TABLE I

FLUORINE NMR SPECTRA

Compound	Solvent	Temp,[a] °C	δ,[b] ppm	J_{WF}, cps	Additional information
WF_6	$CFCl_3$		−165.2	44	
WF_6	Cyclohexane		−165.4	41	
WF_6	Mesitylene		−166.0	39	
WF_6	SO_2		−166.4	44	
WF_6	CH_3CN		−165.9	. . .	
WF_6	CH_3CN	−15	−165.2	48	
$F_6WP(CH_3)_3$	CH_3CN		−135.5	. . .	J_{PF} = 73 cps
$F_6WP(CH_3)_3$	SO_2	−20	−137.4	38	J_{PF} = 73 cps
$F_6WN(CH_3)_3$	SO_2		−144.8	. . .	
$F_6WNC_5H_5$	SO_2		−163.9	. . .	
$F_6WNC_5H_5$	CH_2Cl_2		−162.5	. . .	
$F_6W(NC_5H_5)_2$	SO_2	25	−135.9	. . .	
WOF_4	SO_2		−73.9	64	
$(n\text{-}C_3H_7)_4N^+WOF_5^-$	CH_3CN		Doublet −49.4 Quintuplet +82.8	70	J_{FF} = 53 cps
$(n\text{-}C_3H_7)_4N^+WOF_5^-$	SO_2		Doublet −54.3 Quintuplet +71.9	71	J_{FF} = 52 cps
$(C_6H_5)_2NPF_4$	Toluene	−72	+46.4 (F_a) +73.0 (F_e)		J_{PF_a} = 788 cps; J_{FF} = 81 cps J_{PF_e} = 941 cps
$(C_6H_5)_2NPF_4$	Toluene		+59.8		J_{PF} = 865

[a] Unless otherwise specified the temperature was about 28° without external temperature control. [b] Reference: internal $CFCl_3$.

acetonitrile solutions was markedly temperature dependent. In sulfur dioxide solution, the shift varied from −137.9 ppm at +31° to −121.7 ppm at −30°. No comparable temperature dependence of chemical shift was found in any of the other complexes studied.

The WF_6–CH_3CN System.—A white solid, soluble in acetonitrile, was formed on reaction of WF_6 and CH_3CN but was not isolated in this study. The nmr spectrum of a solution of 0.1 ml of WF_6 dissolved in a mixture of 0.4 ml of CH_3CN and 0.1 ml of $CFCl_3$ consisted of a broad line (70 cps at half-height) at room temperature and of a relatively sharp (9 cps) line at −15° with visible WF satellites.

Preparation of WOF_4 and WOF_5^-.—Tungsten hexafluoride, 14 g (0.047 mole), was condensed into an evacuated Hastelloy-C bomb containing 5.0 g (0.022 mole) of tungsten trioxide. The vessel was sealed and shaken at 400° for 6 hr, cooled to room temperature, vented to a hood, and purged several times with nitrogen at 100 psi. The product was transferred under nitrogen and sublimed in glass equipment at 100° under vacuum. The yield was 5.6 g or 31% based on the equation $WO_3 + 2WF_6 \rightarrow 3WOF_4$. Resublimation yielded 4.3 g (mp 97–102°; lit.,[10] 110°). *Anal.* Calcd for WOF_4: W, 66.7; F, 27.5. Found: W, 67.6; F, 27.6. This material was used without further purification for the preparation of WOF_5^-.

Tetra-*n*-propylammonium fluoride was prepared by neutralization of a 10% solution of tetra-*n*-propylammonium hydroxide in water with an aqueous solution of 48% hydrofluoric acid. The bulk of the water was removed at approximately 3 mm and the resulting semisolid was further dried under vacuum (10^{-5} mm) at 100° for 6 hr. A solution of 2.5 g of this solid dissolved in 10 ml dichloromethane was added under a nitrogen atmosphere to 2.2 g of WOF_4 suspended in 5 ml of dichloromethane. The mixture was filtered and solvent was removed from the filtrate to the point of crystallization of the product $(n\text{-}C_3H_7)_4NWOF_5$. The first crop of product isolated in this manner weighed ~0.6 g and was recrystallized from dichloromethane. *Anal.* Calcd for $C_{12}H_{28}NWOF_5$: C, 30.0; H, 5.9; N, 2.9; F, 19.7; W, 38.2. Found: C, 29.5; H, 5.7; N, 3.3; F, 19.3; W, 38.2.

Nmr Procedures.—Fluorine-19 nmr spectra were obtained at 56.4 and 94 Mc using Varian HR-60 and HA-100 instruments. Samples were maintained in sealed evacuated tubes at liquid nitrogen temperatures prior to examination. Chemical shifts are reported with reference to internal $CFCl_3$.

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Base Hydrolysis of $[Co(NH_3)_5X]^{2+}$ Ions

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The rate law for base hydrolysis of cobalt(III) complexes has been established for a wide variety of complexes[1] as

$$-\frac{d[\text{complex}]}{dt} = k[\text{complex}][OH^-]$$

but mostly for low base concentrations. However, a recent article[2] on the base hydrolysis of the chloropentaamminecobalt(III) ion has described a rate law which deviates substantially from a first-order dependence on $[OH^-]$ at higher OH^- concentrations, Figure 1. This deviation was interpreted on the basis of an ion-pair mechanism, but the possibility of the result arising from the production of an appreciable concentration of the deprotonated intermediate was not excluded.

This note questions the validity of the rate data ob-

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[10] O. Ruff, F. Eisner, and W. Heller, *Z. Anorg. Allgem. Chem.*, **52**, 256 (1907).

(1) For collected references see F. Basolo and R. G. Pearson "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1967.

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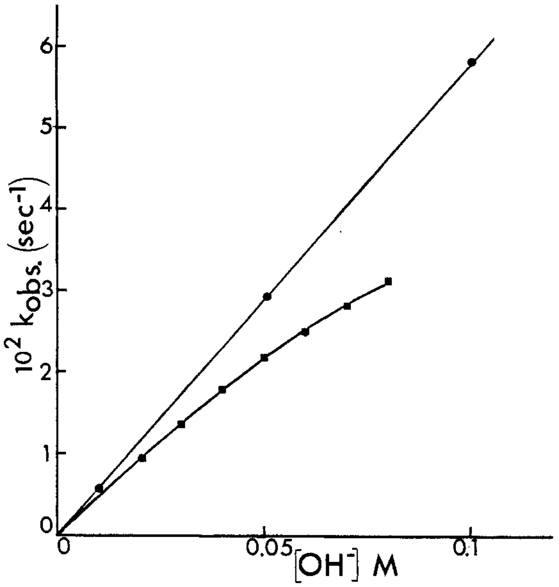

Figure 1.—Rate constants for the base hydrolysis of $[Co(NH_3)_5Cl](ClO_4)_2$ at 25.4°, $\mu = 0.1$, and [complex] $= 3.43 \times 10^{-3}$ *M*: ●, present results; ■, ref 2.

tained by Chan[2] and the base hydrolysis experiments with the $[(NH_3)_5CoCl]^{2+}$ and $[(NH_3)_5CoBr]^{2+}$ ions

$$[Co(NH_3)_5X]^{2+} + OH^- \longrightarrow [Co(NH_3)_5OH]^{2+} + X^-$$

have been repeated over a wide range of OH^- concentrations at 25.4°. The rate constants are given in Tables I and II. The rates were followed spectrophotometrically at constant ionic strength, using a stopped-flow reactor.

TABLE I

RATE CONSTANTS FOR THE BASE HYDROLYSIS OF $[Co(NH_3)_5Cl](ClO_4)_2$ AT 25.4°[a]

C_{NaOH}, *M*	10^2k_{obsd}, sec^{-1} [b]	*k*, M^{-1} sec^{-1}
	(a) $\mu = 0.1$	
0.01	0.547 ± 0.005 (5)	0.63
0.05	2.95 ± 0.07 (6)	0.61
0.1	5.80 ± 0.07 (6)	0.59
	(b) $\mu = 1.0$	
0.01	0.235 ± 0.001 (3)	0.26
0.05	1.25 ± 0.02 (5)	0.26
0.25	6.31 ± 0.11 (5)	0.25
0.5	12.2 ± 0.02 (5)	0.24
1.0	23.5 ± 0.6 (6)	0.24

[a] $C_{complex} = 3.43 \times 10^{-3}$ *M*, measured at 275 mμ. [b] Average values with standard deviations and number of determinations in parentheses.

TABLE II

RATE CONSTANTS FOR THE BASE HYDROLYSIS OF $[Co(NH_3)_5Br](ClO_4)_2$ AT 25.4°[a]

C_{NaOH}, *M*	10^2k_{obsd}, sec^{-1} [b]	*k*, M^{-1} sec^{-1}
0.01	1.33 ± 0.02 (4)	1.40
0.05	6.92 ± 0.10 (5)	1.40
0.25	34.3 ± 0.3 (6)	1.37

[a] $\mu = 1.0$, $C_{complex} = 1.36 \times 10^{-3}$ *M*, measured at 310 mμ. [b] Average values with standard deviations and number of determinations in parentheses.

First, Chan's conditions were duplicated at $\mu = 0.1$, using 0.1, 0.05, and 0.01 *M* $[OH^-]$, and linear plots of log $(D_\infty - D_t)$ against *t* were obtained over the first two half-lives. The observed rate constants (k_{obsd}) show a first-order dependence on $[OH^-]$, Table Ia. These are plotted in Figure 1, along with those reported by Chan.[2] The accuracy of the present data is attested by the small standard deviations obtained, Tables I and II. The average concentration of OH^- ion in $2t_{1/2}$ was used to derive the second-order rate constant.

Second, the measurements were extended to $\mu = 1.0$ so that a wider range in the concentration of base could be used, Table Ib. It is apparent that no significant deviation from a first-order dependence on $[OH^-]$ occurred even at $[OH^-] = 1.0$ *M*. This concentration is more than 10 times greater than the highest concentration of base used by Chan, and a major departure from a first-order dependence would be expected if Chan's effect was real. Moreover the "normal" rate law for base hydrolysis

$$R = k[Co(NH_3)_5X^{2+}][OH^-]$$

was also obtained for the related $[(NH_3)_5CoBr]^{2+}$ ion, Table II, and again no departure from this proportionality was observed in the range $0.01 \leqslant [OH^-] < 0.25$ *M* at 25.4°.

The present results are not consistent with the ion-pair mechanism proposed by Chan[2] unless the ion-pair association constant is small, $K_{ip} < 0.05$ at $\mu = 1.0$. Such a value is not inconsistent with the value expected for the association of a 2+ ion and OH^- if the Bjerrum theory[3] holds and appropriate correction is made for the ionic strength. Some evidence for the validity of the theory might be inferred from the ion association constant for $[Co(NH_3)_6]^{3+}$ and OH^- at $\mu = 0$.[4]

The results are also in keeping with the estimated high pK_a values (>15) for those ions[5] and with repeated failures to determine the pK_a values of related inert species such as $[Co(NH_3)_6]^{3+}$ which might be expected to have a lower pK_a value than the 2+ ions discussed here. Both the ion-pair association constants and the pK_a values for the chloro and bromo complexes would be expected to be similar and this is reflected in the similarity of their kinetic behavior.

Experimental Section

The complexes $[Co(NH_3)_5Br](ClO_4)_2$ and $[Co(NH_3)_5Cl](ClO_4)_2$ were the same as those used previously.[6]

The cobalt complexes were dissolved in water or $NaClO_4$ solutions (pH 5–6) depending on the ionic strength requirements of the final solutions. Similarly NaOH concentrations were prepared in water or in the appropriate $NaClO_4$ solution. The reactant solutions were mixed rapidly at 25.4° in a stopped-flow reactor[7] and the change in absorbance (~4 OD unit) was followed using a Shimadzu RS 27 recording spectrophotometer.

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