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# Kinetics and mechanism of the complex formation between oxalatopentaamminecobalt(III) and aluminium(III) and gallium(III); a comparative study

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## Summary

The reversible complex formation between oxalatopentaammine cobalt(III), aluminium(III) and gallium(III) was investigated by the stopped flow technique at  $30 \pm 0.1^\circ\text{C}$  and  $I = 1.0 \text{ mol dm}^{-3}$ . The reactivity sequence:  $\text{Ga}^{\text{III}} > \text{Al}^{\text{III}}$  is observed, however, the major path for gallium(III) was  $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+} + \text{GaOH}^{2+} \rightarrow (\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{Ga}^{4+} + \text{H}_2\text{O}$ . The formation and dissociation rate constants of the binuclear species have been compared with the analogous data for iron(III) and nickel(II) reported earlier. The results reflect the fact that the half-bonded oxalato moiety of  $(\text{NH}_3)_5\text{CoC}_2\text{O}_4^+$  acts as a chelating agent for the metal ions.

## Introduction

The mechanism of ligand penetration into the coordination sphere of metal ions is a challenging feature of metal ion ligand interactions in solution. Extensive data on the complexation of alkaline earth and first row transition metal ions have accumulated<sup>(1–14)</sup> from which it has been realised that such reactions are extremely sensitive to the charge, size and coordination environment of the metal ions from both kinetic and thermodynamic standpoints. The mechanistic picture ranges from A to D covering Id and Ia. Mechanistic studies on nontransition metal ions such as aluminium(III) and gallium(III) have been comparatively scarcely investigated. We present in this work the results of the kinetics of binuclear complex formation by aluminium(III) and gallium(III) with oxalatopentaamminecobalt(III). Such a study provides the opportunity to examine the complexing ability (from both the kinetic and thermodynamic standpoint) of oxalate, which functions as a bridge between  $(\text{NH}_3)_5\text{Co}^{3+}$  and  $\text{M}^{3+}$  centres. Analogous data on iron(III) and nickel(II) are available for comparison.

## Experimental

$[(\text{NH}_3)_5\text{CoO}_2\text{CCO}_2\text{H}]^{2+}$  was prepared by the standard procedure<sup>(15)</sup>;  $\lambda_{\text{max}} [\text{nm} (\epsilon, \text{M}^{-1} \text{cm}^{-1})] = 500 (72.0)$  for  $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$  in 0.1 (M)  $\text{HClO}_4$  medium, which agrees well with the previously reported values<sup>(16)</sup>. Aluminium(III) and gallium(III) perchlorates were prepared and analysed for the metal ion and free acid contents as described earlier<sup>(17,18)</sup>. Ionic strength was adjusted to  $1.0 \text{ mol dm}^{-3}$  using  $\text{NaClO}_4$  prepared from  $\text{Na}_2\text{CO}_3$  (A.R.) and  $\text{HClO}_4$  (A.R.).  $\text{ClCH}_2\text{CO}_2\text{Na}-\text{ClCH}_2\text{CO}_2\text{H}$  buffer was used to adjust the pH. All solutions were prepared in doubly distilled  $\text{H}_2\text{O}$ , the second distillation being made from alkaline  $\text{KMnO}_4$  in all-glass distillation apparatus. The pH measurements were made using an

Elico digital pH meter LI120 with glass–Ag/AgCl ( $2 \text{ mol dm}^{-3} \text{ NaCl}$ ) combination electrode CL 51. The u.v.–vis. spectra were recorded on a JASCO model 7800 spectrophotometer, with 10 mm matched quartz cells.

## Kinetic measurements

The kinetics of the reversible complexation of the oxalato complex with the  $\text{M}^{3+}$  ions was investigated at  $30 \pm 0.1^\circ\text{C}$  and  $I = 1.0 \text{ mol dm}^{-3}$ . The rate measurements were made on a fully automated SF 51 stopped flow spectrophotometer (HITECH, UK) as described in our earlier work<sup>(19)</sup>. Only a single exponential curve was displayed for any run, even after spreading the reaction over the time scale accessible by the instrument. The initial absorbance is due to the oxalato complex and the final absorbance to the binuclear species and oxalato complex at equilibrium. All calculations were made by the least squares computer programme suitable for an Apple II GS PC.

## Results and discussion

The spectra of the oxalato complex in the absence and presence of aluminium(III) is shown in Figure 1, which illustrates its interaction with the metal ions and, further, corroborates our earlier findings<sup>(16,20)</sup>. A few runs were made at constant  $[\text{Al}^{\text{III}}]_{\text{T}} = 8 \times 10^{-3} \text{ mol dm}^{-3}$  at  $\text{pH} = 2.38 \pm 0.02$  and  $I = 1 \text{ mol dm}^{-3}$ , but with varying concentrations of chloroacetate ( $[\text{Cl}-\text{CH}_2\text{CO}_2^-]_{\text{T}} = 8.24 \times 10^{-3} - 34.2 \times 10^{-3} \text{ mol dm}^{-3}$ ). The  $k_{\text{obs}} (\text{s}^{-1})$  values ( $0.167 \pm 0.002$ ) indicated that the buffer effect is negligible<sup>(18,21)</sup>. Tables 1 and 2 lists the pseudo-first order constants as a function of  $[\text{M}^{\text{III}}]$  and pH at  $30 \pm 0.1^\circ\text{C}$ .

Under the experimental pH conditions the proton dissociation of the bioxalate complex is substantial [ $\text{pK}$  of  $(\text{NH}_3)_5\text{CoO}_2\text{CCO}_2\text{H}^{2+} = ca 2$  at  $25^\circ\text{C}$ ,  $I = 1.0 \text{ mol dm}^{-3}$ ]<sup>(20)</sup> and the hydrolysis of  $\text{Al}(\text{OH})_2^{3+}$  is insignificant ( $\text{pK}_{\text{h}} = 5$  at  $25^\circ\text{C}$ ,  $I = 1.0 \text{ mol dm}^{-3}$ )<sup>(22)</sup> from the equilibrium standpoint. However, the reactivities of  $\text{Al}(\text{OH})_2^{3+}$  and  $\text{Al}(\text{OH})(\text{OH})_2^{2+}$  differ greatly<sup>(21)</sup>. Furthermore, our earlier experiment with  $\text{Fe}(\text{OH})_2^{3+}$ –oxalatopentaamminecobalt(III) system for which there was no kinetic evidence of the reaction between  $\text{Fe}(\text{OH})_2^{3+}$  and  $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$  and acid catalysed aequation of the resulting binuclear complex,  $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{Fe}^{4+}$ , leads us to believe that a similar situation might prevail for the comparatively less reactive and less prone to complex  $\text{Al}(\text{OH})_2^{3+}$ . Furthermore, the proton ambiguity for the reaction of  $\text{Al}(\text{OH})_2^{3+}$  with  $(\text{NH}_3)_5\text{CoC}_2\text{O}_4^+$  and  $\text{Al}(\text{OH})_2^{3+}$  with  $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$  is quite unlikely to be due to substantial difference (by  $ca \text{ pK } 3$  units) between the  $\text{pK}_{\text{a}}$ 's of the reactants. On these grounds, a reasonable reaction is presented below (Scheme 1), for which the pseudo-first order rate constant is given by Equation 1. (Aqua ligands in the coordination sphere of aluminium(III) are not

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**Figure 1.** Spectra of  $[\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4\text{H}]^{2+}$  in the presence and absence of aluminium(III) at pH 2.6 and 30 °C. (a)  $[\text{Al}^{\text{III}}]_{\text{T}} = 0.01 \text{ mol dm}^{-3}$ ; (b)  $[\text{Al}^{\text{III}}]_{\text{T}} = 0.01$ ,  $[\text{complex}]_{\text{T}} = 5 \times 10^{-4} \text{ mol dm}^{-3}$ ; (c)  $[\text{complex}]_{\text{T}} = 5 \times 10^{-4} \text{ mol dm}^{-3}$ .

shown for convenience.

$$k_{\text{obs}} = (k_1 + k_2 K_h / [\text{H}^+]) \cdot \left( \frac{K_1}{K_1 + [\text{H}^+]} \right) [\text{Al}^{\text{III}}]_{\text{T}} + k_{-1} + k_{-2} \frac{K'_h}{[\text{H}^+]} \quad (1)$$

where the  $k_i$ 's are the rate constants and  $K_1$ ,  $K_h$  and  $K'_h$  are the equilibrium constants for the forward reaction ( $\rightarrow$ ) as shown in Scheme 1. Equation 1 further assumes that, like free  $\text{Al}^{\text{III}}$  ( $K_h/[\text{H}^+] \ll 1$ ), the hydrolysis of  $\text{Al}^{\text{III}}$  in  $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{Al}^{4+}$  ( $K'_h/[\text{H}^+] \ll 1$ ) is not substantial under the experimental conditions. The rate data were analysed by successive approximations. To begin, the contributions of  $k_1$ ,  $K'_h$  and  $k_{-2}$  terms were neglected. Strikingly, the  $k_{\text{obs}}$  versus  $\{K_1/(K_1 + [\text{H}^+])\} [\text{Al}^{\text{III}}]/[\text{H}^+]$  plot was reasonably linear (Figure 2), and the intercept and slope were taken to be  $k_{-1}$  and  $k_2 K_h$  respectively. In the second approximation  $k_{\text{obs}} - k_{-1} - k_2 K_h \{K_1/(K_1 + [\text{H}^+])\} [\text{Al}^{\text{III}}]/[\text{H}^+]$  versus  $1/[\text{H}^+]$  plot was constructed

**Table 1.** Rate data for the complexation of aluminium(III) with  $[(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}]^{2+}$  at  $30 \pm 1$  °C,  $[\text{complex}] = 4 \times 10^{-4}$  and  $I = 1.0 \text{ mol dm}^{-3}$

pH	$k_{\text{obs}}(\text{s}^{-1})$	pH	$k_{\text{obs}}(\text{s}^{-1})$
$\text{Al}^{\text{III}} = 0.007 \text{ mol dm}^{-3}$		$\text{Al}^{\text{III}} = 0.020 \text{ mol dm}^{-3}$	
2.27	$0.142 \pm 0.002$	2.43	$0.199 \pm 0.004$
2.45	$0.155 \pm 0.002$	2.77	$0.385 \pm 0.006$
2.71	$0.263 \pm 0.004$	3.28	$1.100 \pm 0.011$
2.80	$0.331 \pm 0.005$	3.46	$1.55 \pm 0.010$
3.16	$0.674 \pm 0.004$	3.48	$1.70 \pm 0.030$
3.22	$0.863 \pm 0.015$		
3.42	$1.100 \pm 0.010$		
$\text{Al}^{\text{III}} = 0.010 \text{ mol dm}^{-3}$		$\text{Al}^{\text{III}} = 0.040 \text{ mol dm}^{-3}$	
2.28	$0.133 \pm 0.003$	2.45	$0.295 \pm 0.007$
2.48	$0.182 \pm 0.003$	2.51	$0.359 \pm 0.002$
2.68	$0.278 \pm 0.001$	2.61	$0.458 \pm 0.002$
2.93	$0.486 \pm 0.008$	2.73	$0.600 \pm 0.006$
3.34	$0.997 \pm 0.009$	3.14	$1.12 \pm 0.030$
3.50	$1.470 \pm 0.040$		
$\text{Al}^{\text{III}} = 0.030 \text{ mol dm}^{-3}$			
2.34	$0.212 \pm 0.003$		
2.52	$0.281 \pm 0.007$		
2.70	$0.384 \pm 0.002$		
2.90	$0.596 \pm 0.003$		
3.10	$0.882 \pm 0.004$		
3.20	$1.090 \pm 0.010$		
3.26	$1.200 \pm 0.010$		

so as to obtain the approximate value of  $k_{-2} K'_h$ . Next, the refined  $k_1$  and  $k_2 K_h$  values were calculated from the plot of  $Y_{(1)}$  [see Equation 2, derived from Equation 1] versus  $1/[\text{H}^+]$ :

$$Y_{(1)} = (k_{\text{obs}} - k_{-1} - k_{-2} K'_h / [\text{H}^+]) / Z = k_1 + k_2 K_h / [\text{H}^+] \quad (2)$$

$$Z = [\text{Al}^{\text{III}}] K_1 / (K_1 + [\text{H}^+])$$

and the  $k_2 K_h$  and  $k_{-2} K'_h$  values were refined making plots of  $Y_{(1)} [\text{H}^+]$  versus  $Z$  as per Equation 3 [see also Equations 1 and 2].

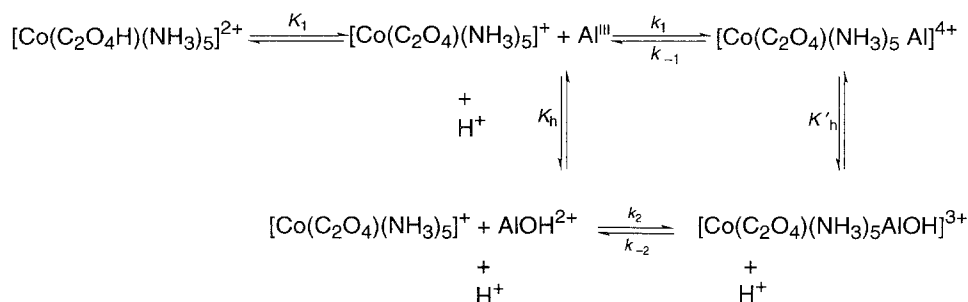
$$Y_{(1)} [\text{H}^+] = (k_{\text{obs}} - k_{-1} - k_{-2} K'_h) [\text{H}^+] = k_2 K_1 Z + k_{-2} K'_h \quad (3)$$

This process was then repeated to yield the best values of the parameters by a double least squares analysis. The final values of the parameters are collected in Table 3.

Gallium(III) complexation was studied at  $[\text{H}^+]_{\text{T}} = 0.115 - 0.20 \text{ mol dm}^{-3}$  in order to avoid appreciable hydrolysis of  $\text{Ga}(\text{OH}_2)_6^{3+}$  ( $\text{p}K_h = 2.938$  at 25 °C and  $I =$

**Table 2.** Rate data for the complexation of gallium(III) with  $[(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}]^{2+}$  at  $30 \pm 0.1$  °C,  $[\text{complex}]_{\text{T}} = 4 \times 10^{-4}$  and  $I = 1 \text{ mol dm}^{-3}$

$[\text{H}^+] = 0.20 \text{ mol dm}^{-3}$ $10^3 [\text{Ga}^{\text{III}}] \text{ mol dm}^{-3}$		$[\text{H}^+] = 0.15 \text{ mol dm}^{-3}$ $10^3 [\text{Ga}^{\text{III}}] \text{ mol dm}^{-3}$		$[\text{H}^+] = 0.115 \text{ mol dm}^{-3}$ $10^3 [\text{Ga}^{\text{III}}] \text{ mol dm}^{-3}$	
	$k_{\text{obs}}(\text{s}^{-1})$		$k_{\text{obs}}(\text{s}^{-1})$		$k_{\text{obs}}(\text{s}^{-1})$
2.5	$2.87 \pm 0.37$	2.5	$3.69 \pm 0.55$	1.50	$2.77 \pm 0.14$
3.0	$3.13 \pm 0.39$	3.0	$4.27 \pm 0.36$	2.00	$4.28 \pm 0.31$
3.5	$3.25 \pm 0.53$	3.5	$4.57 \pm 0.45$	2.50	$4.61 \pm 0.46$
4.0	$3.54 \pm 0.68$	4.0	$5.06 \pm 0.41$	3.00	$5.34 \pm 0.31$
		4.5	$5.62 \pm 0.41$	3.50	$6.14 \pm 0.33$
5.0	$4.12 \pm 0.15$	5.0	$6.50 \pm 0.30$	4.00	$6.68 \pm 0.25$
				4.50	$7.48 \pm 0.14$
				5.00	$8.75 \pm 0.29$



**Scheme 1.**

0.5 mol dm<sup>-3</sup>) and polymerisation of GaOH<sup>2+</sup>, under this condition the cobalt(III) substrate will exist in the bioxalato form ([H<sup>+</sup>] > 10 K<sub>1</sub>). In accord with Scheme I,  $k_{\text{obs}}$  versus [Ga]<sub>T</sub> plot at constant [H<sup>+</sup>]<sub>T</sub> was also linear with positive intercept and positive gradient at each [H<sup>+</sup>]. However, when both the intercepts and gradients of such plots were plotted versus 1/[H<sup>+</sup>], we obtained negative  $k_1$  and  $k_{-1}$  values (see Equation 1) indicating thereby that  $k_{\text{obs}}$  had essentially the form given in Equation 4.

$$k_{\text{obs}} = (k_2 K_h / [\text{H}^+]) \frac{[\text{Ga}]}{[\text{H}^+]} + k_{-2} \frac{K'_h}{[\text{H}^+]} \quad (4)$$

Equation 1 reduces to this form when  $k_1 \ll k_2 K_h / [H^+]$  and  $k_{-1} \ll k_{-2} K'_h / [H^+]$ .

Hence the only significant reaction path for gallium(III) involved  $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^{2+}$  and  $\text{GaOH}^{2+}$ . Values of  $k_2K_b$ ,  $K_{-2}K'_b$  obtained from Equation 4 by the least squares analysis are collected in Table 3, as is a comparison of the rate constants for the binuclear complex formation/dissociation reaction for aluminium(III), gallium(III), iron(III) and nickel(II). Notably among the formation rate constants  $k_1$  and  $k_2$ , the former showed a much wider variation with the nature of the metal ion. The ionic strength effect cannot explain the greater than 1000-fold variation of  $k_1$  for nickel(II) and aluminium(III). This

result must arise from the substantial coulombic repulsion effect for the diffusion controlled encounter complex formation between the substrate and the metal ion as well as rate limiting  $M^{n+} - OH_2$  dissociation for outer sphere—inner sphere conversion of the encounter complex. However, for iron(III) some degree of associative character (Ia)<sup>(24)</sup> is expected in this conversion process. For  $AlOH^{2+}$ ,  $GaOH^{2+}$  and  $FeOH^{2+}$ , the spread of  $k_2$  values is narrow. This fact further supports the strong stabilizing action of the metal-bound hydroxyl group. The substitution mechanism for  $Fe(OH)(OH_2)_5^{2+}$  being Id<sup>(24)</sup>, a similar mechanism is expected for the other two  $MOH^{2+}$  species.

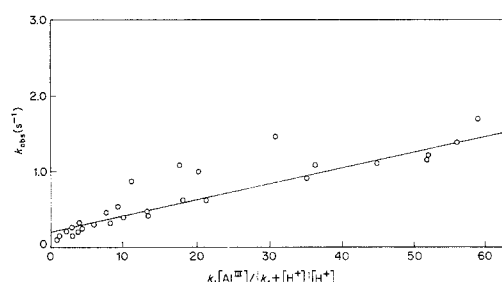
Interestingly, the dissociation rate constant ( $k_{-1}$ ) of the binuclear species  $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{M}^{(n+1)+}$  varies in the order nickel(II) > iron(III) > aluminium(III). Evidently the inherent coulombic repulsion between the like charge centres in the binuclear species is outweighed by the strong metal–ligand interaction which presumably pertains to the chelating action of the oxalato moiety.

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**Figure 2.**  $k_{\text{obs}}(\text{s}^{-1})$  versus  $K_1[\text{Al}^{\text{III}}]/\{K_1 + [\text{H}^+]\}[\text{H}^+]$  plot.

**Table 3.** Rate for formation and dissociation of  $(\text{NH}_3)_4\text{CoC}_2\text{O}_4\text{M}^{4+}$  at  $30 \pm 0.1^\circ\text{C}$  and  $I = 1.0 \text{ mol dm}^{-3}$

$M^{n+}$	$k_1$ ( $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ )	$k_{-1}$ ( $\text{s}^{-1}$ )	$k_2 K_h$ ( $\text{s}^{-1}$ )	$k_2$ ( $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ )	$k_{-2} K'_h$ ( $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ )	$k_{-2}$ ( $\text{s}^{-1}$ )	R
$\text{Al}^{\text{III}}$	$2.47 \pm 0.05$	$(5.0 \pm 1)10^{-2}$	$(0.92 \pm 0.06)10^{-2}$	$0.84 \times 10^3$	$(3.36 \pm 0.12)10^{-4}$	$30.5^a$	this work
$\text{Ga}^{\text{III}}$	—	—	$(19.72 \pm 2)$	$17.14 \times 10^3$	$0.133 \pm 0.05$	$1.15 \times 10^{2a}$	this work
$\text{Fe}^{\text{III}}$	$11.0 \times 10^2$	0.7	—	$4.8 \times 10^3$	—	0.7	23
$\text{Ni}^{\text{II}}$	$(3.99 \pm 0.12)10^3$	$89.6 \pm 1$	—	—	—	—	19

<sup>a</sup>Based on  $K_b = K'_b$ ,  $I = 0.3 \text{ mol dm}^{-3}$ .

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