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The Effects of Multivalent Anions on the Aluminium Ion-assisted Aquation of the Pentaamminefluorocobalt(III) Complex**

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The presence of multivalent anions, such as sulfate, oxalate, and malonate ions, accelerated the aluminium ion-assisted aquation of $\mathrm{CoF(NH_3)_5^{2+}}$ and gave the anionopentaamminecobalt(III), along with the aqua complex. The competition reaction for the sulfate ion showed a saturation of the product percentage (33% $\mathrm{CoSO_4(NH_3)_5^+}$) at nearly $[\mathrm{SO_4^{2-}}]_{\mathrm{total}}=0.1$ mol dm^{-3}, while the saturation of the reaction rate was observed at a higher sulfate concentration. This difference can be explained by a scheme in which the reaction proceeds through two intermediates, $\mathrm{CoF(NH_3)_5^{2+}\cdot SO_4^{2-}\cdot Al^{3+}}$ and $\mathrm{SO_4^{2-}\cdot CoF(NH_3)_5^{2+}\cdot SO_4^{2-}\cdot Al^{3+}}$. The reaction for the oxalate and malonate ions gave extremely large yields (more than 90%) of $\mathrm{CoA(NH_3)_5^+}$ ($\mathrm{A^{2-}}$=oxalate ion or malonate ion) when $[\mathrm{A^{2-}}]_{\mathrm{total}}/[\mathrm{Al^{3+}}]_{\mathrm{total}}>2$, and the reaction rates showed a maximum at approximately $[\mathrm{A^{2-}}]_{\mathrm{total}}/[\mathrm{Al^{3+}}]_{\mathrm{total}}=2$. These specific effects can be attributed both to the strong affinities of the dicarboxylate ions for the aluminium ion and to the residual capacity of the aluminium-bonded dicarboxylate ions for coordinating with cobalt(III).

Our previous studies of $\mathrm{CrF(NH_3)_5^{2+}}$–$\mathrm{Al^{3+}}$ 1) and $\mathrm{CoF(NH_3)_5^{2+}}$–$\mathrm{Al^{3+}}$ 2) reactions have revealed that the reaction rates are approximately first-order with respect to each reactant and that the effects of $\mathrm{ClO_4^-}$ and $\mathrm{Co(CN)_6^{3-}}$ on the former reaction can be explained from a purely electrostatic point of view. The assisted aquations in the presence of competing nucleophiles have been widely studied3–8) and have thrown light on the reaction mechanism, in particular on the reaction intermediate. Among others, Posey and Taube3) and Buckingham *et al.*8) have explained the results in terms of the formation of ion pairs between the reactants and the nucleophiles. The ion pair formed in the intermediate step has, however, not been well characterized.

The present study has been undertaken in order to obtain information about the competition in the $\mathrm{CoF(NH_3)_5^{2+}}$–$\mathrm{Al^{3+}}$ reaction. The nucleophilic anions used were sulfate, oxalate, and malonate ions. As they strongly interact with the reactant cations, they are useful in helping to see the role of the ion pair or complex formation in the reaction. The relationship between the product percentages and the reaction rates will be clarified by observing the effect of the sulfate ion in the pH range where the formation of $\mathrm{HSO_4^-}$ is slight. The strong affinities of the dicarboxylate ions(oxalate ion=$\mathrm{ox^{2-}}$, or malonate ion=$\mathrm{mal^{2-}}$) to the aluminium ion will give their specific behavior in the reaction.

Experimental

Materials. The preparation and confirmation of the $\mathrm{[CoF(NH_3)_5](ClO_4)_2}$ crystals, $\mathrm{NaClO_4}$ crystals, $\mathrm{Al(ClO_4)_3}$ solution, and $\mathrm{Na_3[Co(CN)_6]\cdot 2H_2O}$ crystals were made as has previously been described.1,2) The anhydrous sodium oxalate was a guaranteed reagent from Wako Pure Chemicals Industries, Ltd., and was dried at 300 °C for one hour before use. Anhydrous sodium malonate, an extra pure reagent from Nakarai Chemicals Industries, was recrystallized from a water–methanol (1:1) solution, dried *in vacuo* at 60 °C, and then used. (Found: C, 24.00, H, 1.44%. Calcd for $\mathrm{Na_2C_3H_2O_4}$: C, 24.34, H, 1.36%).

Kinetic Measurements. The sample solutions contained the anion and the aluminium ion in different concentrations and had different pH values, while they contained the complex ion in a constant concentration of 5.0×10^{-3} mol dm^{-3}. The kinetics were studied spectrophotometrically. Absorbance changes were followed at 480 nm in the cases of $\mathrm{Co(CN)_6^{3-}}$ and $\mathrm{SO_4^{2-}}$ and at 500 nm in the cases of $\mathrm{ox^{2-}}$ and $\mathrm{mal^{2-}}$. The pseudo-first-order rate constants, k_{obsd}, were determined by plotting $\ln|D_t-D_\infty|$ *vs.* t, where D_t and D_∞ are the absorbances at the time t and at the time when the absorbance becomes almost constant respectively. The kinetic studies were made at 25.0±0.1 °C unless otherwise stated.

Competition in the Formation of Products. After the reaction had been completely terminated, the reaction solution was added to a column of SP-Sephadex and eluted with a 0.15 mol dm^{-3} sodium-sulfate solution. Two bands were observed; the first was assigned to the aniono complex, and the second, to the aqua complex. The concentration ratios of the two complexes can be calculated by means of the following equation:

$$\frac{c_{\mathrm{X}}}{c_{\mathrm{A}}}=\frac{\varepsilon_{\mathrm{A}}}{\varepsilon_{\mathrm{X}}}\frac{D_{\mathrm{X}}V_{\mathrm{X}}}{D_{\mathrm{A}}V_{\mathrm{A}}},$$

where ε and D are the molar absorption coefficients and the absorbances at the absorption maxima respectively, where V is the volume of the eluate, and where the subscripts, X and A, indicate the aniono complexes and the aqua complex respectively. The ε values used are 47.5 at 492 nm for the aqua complex, 59.3 at 515 nm for the sulfato complex, 78.0 at 503 nm for the oxalato complex, and 74.9 at 503 nm for the malonato complex. We here use the product percentages defined as:

$$F=\frac{c_{\mathrm{X}}}{c_{\mathrm{X}}+c_{\mathrm{A}}}\times 100\%.$$

Measurements of the pH and of the ^{19}F NMR followed previous studies;1,2) the observed pH values were used without correction.

Results and Discussion

In a previous study, hexacyanocobaltate(III) ions have been shown to accelerate the $\mathrm{CrF(NH_3)_5^{2+}}$–$\mathrm{Al^{3+}}$

** A preliminary report on this work has been published in *Chem. Lett.*, **1981**, 781.

TABLE 1. EFFECTS OF $[Co(CN)_6^{3-}]$ ON THE REACTION RATES
(The ionic strength was not controlled. pH: 1.76 ± 0.02. Runs 1—6 were made at 35 °C, and Runs 7—11, at 25 °C.)

Run	$[Al^{3+}]$/mol dm^{-3}	$[Co(CN)_6^{3-}]$/mol dm^{-3}	k_{obsd}/s^{-1}
1	0.10	0	2.6×10^{-4}
2	0.10	0.025	3.9×10^{-4}
3	0.10	0.050	5.5×10^{-4}
4	0.10	0.10	8.1×10^{-4}
5	0.10	0.20	8.9×10^{-4}
6	0.10	0.30	8.7×10^{-4}
7	0.051	0	3.3×10^{-5}
8	0.051	0.050	9.8×10^{-5}
9	0.051	0.10	1.2×10^{-4}
10	0.051	0.15	1.2×10^{-4}
11	0.051	0.20	1.3×10^{-4}

TABLE 2. DEPENDENCE OF THE RATE CONSTANTS ON THE CONCENTRATION OF SULFATE IONS
($[Al^{3+}]_{total}=0.051$ mol dm^{-3}, $[CoF(NH_3)_5^{2+}]_{initial}=5.0\times10^{-3}$ mol dm^{-3}, pH 2.9 ± 0.1.)

$[SO_4^{2-}]$/mol dm^{-3}	$k_{obsd}\times10^4$/s^{-1}	I_{calcd}[a]
0	0.33	0.321
0.010	0.80	0.295
0.025	1.93	0.270
0.050	4.98	0.258
0.075	6.50	0.290
0.10	8.54	0.345
0.20	14.0	0.616
0.30	15.0	0.906

a) The ionic strengths are the values calculated considering the formation of ion pairs, $Al^{3+}\cdot SO_4^{2-}$.

reaction.[1] A similar acceleration effect was shown by the same anion on the $CoF(NH_3)_5^{2+}$–$Al(ClO_4)_3$ reaction systems. This is shown in Table 1, in which the reaction rate approaches saturation above the concentration ratio of $[Co(CN)_6^{3-}]/[Al^{3+}]\approx2$. These results can be understood from the formation of ion-pairs between the anions and the reacting cations.

TABLE 3. THE YIELDS OF $CoSO_4(NH_3)_5^+$
($[Al^{3+}]_{total}=0.051$ mol dm^{-3}, $[CoF(NH_3)_5^{2+}]_{initial}=5.0\times10^{-3}$ mol dm^{-3}, pH 2.9 ± 0.1.)

$[SO_4^{2-}]_{total}$/mol dm^{-3}	F/%
0.010	19.8
0.025	26.4
0.050	29.6
0.075	31.7
0.10	32.5
0.20	32.4
0.30	32.7

Effects of Sulfate Ions. The results of the competition study of the sulfate ion are listed in Tables 2 and 3. A comparison of these tables shows a significant difference between the saturation of the rate constant and that of the yield of $CoSO_4(NH_3)_5^+$; thus, the saturation of the product percentage (33%) for $CoSO_4(NH_3)_5^+$ appears at nearly $[SO_4^{2-}]_{total}=0.1$ mol dm^{-3}, while the reaction rate reaches saturation at the higher sulfate concentration of $[SO_4^{2-}]_{total}>0.2$ mol dm^{-3}. The relation between the reaction rate and the product percentage has not yet been discussed for the competition reactions hitherto studied. In order to explain the relation, we shall describe the rate constants and the yields of $CoSO_4(NH_3)_5^+$ from the reaction scheme containing the sulfate ion. As both the anation,

$$\mathrm{CoOH_2(NH_3)_5^{3+} + SO_4^{2-} \xrightarrow{k_{an}} CoSO_4(NH_3)_5^{+} + H_2O},$$

and the aquation,

$$\mathrm{CoSO_4(NH_3)_5^{+} + H_2O \xrightarrow{k_{aq}} CoOH_2(NH_3)_5^{3+} + SO_4^{2-}},$$

are known to be very slow ($k_{an}=1.49\times10^{-5}$ mol^{-1} dm^3 s^{-1} and $k_{aq}=1.20\times10^{-6}$ s^{-1} at 25 °C, $I=0.5$ mol dm^{-3}),[9] the formation of a considerable quantity of sulfato-complex ions can be attributed to the entry of sulfate ions into the inner sphere of the cobalt(III) ion immediately after the rate-determining step. The following scheme can be considered for the reaction in the presence of the sulfate ion:

$$\mathrm{CoF^{2+} + SO_4^{2-}} \overset{K_1{}^{\mathrm{ip}}}{\rightleftharpoons} \mathrm{CoF^{2+}SO_4^{2-}}$$

$$\mathrm{Al^{3+} + SO_4^{2-}} \overset{K_2{}^{\mathrm{ip}}}{\rightleftharpoons} \mathrm{Al^{3+}SO_4^{2-}}$$

$$\begin{array}{lllllll}
\mathrm{I} & \mathrm{CoF^{2+} + Al^{3+}} & \overset{K_{\mathrm{I}}}{\rightleftharpoons} & \mathrm{CoF^{2+}Al^{3+}} & \xrightarrow{k_{\mathrm{I}}} & \mathrm{CoFAl^{5+}} & \xrightarrow{\text{fast}} \mathrm{CoOH_2(NH_3)_5^{3+}} \\
\mathrm{II} & \mathrm{CoF^{2+} + Al^{3+}SO_4^{2-}} & \overset{K_{\mathrm{II}}}{\rightleftharpoons} & \mathrm{CoF^{2+}Al^{3+}SO_4^{2-}} & \xrightarrow{k_{\mathrm{II}}} & \mathrm{CoFAl^{5+}SO_4^{2-}} & \left.\right\} \\
\mathrm{III} & \mathrm{CoF^{2+}SO_4^{2-} + Al^{3+}} & \overset{K_{\mathrm{III}}}{\rightleftharpoons} & \mathrm{CoF^{2+}SO_4^{2-}Al^{3+}} & \xrightarrow{k_{\mathrm{III}}} & \mathrm{CoFAl^{5+}SO_4^{2-}} & \left.\right\} \xrightarrow{\text{fast}} \left\{\begin{array}{l}\mathrm{CoOH_2(NH_3)_5^{3+}} \\ + \\ \mathrm{CoSO_4(NH_3)_5^{+}},\end{array}\right. \\
\mathrm{IV} & \mathrm{CoF^{2+}SO_4^{2-} + Al^{3+}SO_4^{2-}} & \overset{K_{\mathrm{IV}}}{\rightleftharpoons} & \mathrm{SO_4^{2-}\text{-}CoF^{2+}SO_4^{2-}\text{-}Al^{3+}} & \xrightarrow{k_{\mathrm{IV}}} & \mathrm{SO_4^{2-}\text{-}CoFAl^{5+}SO_4^{2-}} & \xrightarrow{\text{fast}}
\end{array}$$

where $CoF(NH_3)_5^{2+}$ is abbreviated as CoF^{2+} and where $CoFAl^{5+}$ indicates that F and Al are bonded more strongly than in $CoF^{2+}Al^{3+}$. The following conditions will be used in the discussion below:

1) The ion association of sulfate ions with the cobalt-complex ions had only a negligible effect on the sulfate-ion concentration, as the concentration of the cobalt complex was very low.

2) The formation of HSO_4^- ($\log K=1.36$, $I=0.5$ mol dm^{-3})[10] was not significant, as the experiments were carried out in the $(pH)_{obsd}$ range of 2.8—3.0.

3) As soon as the fluoride ligand was extracted by the aluminium ion, a sulfate ion or a water molecule rapidly entered the coordination sphere of the cobalt(III) ion; thus, the extraction of the fluoride ligand is the rate-determining step for the formation

of either the aqua or the sulfato complex.

4) The formation constants (K_I—K_{IV}) of the precursors of the reaction intermediates are small enough in comparison with the ion-pair formation constants, K_1^{ip} and K_2^{ip}.

Letting a, b, and c represent the total initial concentrations of $CoF(NH_3)_5^{2+}$, Al^{3+}, and SO_4^{2-} respectively, the reaction rate can be expressed as:

$$\begin{aligned}\text{Rate} &= k_{obsd}\,a = k_I K_I[CoF^{2+}][Al^{3+}] \\ &\quad + (k_{II}K_{II}K_2^{ip}+k_{III}K_{III}K_1^{ip})[CoF^{2+}][Al^{3+}][SO_4^{2-}] \\ &\quad + k_{IV}K_{IV}K_1^{ip}K_2^{ip}[CoF^{2+}][Al^{3+}][SO_4^{2-}]^2 \\ &= k_0(a-x_1)(b-x_2) + k_1[x_2(a-x_1)+x_1(b-x_2)] \\ &\quad + k_2x_1x_2, \end{aligned} \tag{1}$$

where x_1 and x_2 denote the concentrations of two ion-pairs, $CoF^{2+}SO_4^{2-}$ and $Al^{3+}SO_4^{2-}$ respectively, and where the rate constants,

$$k_0 = k_IK_I,\ k_1 = \frac{k_{II}K_{II}K_2^{ip}+k_{III}K_{III}K_1^{ip}}{K_1^{ip}+K_2^{ip}},$$

and

$$k_2 = k_{IV}K_{IV},$$

have identical dimensions of $mol^{-1}\,dm^3\,s^{-1}$. The value of k_0 in Eq. 1 should be equal to the k_{obsd} value at $c=0$ ($6.6\times10^{-4}\,mol^{-1}\,dm^3\,s^{-1}$). The other rate constants, k_1 and k_2, can be determined from the results given in Table 2 by the use of the x_1 and x_2 values, which were calculated for each run by the method of successive approximations in the following way. The ion-pair formation constants are:

$$K_1^{ip} = \frac{x_1}{(a-x_1)(c-x_2)}, \tag{2}$$

$$K_2^{ip} = \frac{x_2}{(b-x_2)(c-x_2)}, \tag{3}$$

where $c-x_1-x_2$ has been approximated by $c-x_2$. Assuming provisionally the ionic strength based on the analytical concentrations, the known values of the constants, $\log K_1^{ip}=2.46$ ($I=0$)[11] and $\log K_2^{ip}=3.73$ ($I=0$),[12] were corrected for the ionic strength by using the Davies equation:

$$\log y_i = -0.512\,z_i^2\left(\frac{\sqrt{I}}{1+\sqrt{I}}-0.3I\right). \tag{4}$$

The concentrations of the ion pairs, x_1 and x_2, were calculated by the use of Eqs. 2 and 3, and the ionic strength was re-evaluated. The final values of x_1 and x_2 were obtained by repeating such calculations until their values became unchanged within 0.01% of their respective values. Using x_1 and x_2 for each run, one can determine the rate constants, k_1 and k_2, from Eq. 1 so as to fit the observed rate constants, k_{obsd}: $k_1=(4.0\pm0.2)\times10^{-3}\,mol^{-1}\,dm^3\,s^{-1}$ and $k_2=(3.0\pm0.2)\times10^{-2}\,mol^{-1}\,dm^3\,s^{-1}$. These constants were obtained at the ionic strengths of 0.32 for k_0, 0.26—0.34 for k_1, and 0.3—0.9 for k_2 (Table 2); the effective charge of one of the reactants participating in each of the II—IV paths is low (+1 for II, and 0 for III and IV), so that the values of k_1 and k_2 will not be appreciably affected by the ionic-strength change.

The expression for the yields of $CoSO_4(NH_3)_5^+$, F (in %) on the basis of the reaction scheme given above is:

$$F/100 = [r_1k_1\{x_2(a-x_1)+x_1(b-x_2)\} + r_2k_2x_1x_2]/(k_{obsd}a), \tag{5}$$

where r_1 and r_2 are the fractions of SO_4^{2-} entering into the coordination sphere of cobalt(III) in competition with the H_2O solvent when AlF^{2+} leaves $CoF(NH_3)_5^{2+}SO_4^{2-}Al^{3+}$ and $SO_4^{2-}CoF(NH_3)_5^{2+}SO_4^{2-}$-$Al^{3+}$ respectively. In Eq. 5, all the parameter values except for r_1 and r_2 have been obtained in the analysis of the reaction rates. The value of r_2 can be taken as 0.33, which is the F/100 value at the saturation (Table 3). Then, $r_1=0.27\pm0.02$ results, thus fitting the experimental F values listed in Table 3. The r_1 and r_2 values are of comparable magnitude, in contrast to the significant difference between the k_1 and k_2 values. Thus, the reaction through Path IV is very important in determining the reaction rates, while Path IV only slightly increases the fraction of SO_4^{2-} entering into the coordination sphere of the cobalt(III). The second sulfate ion contained in the reaction intermediate assists the two reactant cations in approaching each other, but it rarely enters the coordination sphere of the cobalt(III) in the intermediate step.

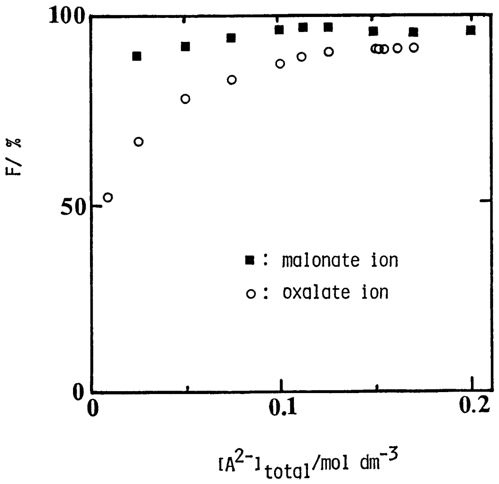

Fig. 1. The yield of $CoA(NH_3)_5^+$ depending on the concentration of the anions.
$[CoF(NH_3)_5^{2+}]_{initial}=5.0\times10^{-3}\,mol\,dm^{-3}$, $[Al^{3+}]_{total}=5.1\times10^{-2}\,mol\,dm^{-3}$.

Effects of Oxalate and Malonate Ions. The competition reactions were also examined in the presence of oxalate ions and of malonate ions. The product percentages and the rate constants are shown in Figs. 1 and 2 respectively. The effects of these ions distinctly differ from that of the sulfate ion in both the reaction rates and the products: (1) The reactions are more effectively accelerated by the dicarboxylate anions, but at high concentrations of the anions the reaction rate decreases instead of reaching saturation, and (2) the yields of the anionopentaamminecobalt(III) ions are unusually high. These specific effects of the anions have not so far been reported for the competition reactions accompanying the assisted aquations of the pentaamminecobalt(III) complexes.[3—8]

As the dicarboxylate ions tend to form complexes with the aluminium ion,[13,14] the present reactions can be regarded as reactions between $CoF(NH_3)_5^{2+}$ and AlA_n^{3-2n}. In order to confirm the stoichiometry, we made a ^{19}F NMR study of the final products existing

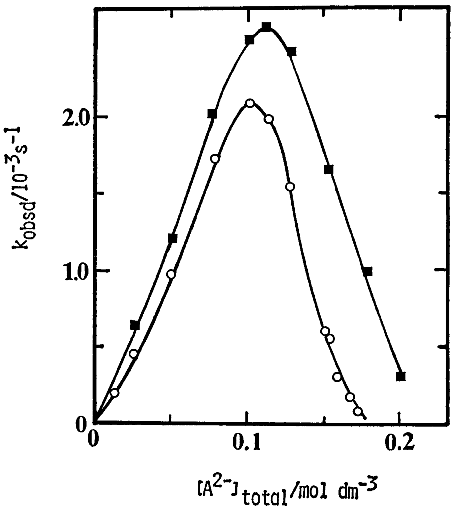

Fig. 2. Dependence of the rate constant on the concentration of the anions.
○: Oxalate ion, ■: malonate ion. $[CoF(NH_3)_5^{2+}]_{initial}=5.0\times10^{-3}$ mol dm^{-3}, $[Al^{3+}]_{total}=5.1\times10^{-2}$ mol dm^{-3}.

in the reaction solutions. The measurements were made for three samples varying in their concentrations of the added sodium oxalate, but with unchanged conditions of $[CoF(NH_3)_5^{2+}]_{initial}=0.050$ mol dm^{-3} and $[Al^{3+}]_{total}=0.20$ mol dm^{-3}. The values of the chemical shift (δ) of the main peak with reference to F^- were -35.2, -38.4, and -38.8 for $[ox^{2-}]_{total}=$ 0.20, 0.41, and 0.61 mol dm^{-3} respectively; the signal of $CoF(NH_3)_5^{2+}$ could not be detected. A solution of $[NaF]=0.050$ mol dm^{-3}, $[Al^{3+}]_{total}=0.20$ mol dm^{-3}, and $[ox^{2-}]_{total}=0.41$ mol dm^{-3} was also measured as a reference; it gave a peak at -38.5 from F^-. As the chemical shift of the AlF^{2+} peak is -36.1 from F^-,[2] the above results suggest the formation of the Al–F bonding. (The small differences among them may be due to the effect of oxalate ligands in the aluminium complexes.) A comparison of the peak areas between the samples and the reference reveals that most of the fluoride ions in the initial $CoF(NH_3)_5^{2+}$ had moved to the aluminium ions in every case. The ^{19}F NMR results, together with the results shown in Fig. 2, lead to the conclusion that the reaction:

$$CoF(NH_3)_5^{2+} + AlA_n^{3-2n} \longrightarrow$$
$$CoA(NH_3)_5^{+} + AlFA_{n-1}^{4-2n},$$

produced about a 90% yield when $[A^{2-}]_{total}>[Al^{3+}]_{total}\gg[CoF(NH_3)_5^{2+}]_{initial}$.[15]

The mechanism of the reaction will be considered next. It is very improbable that the oxalate or the malonate ion enters into the coordination sphere of cobalt(III) after the formation of the aquapentaamminecobalt(III) ion, because the anation reaction of the aqua complex by these anions proceeds much more slowly than the present reaction.[16,17] This was confirmed by examining the reaction of the aqua complex with an excess of the oxalato– or the malonato–aluminium complex. The spectrum of the mixed solution remained unchanged for several days at 25 °C, and only the aqua complex was detected by means of a chromatographic technique using an SP-Sephadex column and a 0.15 mol dm^{-3} sodium–sulfate solution. It can, therefore, be concluded that the anion directly enters into the coordination sphere of cobalt(III) as soon as the aluminium ion extracts the fluoride ion from $CoF(NH_3)_5^{2+}$. The present reaction seems to be interesting as an extreme case of a competition reaction and can be classified as a double-ligand-exchange reaction, which is a very rare type of the reactions of the octahedral inert complexes.[18] This specific reaction will arise from the strong affinity of the aluminium ion to the dicarboxylate ions, combined with the residual capacity of the aluminium-bonded dicarboxylate ions for coordinating with cobalt(III). The latter factor is probably important, for the yield of the acetatopentaamminecobalt(III) in the $CoBr(NH_3)_5^{2+}$–$Hg(CH_3CO_2)_2$ system[7] was low (18.0 or 19.0%) in spite of the large formation constants of mercury–acetate complex. ($\log K_1=5.55$, $\log \beta_2=9.30$, at $I=1.0$ mol dm^{-3}).[19] A general rule for a high yield of the anionopentaamminecobalt(III) to be obtained in the competition reactions will be found by further studies of various systems.

An attempt was made to detect the formation of an intermediate in the present reaction. A binuclear complex such as $[(NH_3)_5Co\genfrac{}{}{0pt}{}{\cdot F\cdot}{\cdot A\cdot}Al]^{3+}$ might be present in the intermediate step. A rapid-scan spectrophotometer was used to follow the absorption change in the $CoF(NH_3)_5^{2+}$–Al^{3+}–ox^{2-} system (1:10:20, concentration ratio) in the wavelength region of about 290 to 350 nm, where $Coox(NH_3)_5^{+}$ or $CoHox(NH_3)_5^{2+}$ has a specific charge-transfer band originating in the Co–ox bonding. No species other than reactants and products were, however, detected in the time scale of 10 ms—10 s. This experiment was not able to distinguish between the dissociative and associative mechanisms.

The rate constants shown in Fig. 2 have a maximum approximately at the position of $[A^{2-}]_{total}/[Al^{3+}]_{total}=2$, decreasing on both sides with a less steep slope on the left side. These characteristics of the curve may result from different reactivities of the AlA_n^{3-2n} complexes with different n values. Thus, the concentrations of a series of aluminium–dicarboxylate species in each solution were calculated on the basis of the literature values of the successive formation constants, K_n and the acid dissociation constants, K_{a1} and K_{a2}, of the dicarboxylic acid: $\log K_1=6.06$, $\log K_2=5.03$, and $\log K_3=4.03$ for the Al^{3+}–ox^{2-} system ($I=1.0$ mol dm^{-3}),[13] $\log K_1=5.24$, $\log K_2=4.16$, and $\log K_3=4.06$ for the Al^{3+}–mal^{2-} system ($I=0.2$ mol dm^{-3}),[14] $pK_{a1}=3.5$ and $pK_{a2}=1.1$ for oxalic acid, and $pK_{a1}=5.1$ and $pK_{a2}=2.6$ for malonic acid at $I=1.0$ mol dm^{-3}.[20] The results are listed in Table 4, together with the kinetic results and the observed pH value. For $[A^{2-}]_{total}/[Al^{3+}]_{total}=1.0$ and 2.0, the calculated concentration of each aluminium complex and the observed rate constant vary in proportion to $[Al^{3+}]_{total}$ or $[A^{2-}]_{total}$, while the pH value changes without affecting their proportionality. From Fig. 2, the reactivities of the aluminium species can be expected to decrease in this order: $AlA_2^{-}>AlA^{+}>AlA_3^{3-}$

TABLE 4. DEPENDENCE OF THE RATE CONSTANTS ON THE CONCENTRATION OF THE ALUMINIUM COMPLEX
($[CoF(NH_3)_5^{2+}]=5.0\times10^{-3}$ mol dm^{-3}, I[a)]$=0.80\pm0.02$ mol dm^{-3}; 25 °C.)

(I) A=ox	$[Al^{3+}]$	$[Alox^+]$	$[Alox_2^-]$	$[Alox_3^{3-}]$	k_{obsd}/s^{-1}	$(pH)_{obsd}$
(a) $[Al^{3+}]_{total}$[b)] $=[ox^{2-}]_{total}$						
0.202	4.34×10^{-2}	1.18×10^{-1}	3.92×10^{-2}	1.73×10^{-3}	3.46×10^{-3}	1.70
0.101	2.18×10^{-2}	5.88×10^{-2}	1.95×10^{-2}	8.56×10^{-4}	1.72×10^{-3}	1.80
0.0505	1.09×10^{-2}	2.94×10^{-2}	9.79×10^{-3}	4.29×10^{-4}	9.28×10^{-4}	2.10
0.0303	6.54×10^{-3}	1.76×10^{-2}	5.85×10^{-3}	2.56×10^{-4}	5.54×10^{-4}	2.20
(b) $[Al^{3+}]_{total}=\dfrac{[ox^{2-}]_{total}}{2.0}$						
0.202	2.15×10^{-3}	4.50×10^{-2}	1.16×10^{-1}	3.92×10^{-2}	5.68×10^{-3}	1.51
0.101	8.67×10^{-4}	2.02×10^{-2}	5.80×10^{-2}	2.19×10^{-2}	2.75×10^{-3}	3.88
0.0505	4.34×10^{-4}	1.01×10^{-2}	2.90×10^{-2}	1.10×10^{-2}	1.38×10^{-3}	3.97
	4.40×10^{-4}	1.02×10^{-2}	2.90×10^{-2}	1.09×10^{-2}	1.35×10^{-3}	3.07
0.0303	2.61×10^{-4}	6.08×10^{-3}	1.74×10^{-2}	6.56×10^{-3}	7.61×10^{-4}	4.07
(c) $[Al^{3+}]_{total}=\dfrac{[ox^{2-}]_{total}}{3.0}$						
0.0909	8.51×10^{-8}	6.74×10^{-5}	6.56×10^{-3}	8.43×10^{-2}	3.22×10^{-4}	3.10
0.0505	1.07×10^{-7}	6.42×10^{-5}	4.72×10^{-3}	4.57×10^{-2}	1.43×10^{-4}	3.12
	2.16×10^{-7}	1.01×10^{-4}	5.85×10^{-3}	4.45×10^{-2}	2.32×10^{-4}	2.89
0.0303	1.31×10^{-7}	6.14×10^{-5}	3.53×10^{-3}	2.67×10^{-2}	1.01×10^{-4}	3.13

(II) A=mal	$[Al^{3+}]$	$[Almal^+]$	$[Almal_2^-]$	$[Almal_3^{3-}]$	k_{obsd}/s^{-1}	$(pH)_{obsd}$
(a) $[Al^{3+}]_{total}=[mal^{2-}]_{total}$						
0.182	5.97×10^{-2}	1.08×10^{-1}	1.34×10^{-2}	1.11×10^{-3}	6.01×10^{-3}	1.83
0.101	2.87×10^{-2}	6.21×10^{-2}	9.31×10^{-3}	9.22×10^{-4}	3.42×10^{-3}	2.33
0.0505	1.26×10^{-2}	3.17×10^{-2}	5.52×10^{-3}	6.35×10^{-4}	1.76×10^{-3}	2.68
0.0303	6.89×10^{-3}	1.92×10^{-2}	3.71×10^{-3}	4.74×10^{-4}	1.09×10^{-3}	3.02
(b) $[Al^{3+}]_{total}=\dfrac{[mal^{2-}]_{total}}{2.0}$						
0.182	5.25×10^{-3}	7.06×10^{-2}	6.57×10^{-2}	4.04×10^{-2}	8.31×10^{-3}	2.50
0.101	3.03×10^{-3}	3.99×10^{-2}	3.63×10^{-2}	2.18×10^{-2}	4.10×10^{-3}	2.75
0.0505	8.28×10^{-4}	1.50×10^{-2}	1.89×10^{-2}	1.57×10^{-2}	1.76×10^{-3}	4.09
	1.69×10^{-3}	2.09×10^{-2}	1.79×10^{-2}	1.01×10^{-2}	1.95×10^{-3}	2.90
	7.70×10^{-3}	3.18×10^{-2}	1.09×10^{-2}	7.52×10^{-5}	1.97×10^{-3}	1.98
0.0303	9.34×10^{-4}	1.21×10^{-2}	1.08×10^{-2}	6.42×10^{-3}	1.24×10^{-3}	3.13
(c) $[Al^{3+}]_{total}=\dfrac{[mal^{2-}]_{total}}{3.0}$						
0.0909	5.43×10^{-6}	9.05×10^{-4}	1.04×10^{-2}	7.95×10^{-2}	1.70×10^{-3}	3.96
0.0505	4.99×10^{-7}	1.55×10^{-4}	3.32×10^{-3}	4.70×10^{-2}	5.04×10^{-4}	4.95
	6.25×10^{-6}	8.07×10^{-4}	7.20×10^{-3}	4.25×10^{-2}	9.25×10^{-4}	3.99
	2.13×10^{-3}	2.29×10^{-2}	1.71×10^{-2}	8.40×10^{-3}	1.92×10^{-3}	2.39
0.0303	7.46×10^{-6}	7.53×10^{-4}	5.26×10^{-3}	2.43×10^{-2}	5.85×10^{-4}	4.00

a) The ionic strength was controlled with $NaClO_4$, considering the formation of the Al^{3+}-A^{2-} complexes shown in this table. b) All brackets denote the concentration in mol dm^{-3}.

and Al^{3+}. Therefore, when $[A^{2-}]_{total}/[Al^{3+}]_{total}=1.0$ and 2.0, the contribution of AlA_3^{3-} and Al^{3+} to the reaction can be neglected, and the observed rate constant can be expressed as: $k_{obsd}=k_1[AlA^+]+k_2[AlA_2^-]$. The values of k_1 and k_2 can be obtained so as to fit the experimental values, starting from the first approximate value of $k_2=k_{obsd}/[AlA_2^-]$ for the case of $[A^{2-}]_{total}/[Al^{3+}]_{total}=2.0$. The k_1 and k_2 values thus obtained are: $(1.5\pm0.1)\times10^{-2}$ mol^{-1} dm^3 s^{-1} and $(4.5\pm0.3)\times10^{-2}$ mol^{-1} dm^3 s^{-1} for A=ox, and $(4.2\pm0.3)\times10^{-2}$ mol^{-1} dm^3 s^{-1} and $(7.5\pm0.5)\times10^{-2}$ mol^{-1} dm^3 s^{-1} for A=mal. When $[A^{2-}]_{total}/[Al^{3+}]_{total}=3.0$, the concentrations of the aluminium complexes are more sensitive to the pH value; therefore, the calculated concentrations may be accompanied by considerable errors resulting from possible errors in the equilibrium constants and in the pH values. The gross rate constants calculated with the k_1 and k_2 values obtained above are 10—50% larger than the experimental values for A=ox, even when $Alox_3^{3-}$ is assumed to be nonreactive, while, for A=mal, they are 10—50% smaller than the experimental values

TABLE 5. DEPENDENCE OF THE RATE CONSTANTS ON THE TEMPERATURES

([cobalt complex] $=5.0\times10^{-3}$ mol dm^{-3}, $I_{app}=0.61$ mol dm^{-3}.)

(I) $[Al^{3+}]_{total} = \frac{1}{2.0}[ox^{2-}]_{total} = 0.051$ mol dm^{-3}

T/°C	$10^3 \times xk_{obsd}$/s^{-1}
20	1.17
25	1.97
30	3.02
35	4.17

(II) $[Al^{3+}]_{total} = \frac{1}{2.0}[mal^{2-}]_{total} = 0.051$ mol dm^{-3}

T/°C	$10^3 \times k_{obsd}$/s^{-1}
20	1.73
25	2.35
30	3.58
35	5.37

when calculated on the assumption that $Almal_3^{3-}$ is not reactive. It may, therefore, be said that the reactivity of $Alox_3^{3-}$ is low, while $Almal_3^{3-}$ is reactive to some extent.

The fact that the reactivity of AlA_2^- is the largest among the consecutive complexes can be attributed to the favorable characteristics that the complex electrostatically assists the two reactant cations in approaching each other and that it can easily react with the fluoride ligand of the cobalt complex. On the other hand, in spite of its larger negative charge, AlA_3^{3-} is not so reactive, probably because the aluminium ion is masked by the ligands in this complex. The malonate ion more effectively accelerates the reaction and increases the yield of $CoA(NH_3)_5^+$. This may be attributable to the flexibility of the chelate ring formed by malonate ligands; the central aluminium ion of the more flexible malonato complex may more easily come in contact with the fluoride ligand of the cobalt(III) complex, and the malonate ion may be more easily transferred to the cobalt(III).

The yields of $CoA(NH_3)_5^+$ are not listed in Table 4, because they scarcely depended at all on the concentration of the aluminium complex (varying only within 1%); they depended only on the $[A^{2-}]_{total}/[Al^{3+}]_{total}$ ratio (see Fig. 1).

Table 5 shows the rate constants at different temperatures with $[A^{2-}]_{total}/[Al^{3+}]_{total}=2.0$ (the ionic strength is given in the analytical concentration). They give the values of ΔH^* and ΔS^* as 57 ± 3 kJ mol^{-1} and -92 ± 14 J K^{-1} mol^{-1} respectively for A=ox, and as $\Delta H^*=55\pm2$ kJ mol^{-1} and $\Delta S^*=-110\pm11$ J K^{-1} mol^{-1} respectively for A=mal. These values approximately agree with each other, but they are significantly different from the values, $\Delta H^*=74$ kJ mol^{-1} and $\Delta S^*=-72$ J K^{-1} mol^{-1}, for the reaction in the $CoF(NH_3)_5^{2+}$–Al^{3+} system ($I=0.61$ mol dm^{-3}).[2)] The activation enthalpies are depressed by the electrostatic attraction of the anions to both the reactant cations, while the activation entropies decrease as a result of a stringent geometrical condition to form the activated complex. These effects are similar to that of added salts on the activation parameters in a cation-cation reaction.[21)]

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