} , and it can be concluded that at this pH the predominant route for hydrolysis of **III** is via the intramolecular reaction of **IV**.

Comparison with other systems. The kinetic and thermodynamic data for the reactions shown in Scheme 1 are listed in Table 6. The activation enthalpies for the carboxylato-bridge cleavage and formation reactions (k_1 and k_{-1}) are

both about 13 kJ smaller than the respective values for the reactions of **V** and **VII** (k_5 and k_{-5}). This result is in keeping with the observation that the activation enthalpy for water exchange¹⁸ in $\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$ (99 kJ mol⁻¹) is 17 kJ mol⁻¹ larger than the activation enthalpy for aquation¹⁹ of the corresponding trifluoroacetato complex (82 kJ mol⁻¹). When comparing the two systems one must, however, also consider the effects due to strain in the bridging ring system. The enhanced reactivity of the dihydroxo-bridged species has been explained in part by strain in the four-membered bridging ring. The carboxylato-bridged species has a six-membered bridging ring with negligible strain, and the unusual lability therefore reflects a weak bonding of the trifluoroacetato bridge. In both systems the bridge formation reactions are facilitated by proximity effects, and the trifluoroacetato complex is favoured in the sense that the formation of the transition state does not afford a strained structure. For both systems these kinetic properties lead to an equilibrium constant close to 1, with only a small temperature dependence (Table 6).

The formation of **V** by an intramolecular reaction (k_3) is the first example of the formation of a chromium(III) hydroxo bridge where the leaving group is not water (or hydroxide). The reaction may be compared with the reaction of **VII** (k_{-5}), where the leaving group is water, and again it should be noted that the trifluoroacetate is a better leaving group than water. The activation entropies for the two reactions are similar.

The intramolecular reaction discussed above (k_3) competes with an intermolecular base-catalyzed hydrolysis of the carboxylate ligand (k_4), and the latter process dominates in 1 M hydroxide ($t_{1/2} = 14$ and 0.15 s, respectively, at 25 °C). Base catalysis of monodentate carboxylate in mononuclear complexes with, for example, cobalt(III), rhodium(III), iridium(III) or chromium(III) has been reported to occur by two routes: cleavage of the metal–oxygen bond (first-order in hydroxide) and cleavage of the carbon–oxygen bond (second-order in hydroxide).¹⁹ The reaction of the binuclear complex follows strictly a first-order dependence in hydroxide, and the activation enthalpy lies in the region normally found for Cr–O bond cleavage reactions. It is therefore fairly certain that k_4 corresponds to Cr–O cleavage.

The base hydrolysis of the carboxylato bridge in **I** (and its deprotonated form **II**) is extremely fast with half-lives varying from 3 s to 1.6 ms in the pH region 8–11 (25 °C). The reaction is first-order in hydroxide for $[\text{OH}^-] = 0.002$ –0.1 M. In this region the oxo-bridged species **II** is the dominant form, and it is therefore tentatively assumed that **II** is the reactive species (k_2). It is noted, however, that the kinetic data do not exclude cleavage of **I** by a $[\text{OH}^-]^2$ -dependent path, since this would give the same rate expression. The very small activation energy indicates that k_2 is a composite term. Very small activation energies were also reported for the $[\text{OH}^-]^2$ -dependent path in the hydrolysis of the mononuclear carboxylato complexes; for $\text{Cr}(\text{NH}_3)_5(\text{OCOCF}_3)^{2+}$ the values $\Delta H^\ddagger = 28$ kJ mol⁻¹ and $\Delta S^\ddagger = -115$ J mol⁻¹ K⁻¹

have been reported.¹⁹ Also, in these cases the hydrolysis was assumed to occur by a concerted process, and, as mentioned, this path was shown to involve C–O bond fission. On the basis of the present results it is not possible to decide if the carboxylato bridge cleavage in **II** occurs by Cr–O or C–O bond cleavage, but it seems very probable that it is a C–O cleavage. The observation that the reaction in ammonia and tris buffers is subject to general base catalysis is unambiguous, but at present we have no explanation for this effect.

The monohydroxo-bridged species **III** is a relatively strong acid ($pK_a = 3.4$ at 25°C). It is well established that the acid strength of terminally coordinated water in oligomers may vary significantly because of the different degrees of stabilization of the acid and base forms caused by intramolecular hydrogen bonds between coordinated water and hydroxide.¹ The monohydroxo-bridged species **VII** in Scheme 1 is the hydroxo analogue to **III** and has $pK_a = 7.5$ at 25°C. The predominant form of this cation is characterized by an intramolecular hydrogen bond between terminally coordinated water and hydroxide, which weakens the acid strength by 3.0 pK_a units.^{1,16} It follows that the microscopic pK_a value for the form with no intramolecular hydrogen bond must be approximately 4.5. Since the intramolecular hydrogen bonds in **III** or **IV** are probably weak, it is the latter value which should be compared with the pK_a value of **III**, which therefore seems to be more acidic than expected.

The hydroxo bridge in **I** is much more acidic ($pK_a = 9.4$) than is the hydroxo bridge in the acetato-bridged analogue, which has $pK_a \approx 12$.⁹ This is a surprisingly large difference, although it is well established that the acidity of hydroxo bridges in chromium(III) oligomers is very sensitive to the properties of the other ligands.¹ In the present case the difference may be explained as a consequence of acetate being bound more strongly than trifluoroacetate to the two chromium(III) centres (cf. the difference in acid strength of the two carboxylic acids, $pK_a = 0.23$ and 4.76), which is expected to cause an increased π -electron donation from the oxo bridge to chromium(III) in the trifluoroacetate complex, thereby causing stabilization of this species.

Acknowledgement. Financial support by the Carlsberg Foundation and the Danish Natural Research Council is gratefully acknowledged. Prof. R. G. Wilkins (University of New Mexico, Las Cruces) and Prof. J. Ulstrup (Danish Technical University, Lundtofte) are both thanked for use of their stopped-flow facilities. Dr. Peter Andersen is thanked for valuable discussions. *Acta Chemica Scandinavica* is thanked for a travel grant.

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Received January 27, 1992.