1818 © 1981 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 54, 1818—1820 (1981) [Vol. 54, No. 6

The Aluminium Ion-assisted Aquation of $[CoF(NH_3)_5]^{2+}$

Masayasu Iida,* Eiko Kai,** Kichisuke Nishimoto,** and Hideo Yamatera***
Department of Chemistry, Faculty of Science, Nara Women's University, Nara 630
***Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558*
****Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464*

(Received September 25, 1980)

A kinetic study of the aluminium ion-assisted aquation of $CoF(NH_3)_5{}^{2+}$ was carried out. The pseudo-first-order rate constant obtained can be expressed as $k_{obsd}=k_{Al}[Al^{3+}]$, where $k_{Al}=(1.6\pm0.2)\times10^{-3}\ dm^3\ mol^{-1}\ s^{-1}$ ($I=2.0$ mol dm^{-3}, 25 °C). The reaction rate is independent of the pH in the $(pH)_{obsd}<3.3$ range, in contrast with the pH-dependent rate for the $CrF(NH_3)_5{}^{2+}$–Al^{3+} system. The different behavior between $CoF(NH_3)_5{}^{2+}$ and $CrF(NH_3)_5{}^{2+}$ in aquation can be explained in terms of their electronic structures, as calculated on the basis of the CNDO/2 method.

There has been much interest in the reactions of the metal ion-assisted aquations of transition-metal complexes.1) We ourselves have been studying this type of reaction from the point of view that this is a good and simple model to explain the mechanism of an inorganic reaction.2,3)

In a previous paper, we reported the kinetics for the aluminium ion-assisted aquation of the pentaamminefluorochromium(III) ion and attributed the pH dependency of the reaction rate to an easy protonation of $CrF(NH_3)_5{}^{2+}$.3) The present paper is concerned with an aluminium ion-assisted aquation of $CoF(NH_3)_5{}^{2+}$, which showed a pH dependence entirely different from that of $CrF(NH_3)_5{}^{2+}$.

Different behavior has also been observed between $CrF(NH_3)_5{}^{2+}$ and $CoF(NH_3)_5{}^{2+}$ in their spontaneous aquation.3,4) In order to understand the differences, the CNDO/2 calculation has been carried out on these complexes.

Experimental

Materials. Pentaamminefluorocobalt(III) nitrate was prepared according to the literature.5) The nitrate was converted to perchlorate by the addition of $NaClO_4$. The purity of the crystals was confirmed by means of SP-Sephadex column chromatography with spectrophotometric detection. Found: Co, 15.80; N, 18.90; H, 3.93%. Calcd for $[CoF(NH_3)_5](ClO_4)_2$: Co, 16.28; N, 19.34; H, 4.17%.

The preparation of sodium perchlorate and aluminium perchlorate and the confirmation of their purity were carried out as previously described.3)

The other chemicals used were guaranteed reagents from Wako Pure Chemicals Industries, Ltd.

Kinetic Procedure. Kinetic measurements were made in a manner similar to that previously described.3) The concentration of the complex was controlled to 5.0×10^{-3} mol dm^{-3}. The absorbance changes were followed at 330 nm for all the sample solutions. The pseudo-first-order rate constants were determined by plotting $\ln(D_t-D_\infty)$ against the time, where D_t and D_∞ are the absorbances at the time t and at an infinite time respectivey.

pH Measurements. The procedure of pH measurements has been described previously.3) We used this relation: $(pH)_{obsd}+\log[H^+]=-0.21$ for a 0.1 mol dm^{-3} $Al(ClO_4)_3$ solution. The pH of the sample solution was controlled by mixing a 0.2 mol dm^{-3} $Al(ClO_4)_3$ solution with a NaOH solution of an appropriate concentration.

^{19}F NMR Measurements. A JEOL FX 60Q spectrometer was used in the pulse Fourier transform mode at 56.26 MHz, with a deuterium lock to obtain the ^{19}F spectra. The water used in the sample solution was doubly distilled; it contained 5% by volume D_2O to provide a lock signal for the NMR spectrometer. The sample temperature was controlled to 30±1 °C, and the concentration of the complex was controlled to 0.05 mol dm^{-3}. All samples were examined in 5-mm tubes using $BF_3(C_2H_5)_2O$ as an external reference. The values of the chemical shifts obtained with reference to the external $BF_3(C_2H_5)_2O$ was converted to those with reference to F^- (in a neutral aqueous solution); the latter will be designated by δ below.

Calculations

In the present calculation, the standard values6) are used for the CNDO/2 parameters associated with the H, N, and F atoms. The parameter values for the Co and Cr atoms, including those previously reported,7) are summarized in Table 1. The geometries of the complexes are given by the experimental data:8) 1.97 Å (Co–N), 1.87 Å (Co–F), 2.06 Å (Cr–N), 1.96 Å (Cr–F), and 1.01 Å (N–H).

Table 1. CNDO/2 parameters

		Cr	Co
$1/2(I_\mu+A_\mu)$/eV$^{a)}$	4s	3.909	4.17
	4p	0.876	1.16
	3d	4.822	5.839
$-\beta_\mu{}^\circ$/eV$^{b)}$	4s	15.70	17.10
	4p	3.52	4.76
	3d	23.00	28.00
$\zeta_\mu{}^{c)}$	4s, 4p	1.31	1.423$^{d)}$
	3d	2.48	2.83$^{d)}$

a) Clack's parameter.6) I_μ: ionization potential. A_μ: electron affinity. b) $\beta_\mu{}^\circ$: bonding parameter. c) ζ_μ: orbital exponent. d) Zerner's parameter.15)

Results and Discussion

Al^{3+}-assisted Aquation. The aquation of $CoF(NH_3)_5{}^{2+}$ yielding $CoOH_2(NH_3)_5{}^{3+}$ was promoted by aluminium ions. The spectrum of the sample solution changed with the time, showing isosbestic points at 360 and 506 nm, which indicates that no by-products were formed. Table 2 shows that the pseudo-first-order-rate constant obtained is approximately proportional to the aluminium-ion concentration, *i.e.*, $k_{obsd}=$

TABLE 2. DEPENDENCE OF THE RATE CONSTANT ON THE CONCENTRATION OF THE ALUMINIUM ION
(The ionic strength is controlled to 2.0 mol dm^{-3} by $NaClO_4$; at 25 °C, pH 2.5, and [complex] = 5.0×10^{-3} mol dm^{-3}.)

$\frac{[Al^{3+}]}{\text{mol dm}^{-3}}$	k_{obsd}/s^{-1}	$\frac{k_{obsd}}{[Al^{3+}]}/\text{dm}^3\ \text{mol}^{-1}\ s^{-1}$
0.030	4.54×10^{-5}	1.51×10^{-3}
0.050	7.59×10^{-5}	1.52×10^{-3}
0.10	1.57×10^{-4}	1.57×10^{-3}
0.15	2.46×10^{-4}	1.64×10^{-3}
0.20	3.58×10^{-4}	1.79×10^{-3}

$k_{Al}[Al^{3+}]$, where $k_{Al}=(1.6\pm0.2)\times10^{-3}$ dm^3 mol^{-1} s^{-1}. The small systematic variation in k_{Al} may result from the change in the perchlorate concentration (1.91—1.40 mol dm^{-3}) for the solutions of equal ionic strength. Considering the results of Swaddle and Jones[4] and of Chan,[9] we can write the total rate constant as:

$$k_{obsd} = k_0 + k_H[H^+] + k_{Al}[Al^{3+}],$$

where $k_0=3.3\times10^{-7}$ s^{-1} [4] (2.44×10^{-7} s^{-1} [9]), $k_H=5.2\times10^{-4}$ dm^3 mol^{-1} s^{-1} [9] at 35 °C and $I=0.112$—0.12 mol dm^{-3}. Under the present conditions, the first and second terms can be neglected in comparison with the third term.

The dependency of the reaction rate on the pH is shown in Fig. 1, together with the degree of hydrolysis of aluminium ions.[10] Previous results for the CrF-$(NH_3)_5{}^{2+}$–Al^{3+} reaction are also depicted for comparison.

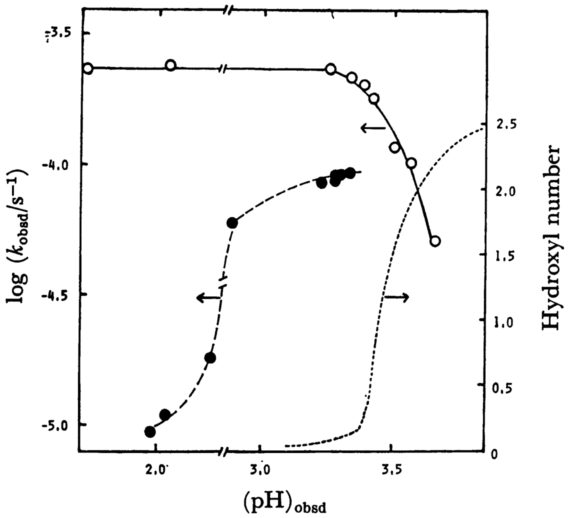

Fig. 1. pH dependence of the pseudo-first-order rate constants for $CoF(NH_3)_5{}^{2+}$–Al^{3+} system (—○—) and for $CrF(NH_3)_5{}^{2+}$–Al^{3+} system (---●---),[3] and the degree of hydrolysis of aluminium ions (------).[10] The hydroxyl number means the $[OH^-]/[Al^{3+}]$ ratio in hydrolysis products. Aveston (Ref. 10) gave the degree of the hydrolysis as a function of log[H$^+$], which is transformed to (pH)$_{obsd}$ (see pH measurements in the text). The experimental conditions for the reaction rates are: [complex] = 5.0×10^{-3} mol dm^{-3}, $[Al(ClO_4)_3]=0.10$ mol dm^{-3}, and at 35 °C, and for the hydrolysis: $[Al(ClO_4)_3]=0.10$ mol dm^{-3}, at 25 °C.

A distinct difference exists in the reactivity between the chromium(III) and cobalt(III) complexes. The chromium(III) complex was considered to be easily protonated at the site of the fluoro ligand, and the complex is blocked from the approach of aluminium ions in the pH region lower than 3.0.[3] On the other hand, the present results show that the cobalt(III) complex is not so easily protonated as the chromium(III) complex and that the contribution of the protonated species to the reaction can be neglected even at a pH lower than 3.0. The reaction rate decreases with an increase of pH above $(pH)_{obsd}=3.4$, where a marked change occurs in the degree of hydrolysis of aluminium ions. According to Aveston[10] and Turner,[11] the formation of polycationic complexes begins to occur around this pH region, and their reactivity may be considerably smaller than that of Al^{3+} or $AlOH^{2+}$.

TABLE 3. SECOND-ORDER RATE CONSTANTS AT VARIOUS TEMPERATURES
([complex] = 5.0×10^{-3} mol dm^{-3}, $[Al^{3+}]=0.10$ mol dm^{-3}.)

t/°C	k_{Al}/dm^3 mol^{-1} s^{-1}
20	4.9×10^{-4}
25	1.2×10^{-3}
30	1.7×10^{-3}
35	2.6×10^{-3}
40	4.2×10^{-3}

Table 3 lists the rate constants at different temperatures; those rate constants give the values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ as 74±5 kJ mol^{-1} and -72 ± 15 J mol^{-1} K^{-1} respectively. On the other hand, the activation parameters for the electron-transfer reaction, $CoF(NH_3)_5{}^{2+}+Fe^{2+}\rightarrow Co^{2+}+FeF^{2+}+5NH_3$, are $\Delta H^{\neq}=56$ kJ mol^{-1} and $\Delta S^{\neq}=-96$ J mol^{-1} K^{-1}.[12] The comparison of the $\Delta S^{\neq}$ values for the aquation and the reduction satisfies the general tendency that more stringent geometrical conditions have to be satisfied in the reduction.[13]

^{19}F NMR Study. The ^{19}F NMR signal of $CoF(NH_3)_5{}^{2+}$ cannot be detected even by 5000 scans for a 0.15 mol kg^{-1} solution of the complex. However, when an excess of aluminium ions was added to the solution of the cobalt(III) complex, a signal appeared which was assigned to the AlF^{2+} species (chemical shift $\delta=-36.1$ ppm from F^-).[14] As the reaction proceeds, the signal grows and approaches a constant height. This change corresponds to the formation of AlF^{2+} in the $CoF(NH_3)_5{}^{2+}+Al^{3+}\rightarrow CoOH_2(NH_3)_5{}^{3+}+AlF^{2+}$ reaction. When the aluminium-ion concentration was so low as to be compared with the $CoF(NH_3)_5{}^{2+}$ concentration ($[Al^{3+}]/[CoF(NH_3)_5{}^{2+}]<5$), an additional peak appeared. This peak had a chemical shift 0.65 ppm lower than that of the AlF^{2+} peak and was assigned to $AlF_2{}^+$.[14] All the kinetic studies were, therefore, carried out in the concentration range of $[Al^{3+}]/[CoF(NH_3)_5{}^{2+}]>5$, where the formation of by-products can be disregarded.

Electronic Effects on the Aquation of $CrF(NH_3)_5{}^{2+}$ and $CoF(NH_3)_5{}^{2+}$. In the spontaneous aquation of $CrF(NH_3)_5{}^{2+}$, the ammonia ligands are more easily displaced than the fluoro ligand, but the tendency

TABLE 4. THE CALCULATED BOND ORDERS ASSOCIATED WITH METAL-LIGAND BONDS

	$CrF(NH_3)_5^{2+}$		$CoF(NH_3)_5^{2+}$		$CrFH(NH_3)_5^{3+}$	
	Cr–F	Cr–N[a)]	Co–F	Co–N[a)]	Cr–F	Cr–N[a)]
σ-Donation						
4s-2s	0.238	0.260	0.235	0.258	0.217	0.267
4s-2p_σ	0.242	0.221	0.250	0.242	0.129	0.226
4p_σ-2s	0.357	0.340	0.360	0.351	0.334	0.350
4p_σ-2p_σ	0.384	0.318	0.417	0.355	0.213	0.338
3d_σ-2s	0.134	0.184	0.116	0.178	0.178	0.196
3d_σ-2p_σ	0.620	0.322	0.645	0.323	0.253	0.359
π-Donation						
3d_π-2p_π	0.101	—	0.0	—	0.061	—

a) The N atom here refers to the *cis*-N atom to F^-, because *cis*-$[CrF(OH_2)(NH_3)_4]^{2+}$ is the main product in the spontaneous aquation of $CrF(NH_3)_5^{2+}$ (Ref. 3).

is reversed in $CoF(NH_3)_5^{2+}$.[4,9)] These results suggest that the Cr–F bond is stronger than the Cr–N bond, but Co–F is weaker than Co–N. The strength of the metal-ligand bond can be measured by the corresponding bond order. Table 4 lists the calculated bond orders of the complexes. The results show that the 3dπ-2pπ interaction strengthens the Cr–F bond, but makes no contribution to the Co–F bond, which explains the significantly greater stiffness of the Cr–F bond as compared with the Co–F bonds. On the other hand, the bond-order values show only a slight difference between Cr–N and Co–N. Therefore, it is possible that Cr–F is stronger than Cr–N, but Co–F is weaker than Co–N, although a simple comparison of bond orders cannot predict which is the stronger between bonds of different types, *i.e.*, between ionic M–F and ion-dipolar M–N.

As has been stated above, $CrF(NH_3)_5^{2+}$ is more easily protonated than $CoF(NH_3)_5^{2+}$. This can be explained by the greater value of the net negative charge of F in the chromium complex than in the cobalt analogue, as is shown in Table 5. The experimental results can also be explained qualitatively from the viewpoint of electronegativities; the less electronegative chromium forms a more ionic bond and the F linked to Cr should be more easily protonated than that bonded to Co. Therefore, the pH dependency of the aquation in the $CrF(NH_3)_5^{2+}$–Al^{3+} system can be well understood.

TABLE 5. THE CALCULATED NET CHARGES OF $CrF(NH_3)_5^{2+}$ AND $CoF(NH_3)_5^{2+}$

	M(Cr or Co)	*cis*-N	F
$CrF(NH_3)_5^{2+}$	+0.653	−0.202	−0.387
$CoF(NH_3)_5^{2+}$	+0.480	−0.183	−0.342

Table 4 also gives the results for the protonated complex, $CrFH(NH_3)_5^{3+}$, for the sake of comparison. Although it shows that the Cr–F bond is considerably weakened by the protonation, this is not well reflected in the experimental results shown in a previous paper:[3)] the ammonia ligands in $CrF(NH_3)_5^{2+}$ are more easily removed than the fluoro ligand at pH 2, where most of the $CrF(NH_3)_5^{2+}$ should be protonated ($\log K_H = 3.0$).

References

1) R. G. Wilkins, "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes," Allyn and Bacon, Boston (1974), p. 213.

2) M. Iida and H. Yamatera, *Bull. Chem. Soc. Jpn.*, **52**, 2290 (1979).

3) M. Iida and H. Yamatera, *Bull. Chem. Soc. Jpn.*, **54**, 441 (1981).

4) T. W. Swaddle and W. E. Jones, *Can. J. Chem.*, **48**, 1054 (1970).

5) F. Basolo and R. K. Murmann, *Inorg. Synth.*, **4**, 172 (1953).

6) D. W. Clack, N. S. Hush, and J. R. Yandle, *J. Chem. Phys.*, **57**, 3503 (1972).

7) E. Kai and K. Nishimoto, *Int. J. Quantum. Chem.*, **18**, 403 (1980).

8) Y. Kushi, 37th National Meeting of the Chemical Society of Japan, 2J28, Tokyo, April 1978; S. A. Goldfield and K. N. Raymond, *Inorg. Chem.*, **10**, 2604 (1971).

9) S. C. Chan, *J. Chem. Soc.*, **1964**, 2375.

10) J. Aveston, *J. Chem. Soc.*, **1965**, 4438.

11) R. C. Turner, *Can. J. Chem.*, **53**, 2811 (1975).

12) H. Diebler and H. Taube, *Inorg. Chem.*, **4**, 1029 (1965).

13) A. E. Ogard and H. Taube, *J. Am. Chem. Soc.*, **80**, 1084 (1958).

14) R. E. Connick and R. E. Poulson, *J. Phys. Chem.*, **79**, 5153 (1957).

15) M. Zerner and M. Gouterman, *Theor. Chim. Acta.*, **4**, 44 (1966).