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LEAVING GROUPS ON INERT METAL COMPLEXES WITH INHERENT OR INDUCED LABILITY

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I. Introduction

The terms *labile* and *inert* represent the two extremes of kinetic reactivity (*273*). Like any simple bifurcation, membership of either group involves a degree of ambiguity. For simple water-exchange reactions of aqua metal cations, for example, it would seem reasonable to describe Ba_{aq}^{2+} as a labile metal ion (k_{ex} $\sim 10^9$ sec^{-1} at 25°C) (*91*) whereas Al_{aq}^{3+} (k_{ex} 0.13 sec^{-1}) (*102*) could be called inert because of the markedly (10^{10}-fold) slower rate constant. However, even this substantial difference pales when comparison is made with ions such as Rh_{aq}^{3+} (k_{ex} 5.9×10^{-9} sec^{-1}) (*229*), in which aqua ligand exchange is $\sim 10^{19}$ times slower than for Ba_{aq}^{2+}. It is relatively simple to assign a metal-ion complex at an extreme of reactivity to one or other group since the reactions are generally slow or fast, irrespective of the type of ligands involved. Consequently, we have come to accept particularly octahedral d^3 or d^6 metal–ion complexes as inherently inert in nature. Indeed, the kinetic (though not necessarily thermodynamic) stability of complexes of cobalt(III) and chromium(III), for example, has promoted this century an extensive study of their chemistries.

It has been recognized for many decades that there is an intimate relationship between coordinated ligand type and physical properties. In particular, the rate at which a donor ligand can be displaced by another in the coordination sphere of an inert metal ion is markedly dependent on the type of ligand involved. If a variety of donors are bound to a metal ion, one particular site may be far more likely to undergo ligand exchange or substitution than others; this selectivity is important in the efficient operation of many metalloenzymes and in the operation of certain catalysts. Even with simple octahedral complexes, solvolytic reactions are sensitive to the nature and position of other ligands relative to that of the leaving group and the entering group, which indicates that factors other than the leaving group type operate. These influences make the isolation and systemization of effects, based simply on the nature of the leaving group, difficult because of the intimate connection with the nature of both the nonleaving ligands and the entering nucleophile.

When we are dealing with reactions in solution, the solvent structure obviously influences the behavior of dissolved compounds. It is convenient to consider reactions in aqueous solution generally, though not exclusively, since the bulk of studies reported in the literature refer to aqueous media. Some of the effects described in this review result in part from significant perturbation of the solvent structure. Since we will be dealing largely with ionic compounds, it is important to remind ourselves that the solvent molecules in the vicinity of the ion differ in properties from those in the bulk solution. A series of progressively ordered and electrostricted hydration sheaths surround the ion. Water molecules in the first hydration sheath of a $[ML_6]^{3+}$ complex ion are subjected to a significant electrostatic pressure and contract by 2–3 $cm^3 mol^{-1}$ in molar volume and, if transferred to the coordination shell of an ion, may contract up to a further 9 $cm^3 mol^{-1}$ (*267*). Subsequently, reactions involving formation of new charge centers, such as occur for simple displacement of an anionic ligand from a complex ion, involve substantial solvent rearrangement as charge centers gain or lose electrostricted solvent layers. Although these effects can be of consequence to the reaction mechanist, since they invariably complicate the task, in much of this discussion we endeavor to limit consideration of minutiae of the role of the solvent.

Further, and again largely as a reflection of the bulk of the literature, we deal with complex ions with amine donors in the majority of coordination sites. Except where the effect of the nonleaving group is discussed specifically, these groups are largely treated as a necessary adjunct of the metal ion. In general, reactivity at one site of a metal complex is addressed. Often, simple pentaamminemetal complexes serve as the basis of discussion. For coordination chemists, the $[M(NH_3)_5]^{n+}$ unit can be considered almost as the equivalent of the methyl group for an organic chemist; that some papers in the literature abbreviate this unit as Ro (or a similar shorthand) is perhaps indicative of such a progression.

It is therefore the purpose of this review to deal with traditional and simple inert metal–ion complexes, mainly octahedral, in which the rate of displacement of at least one ligand permits it to be defined as labile relative to the normal reactivity of complexes of that metal ion. This reactivity may be an inherent property of the ligand as a consequence of poor nucleophilicity (as for $^{-}OClO_3$ or $^{-}OSO_2CF_3$, for example) (*179*). Alternatively, lability may be induced as a result of effects such as the influence of other nonleaving donors, reactions of the ligand with reagents external to the complex ion, or solvation phenomena. Because it touches on areas of chemistry previously well reviewed, no exhaustive literature citation is attempted in certain sections. Apart from purely cataloguing trends in reactivity, the role of labile leaving groups in both mechanistic studies and in chemical synthesis are addressed also.

Throughout, the artificial stance of assigning lability or inertness as essentially a property of the ligand has been adopted. This is simply a consequence of restricting discussion to the traditional inert metal-ion complexes. Variations in reactivity resulting from altering the metal ion occur and are discussed during the review. Nevertheless, it is convenient to 'scale' lability in terms of the rate of substitution of a ligand. A ligand-based order of lability derived for a particular d^3 or d^6 metal ion can be largely transposed to another, at least as regards the more reactive ligands. The terms *labile* and *inert*, as first employed by Taube (*273*), should properly be applied only to a complete system involving metal complex, leaving group and entering group. The application of the term *labile* here as effectively a leaving-group property is merely a convenient device resulting from the defined limitations of this review, rather than an attempt to redefine the terminology.

II. Inherent Lability

A. TOWARD GOOD LEAVING GROUPS

It is common practice to consider the traditional Werner octahedral complex ions $[M(LN)_6]^{n+}$ [M = Co(III), Rh(III), Ir(III), Cr(III), Ru(III), Pt(IV); LN = donor atom of unidentate or polydentate ammine or amine] as well as square-planar $[M(LN)_4]^{2+}$ [M = Pt(II), Pd(II)] as kinetically inert compounds. Bound ammonia is generally less labile than bound water, and it has been suggested that this observation can be related to the presence of an extra and exposed electron pair in water. This may make it more sensitive to electrophilic groups in the solvation sheath, which could assist its dissociation from the metal ion (*274*). If we take the stance of assigning lability as a property of the ligand in such complexes, then ammonia and amines in general can be designated as relatively inert or poor leaving groups. Although the rate of ammine loss varies with the metal ion, being ~10^4-fold more rapid for Cr(III) than for Co(III), for example (*25, 209*), the general robustness of polyamine complexes led to an intense study of particulary $M(NH_3)_5X^{n+}$ compounds, where overwhelmingly (but not exclusively), substitution processes involve replacement of the X-group (*90*).

In aqueous solution, the $M(NH_3)_5(OH_2)^{n+}$ ions permit a reasonable definition of inertness for the metal–ion complexes in terms of water-exchange rates. Although not directly analogous to the extensive data for $M_{aq}{}^{n+}$ systems in general (*125*), which permit a now classic assignment of lability or inertness, the results provide a sufficient comparison.

Studies of water-exchange reactions of aqua transition metal ions have implied that the structure of the ion in the ground state is an important factor in defining lability. Ion charge plays a role since more highly charged ions are less likely to exchange rapidly. The ionic radius is involved, but more particularly, peculiarities in shape; for example, elongation of axial bonds in $Cu_{aq}{}^{2+}$ contributes markedly to the rapid exchange rate constant (~10^9 sec^{-1}) (*125*) observed. Electronic effects related to variation in the number and location of *d*-electrons are also important. Considerations such as these cast ions such as Cr^{3+} into the inert regime. Data for several $[M(NH_3)_5(OH_2)]^{3+}$ ions exist (Table I) and illustrate the typically slow rate constants for these systems. Moreover, exchange rates for known $[M(OH_2)_6]^{3+}$ analogs are not excessively different, with the exception of $[Co(OH_2)_6]^{3+}$, where substitution may take place through the high-spin labile state (*274*). This suggests that the effects of the nonleaving groups on a common leaving group (Section III,A) may not be a major factor usually, and concentration on the leaving group itself then becomes reasonable. The water-exchange rate constants for metal ions span a range of ~10^{20}, with the complexes under discussion clearly in the inert regime.

TABLE I

RATE CONSTANTS FOR EXCHANGE OF A WATER MOLECULE IN SOME AQUA COMPLEXES

Complex	k_{ex} (sec^{-1})[a]	Reference	Complex	k_{ex} (sec^{-1})[a]	Reference
$[Cr(OH_2)_6]^{3+}$	4.5×10^{-7}	*128, 259*	$[Cr(NH_3)_5(OH_2)]^{3+}$	6.1×10^{-5}	*88, 270*
$[Co(OH_2)_6]^{3+}$	1×10^{2}	*274*	$[Co(NH_3)_5(OH_2)]^{3+}$	5.7×10^{-6}	*127*
$[Rh(OH_2)_6]^{3+}$	5.9×10^{-9}	*229*	$[Rh(NH_3)_5(OH_2)]^{3+}$	8.6×10^{-6}	*203, 270*
$[Al(OH_2)_6]^{3+}$	1.3×10^{-1}	*102*	$[Ir(NH_3)_5(OH_2)]^{3+}$	6.1×10^{-8}	*30, 279*
$[Ba(OH_2)_6]^{2+}$	$\sim 1 \times 10^{9}$	*91*	$[Ru(NH_3)_5(OH_2)]^{3+}$	2.3×10^{-4}	*80*

[a] At 25°C.

1. *Pentaamminecobalt*(III) *Compounds*

In the extensive range of $[Co(NH_3)_5X]^{n+}$ complexes reported in the literature, observed rate constants for substitution of the X-group are commonly slow (*19, 51, 90, 258, 289*). Aquation reactions in acidic or neutral solution generally take several hours or at least many minutes to reach completion; selected data appear in Table II. The conception of what merits accreditation as a good leaving group has, of course, been amended with the passage of time. For a considerable period, nitrate ion represented the most accessible ligand for cobalt(III) that departed at any reasonable rate (*35*), but still with a half-life of ~7 hr at 25°C. It had long been recognized that many molecules should be very poor ligands for cobalt(III) and other metal ions. The hurdle for the coordination chemist involved devising ways of replacing a usually far better ligand by the presumed poor ligand. It is only in the last few decades that significant advances in introducing good leaving groups into a normally inert coordination sphere have been achieved.

One early and successful route to better leaving groups involved the use of metal ions that are external to the complex cation under study to promote the loss of a halide or thiocyanate ion from the coordination sphere (*158*). This occurs by complexation of the added metal ion with the coordinated ligand, effectively generating a cationic or neutral leaving group that departs more rapidly (see Section III,B). Conducted in potentially coordinating solvents, this chemistry permits the syn-

TABLE II

AQUATION RATE CONSTANTS FOR (LIGAND)PENTAAMMINECOBALT(III) COMPLEXES

Ligand	k_{obs} (sec^{-1})[a]	Reference	Ligand	k_{obs} (sec^{-1})[a]	Reference
NH_3	5.8×10^{-12}	*209*	CH_3SO_3	2.0×10^{-4}	*42*
PO_4^{3-}	1.5×10^{-9}	*189*	$OP(OCH_3)_3$	2.5×10^{-4}	*251*
NO_2^-	1.2×10^{-8}	*169*	NH_2COCH_2F	1.1×10^{-3}	*98*
CH_3COO	2.7×10^{-8}	*202*	$NH_2SO_2NH_2$	1.3×10^{-2}	*168*
CF_3COO^-	1.5×10^{-7}	*202*	Sulfolane	$\sim 2 \times 10^{-2}$	*129*
SO_4^{2-}	8.9×10^{-7}	*201*	CH_3COOCH_3	$\sim 2 \times 10^{-2}$	*129*
Cl^-	1.7×10^{-6}	*3*	FSO_3^-	2.2×10^{-2}	*145*
OH_2	5.7×10^{-6}	*127*	$CF_3SO_3^-$	2.7×10^{-2}	*82*
Br^-	6.5×10^{-6}	*3*	$NH_2SO_2C_6H_4 \cdot NO_2$	3.8×10^{-2}	*168*
$OS(CH_3)_2$	2.2×10^{-5}	*241*	$OC(CH_3)_2$	$\sim 4 \times 10^{-2}$	*82*
NO_3^-	2.7×10^{-5}	*35*	$NH_2SO_2C_6H_4 \cdot CH_3$	$\sim 1 \times 10^{-1}$	*168*
$OHCH_3$	5.9×10^{-5}	*82*	ClO_4	$\sim 1 \times 10^{-1}$	*121*

[a] At 25°C.

thesis of a range of $[M(NH_3)_5L]^{3+}$ compounds with molecules such as dimethylsulfoxide (Me_2SO) coordinated as ligands.

The concept of altering the displacement rate of a leaving group by altering its character was carried further with experiments in which chemical reactions involving solely one ligand were performed with a view to generating a good leaving group. In particular the cobalt(III)–azido bond, usually robust, could be broken by reaction of the azido complex with NO^+, available as HONO commonly (*118*). The generated Co(III)—N_4O intermediate is particularly short-lived, releasing N_2O and N_2 and providing a "naked" coordination site for solvent or anions to occupy (Section I,D). This chemistry permitted the introduction of tetramethylenesulfone (sulfolane) under well-controlled conditions (*129*); this remains one of the most readily displaced ligands for cobalt(III), even permitting coordination of the ester methyl acetate on dissolution of the former complex in the ester. This chemistry also permitted the introduction of even the poor nucleophile ClO_4^- into the coordination sphere of cobalt(III) (*121*). With complexes containing such ligands, aquation is exceptionally fast (Table I); we have reached the time regime in which reaction and equilibration is effectively complete in the time of mixing, or less than one minute, which equates with Taube's definition of labile as it appears in his 1952 review (*273*).

Subsequently, further examples of labile groups on cobalt(III) have appeared. The sulfamido ($NH_2SO_2NH^-$) ligand itself aquates from the pentaamminecobalt(III) complex only slowly, but in aqueous acid unusually large aquation rate constants are observed and are tied to facile release of the protonated form, $NH_2SO_2NH_2$ ($t_{1/2}$ ~ 50 sec) (*168*). The related protonated ligands $NH_2SO_2C_6H_4CH_3$ and $NH_2SO_2C_6H_4NO_2$ are displaced even more rapidly. The acid dependence of the observed rate constant in these systems is consistent with a process, Eq. (1), where $k_2 \gg k_1$.

$$\begin{array}{ccc}
[(NH_3)_5CoNHSO_2NH_2]^{2+} + H^+ & \overset{K_a}{\rightleftharpoons} & [(NH_3)_5Co(NH_2SO_2NH_2)]^{3+} \\
\downarrow k_1 & & \downarrow k_2 \\
[(NH_3)_5CoOH_2]^{3+} + {}^-NHSO_2NH_2 & & [(NH_3)_5CoOH_2]^{3+} + NH_2SO_2NH_2
\end{array} \tag{1}$$

In effect, this represents an extreme case of acceleration by an external reagent (H^+) and aspects of this chemistry are discussed in Section III,B.

The ready availability of the strong anhydrous acids fluorosulfuric acid and trifluoromethanesulfonic acid in recent decades prompted more chemistry (*179*). The electron-withdrawing properties of the CF_3—, F—, and —SO_2— groups suggested that FSO_3^- and $CF_3SO_3^-$

(trifluoromethane sulfonate, or triflate) anions could be good leaving groups, a role established earlier for the latter anion in organic chemistry (*124*). Access to complexes of these anions came about from the recognition that the strong anhydrous acids would protonate many simple ligands and promote their loss from the coordination sphere; subsequently, in the absence of any competing ligands, FSO_3^- or $CF_3SO_3^-$ occupies the vacant site. With $[Co(NH_3)_5Cl]^{2+}$, for example, CF_3SO_3H reacts according to Eq. (2).

$$[Co(NH_3)_5Cl]^{2+} + CF_3SO_3H \longrightarrow [Co(NH_3)_5(OSO_2CF_3)]^{2+} + HCl\uparrow \qquad (2)$$

The displaced HCl is readily removed as a gas in a stream of an inert gas (*82, 85*). The reaction is conveniently performed at elevated temperature but works at or below room temperature, particularly if reaction time is extended. The product can be simply precipitated from the anhydrous acid solution by careful addition of diethyl ether. Anions other than Cl^- can be removed (e.g., Br^- and NO_2^-), and the procedure has been extended to accommodate a range of metal ions and nonleaving groups (*85, 179*). Further, it has been shown that the $CF_3SO_3^-$ ligand in $[Co(NH_3)_5(OSO_2CF_3)]^{2+}$ hydrolyzes cleanly and rapidly with simple Co—O cleavage (*42*); this permits its use in chemical synthesis (Section V). On the other hand, $[Co(NH_3)_5(OSO_2F)]^{2+}$ in dilute aqueous acid and dimethylsulfoxide undergoes both Co—O and S—F cleavage, with F^- and SO_4^{2-} detected (*145*). This propensity for scission of bound FSO_3^- limits its synthetic use, and the $CF_3SO_3^-$ ligand has developed as a preferred good leaving group. Alternative routes to the introduction of $CF_3SO_3^-$ as a ligand have been developed and have been reviewed (*179*).

Electronic spectroscopy of pentaamminemetal complexes has located $CF_3SO_3^-$ between Cl^- and N_3^- in the spectrochemical series (*84*). Moreover, estimated ligand field parameters Δ and B yielded a nephelauxetic ratio of 0.70, high in comparison with other ligands and indicative of a very low covalent contribution to bonding. Tied to the low energy of the purely electrostatic component of bonding evident from the determined Δ value, this offers an interpretation of the ease with which $CF_3SO_3^-$ leaves the coordination sphere of most metal ions. In cobalt(III) chemistry, $CF_3SO_3^-$ remains the most accessible and labile leaving group. This is also the case for a range of other metal ions. Of the simple ligands, only ClO_4^- is a better leaving group. However, perchlorato complexes are less accessible, may be difficult to handle as a consequence of the oxidizing properties of the anion, and consequently represent a far less compelling source of a labile site for synthetic purposes.

2. *Other Pentaamminemetal Compounds*

Octahedral $[M(NH_3)_5X]^{n+}$ compounds are known for a range of metal ions, and with central metal ions such as Rh(III), Ir(III), Cr(III), and Ru(III) substitution reactions are usually slow for most X-groups (Table III). Prior to recent work with $CF_3SO_3^-$ as a ligand, few attempts at introducing inherently good leaving groups (beyond ions such as nitrate) appeared with metals other than cobalt(III). In chromium(III) chemistry it had long been recognized that the hydrolysis rates of $[Cr(NH_3)_5X]^{n+}$ and $[Cr(OH_2)_5X]^{n+}$ compounds were similar (Table III), and the $Cr(OH_2)_5(OClO_3)^{2+}$ ion was known to aquate rapidly (*253*; so presumably inherently good leaving groups should exist for pentaamminechromium(III). Further, the redox reaction between the pentaammineruthenium(III) complex with the substituted pyridine NC_5H_4—$COOCH_3$ and Cr_{aq}^{2+} generated an intermediate pentaaqua(ester)chromium(III) ion that aquated with a rate constant of 0.035 sec^{-1} at 25°C (*109*). The expectation that inherently good leaving groups should exist with metal complexes beyond cobalt(III) was satisfied with coordination of $CF_3SO_3^-$ in a range of metal-ion complexes.

The $[M(NH_3)_5(OSO_2CF_3)]^{2+}$ ions actually show an increase in relative lability, compared with $[M(NH_3)_5Cl]^{2+}$ ions, for second- and third-row members of the cobalt triad; the ratio of aquation rate constants $k(CF_3SO_3^-)/k(Cl^-)$ varies from 1.4×10^4 (Co) to 5.0×10^5 (Rh) and 2.1×10^5 (Ir) (*84*). Likewise, the ratio of aquation rate constants for triflate and nitrate is substantial, with $k(CF_3SO_3^-)/k(NO_3^-)$ varying

TABLE III

AQUATION RATE CONSTANTS FOR SELECTED (LIGAND)PENTAAMMINEMETAL(III) COMPLEXES[a]

	Rhodium(III)		Iridium(III)		Chromium(III)			
Ligand	k_{obs} (sec^{-1})	Ref	k_{obs} (sec^{-1})	Ref	k_{obs} (sec^{-1})	Ref	(k_{obs} (sec^{-1})	Ref)[b]
SO_4^{2-}	1.6×10^{-6}	*201*	—		1.2×10^{-6}	*6*	(7.5×10^{-7}	*103*)
CF_3COO^-	2.0×10^{-7}	*202*	5.1×10^{-9}	*189*	—		—	
NO_3^-	1.2×10^{-5}	*204*	6.9×10^{-8}	*85*	7.0×10^{-4}	*200*	(7.2×10^{-5}	*10*)
OH_2	8.6×10^{-6}	*270*	6.1×10^{-8}	*279*	6.1×10^{-5}	*270*	(2.3×10^{-5}	*259*)
Br^-	3.4×10^{-8}	*231*	1.1×10^{-9}	*250*	6.8×10^{-5}	*212*	(4.3×10^{-6}	*114*)
Cl^-	3.8×10^{-8}	*231*	1.1×10^{-9}	*249*	7.3×10^{-6}	*212*	(2.8×10^{-7}	*269*)
$CF_3SO_3^-$	1.9×10^{-2}	*84*	2.3×10^{-4}	*84*	1.1×10^{-2}	*84*	($\sim 1 \times 10^{-3}$	*253*)

[a] At 25°C.

[b] Values in parentheses refer to the $[Cr(OH_2)_5X]^{n+}$ analog.

from 1.1 × 10^3 (Co) to 1.5 × 10^3 (Rh) and 3.4 × 10^3 (Ir). Aquation rate constants of the triflato complexes of Cr(III) (1.24 × 10^{-2} sec^{-1} at 25°C) (*84*), Ru(III) (9.2 × 10^{-2} sec^{-1}) (*84*), and even Os(III) (1.8 × 10^{-3} sec^{-1}) (*185*) are fast also. Including the $[M(NH_2CH_3)_5(OSO_2CF_3)]^{2+}$ analogs that have been reported for Co(III), Rh(III), and Cr(III) (*71*), the triflato ion aquates some 10^3 to 10^6 times faster than the chloride ion from pentaamine complexes. This general behavior, despite the variety of metal ions involved, defines the good leaving group properties of $CF_3SO_3^-$ as tied to the poor nucleophilicity of the ligand, that is, there is some validity in describing $CF_3SO_3^-$ as a labile ligand.

Although there are few examples for octahedral complexes of other good leaving groups beyond cobalt(III) chemistry, it should be noted that certain rearrangement reactions can occur rapidly. For example, hydrolysis of the ethylglycinate complex of pentaammineruthenium(III) involves competition between ester hydrolysis and direct ligand hydrolysis and has been interpreted in terms of involvement of a facile N- to O-bonded rearrangement ($k = 1.14 \times 10^{-3}$ sec^{-1} at 25°C) (*291*). Such facile rearrangements are well known in cobalt(III) chemistry also, such as the rapid N- to O-isomerization of the urea NH_2CONMe_2 in acid, which follows a rate law of the form $k[H^+]/(K_a + [H^+])$, where $k = 1.6 \times 10^{-2}$ sec^{-1} at 25°C and $pK_a = 2.92$ for the bound nitrogen (*81*). Because such reactions involve capture of a donor from the same ligand, the description of the ligand as a leaving group is possibly inappropriate; this class of reaction is not treated.

3. *Other Compounds*

The square-planar complexes of Pt(II) and Pd(II) are relatively inert, and the good leaving-group properties of $CF_3SO_3^-$ noted in octahedral complexes carry through to such systems (*86*). Relative rates of aquation, $k(CF_3SO_3^-)/k(Cl^-)$, are 3 × 10^2 for *trans*-$[Pd(NH_3)_2Cl(X)]$ and 1.4 × 10^3 for [Pt(en)Cl(X)] analogs (en = ethane-1,2-diamine), again defining $CF_3SO_3^-$ as a much superior leaving group. A range of Pt(II) and Pd(II) compounds of $CF_3SO_3^-$ with amine, imine, or phosphine ligands also coordinated, have been reported (*9, 86, 104*); all aquate rapidly and also indicate ready replacement of triflate by coordinating solvents generally. The organometallic cyclopentadienyl compound $(\pi\text{-}C_5H_5)_2Ti(OSO_2CF_3)_2$ reacts in aprotic solvent with an alkylammonium nitrate salt to form $(\pi\text{-}C_5H_5)_2Ti(NO_3)_2$ (*164*), indicating that nitrate is a better ligand than triflate in such systems. The triflate ion in $[Mn(CO)_5(OSO_2CF_3)]$ is particularly labile, being rapidly replaced by

CO (*280*). Indeed, it appears that Mn(I)—$OClO_3$ association is stronger than Mn(I)—OSO_2CF_3 association in [$Mn(CO)_5(X)$].

Although there are few comparative kinetic studies for organometallic compounds, half-lives for reactions of triflato complexes are commonly short (*89, 108, 164, 166, 255, 263, 280*). Reactivity trends define $CF_3SO_3^-$ as a better leaving group than a range of other anions including Cl^-, NO_3^-, and SCN^-. For example, [$IrCl(CO)(PR_3)_2(H)(OSO_2CF_3)$] shows ready displacement of $CF_3SO_3^-$ (and also FSO_3^-) by Cl^-, Br^-, SCN^-, and $SeCN^-$ (*217*). Replacement of $CF_3SO_3^-$ by relatively weak σ- and π-donor ligands $P(C_6H_5)_3$, $NCCH_3$, OH_2, $OC(CH_3)_2$, and C_2H_4 occurs readily (*218*). A range of chemistry thus defines both $CF_3SO_3^-$ (and FSO_3^-) as good leaving groups in organometallic compounds in addition to Werner coordination compounds.

Recently, a good deal of chemistry involving the $^-OTeF_5$ (teflate) anion as a ligand has appeared (*2, 60, 210, 260–262*). For example, the Pt(II) norbornadiene (NBD) complex of teflate, [$Pt(NBD)(OTeF_5)_2$], has relatively long Pt—O bonds, and $^-OTeF_5$ dissociates in the donor solvents $NCCH_3$, CH_3NO_2, and $(CH_3)_2CO$ (*60*). There is an accumulation of evidence that clearly defines teflate as a weaker ligand than chloride, but still generally not as good a leaving group as perchlorate or triflate. Nevertheless, teflate can be added to a range of labile ligands that have been identified for commonly inert coordination and organometallic compounds. Of those available, triflate appears to be the most accessible and useful.

Although discussion has largely centered on compounds with one good leaving group, there are now numerous examples of inert complexes with several labile ligands. In cobalt(III) chemistry, the simple compound *cis*-[$Co(en)_2(OSO_2CF_3)_2$]$^+$ is known (*82*), in which both triflates are lost rapidly and sequentially in acid hydrolysis. Aquation leading to the aqua(triflato) complex ($k_1 = 2.2 \times 10^{-2}$ sec^{-1}, 25°C) and then to the diaqua complex ($k_2 = 8.6 \times 10^{-3}$ sec^{-1}) is somewhat unusual since the ratio k_1/k_2 of 2.6 corresponds closely to the purely statistical expectation of $k_1 = 2k_2$. This behavior has also been noted for the Rh(III), Ir(III), and Cr(III) analogs (*84*) and for the [Co(tren)-$(OSO_2CF_3)_2$]$^+$ analog (tren = *N*,*N*-bis(2-aminoethyl)-1,2-ethanediamine) (*69*). Normally, [$M(en)_2X_2$]$^+$ complexes aquate with $k_2 \ll k_1$; with the dichlorocobalt(III) compound, $k_1/k_2 = 150$, for example (*55*). The behavior with triflate is consistent with the relatively weak covalent bonding of this ion, the loss of the first from the coordination sphere having little effect on the second bound triflate. For [Co-(dien)$(OSO_2CF_3)_3$] (dien = 1,5-diamino-3-azapentane), all three triflates depart rapidly (*82*). The consequence of these observations is that poly(triflato) compounds can offer multiple labile sites, with compounds with as many as three triflate ligands relatively stable and readily isolable.

Compounds of triflate of selected geometry have been developed. Compounds of cis geometry tend to dominate bis(triflato) systems, but *trans*-$[M(cyclam)(OSO_2CF_3)_2]^+$ and also *trans*-$[M(cyclam)Cl(OSO_2CF_3)]^+$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) complexes of both Co(III) and Ru(III) have been reported in which the geometry is directed by coordination of the macrocyclic tetraamine ligand incorporating the metal ion in its donor plane (*22*). Partial substitution of chloride permits synthesis of *trans*-$[Co(en)_2Cl(OSO_2CF_3)]^+$ from its dichloro precursor (*61*). All these compounds undergo rapid reaction in solution. In general, reactivity is not influenced greatly for triflato complexes by the nonleaving groups. Even polypyridyl triflato complexes of Ru(II), Ru(III), Os(II), and Os(III) display a lability not unlike the polyamine complexes (*26, 27, 186, 265*).

The relatively facile routes developed for syntheses of triflato complexes, tied to the general stability of such compounds in the solid state, has led to their dominance as sources of complexes with substitution-labile sites. For even the simple pentaamines, the triflato complexes are accessible by dehydration of triflate salts of aqua complexes (*167*), convenient reaction of chloro complexes with the anhydrous acid (*85*), or displacement of other groups by the anhydrous acid [such as dinitrogen in the case of Os(III) (*185*)]. Octahedral bis(chelate) compounds with up to two triflato ligands can also be approached in a number of ways (*179*). With organometallic compounds, further routes involving reactions with anhydride and esters or oxidation-coordination reactions of the acid may be available (*179*). Our progress toward good leaving groups has brought us to an anion that is not necessarily the best leaving group but definitely one of the most versatile. Compounds containing bound $CF_3SO_3^-$ are both inherently labile and synthetically useful.

B. Role of the Metal Ion

Although certain families of metal-ion complexes exhibit similar kinetic behavior, and the same mechanism may operate, there are still obvious and distinct differences from one metal ion to another. The variation with metal ion may be obvious merely from inspection of reaction products. For example, the series of compounds $[M(NH_3)_5X]^{n+}$ [X = $HCOO^-$, $OCH{\cdot}N(CH_3)_2$, or F^-] show in acid formation of only $M(NH_3)_5(OH_2)^{3+}$, where M = Co(III) (*90*), yet exhibit a variety of behaviors for M = Cr(III), in which only ammonia loss ($X = HCOO^-$), only X-group loss [$OCH{\cdot}N(CH_3)_2$], or both ($X = F^-$) occur (*7*). Selectivity of metal ions by various ligands can be distinctive. The ratio of the rate constants for anation of aqua metal ions by SCN^- and Cl^-, $R = k_{an}(SCN^-)/k_{an}(Cl^-)$ has been suggested as a measure of $M_{aq}{}^{n+}$ selectivity (*248*); for example, $R \geq 36$ for $V(OH_2)_6{}^{3+}$ but only 0.6 for $Fe(OH_2)_5(OH)^{2+}$, and distinctly different mechanisms are presumed to operate. Simple comparisons of rate data can mask mechanistic differences; for example, cobalt(III) and chromium(III) pentaammine complexes aquate commonly at similar rates, and common trends (e.g., rate of displacement of $SO_4{}^{2-} < NO_3{}^- < CF_3SO_3{}^-$) can exist. Nevertheless, these metal ions represent the most closely studied systems in which differing mechanisms appear to operate (*73, 90*).

Comparison of data in Tables II and III for the cobalt triad indicates that aquation proceeds, on average, about the same for Rh(III) as for Co(III) and substantially slower for iridium(III). As has been observed earlier, however, lability of $CF_3SO_3{}^-$ complexes is actually enhanced relative to other complexes (such as Cl^- complexes) for iridium(III), and for second- and third-row metal ions generally. The property of $CF_3SO_3{}^-$ as a good leaving group is essentially constant, but the rate of displacement is clearly mediated by the metal ion; aquation of the iridium(III) complex is over 100 times slower than for cobalt(III) whereas loss from the exceptionally inert platinum(IV) is slower still (*84*).

Simple "hard" and "soft" acid–base concepts play a role since the heavier elements generally form softer metal ions; preference for soft chloride ion over hard water molecules can be read into the variable kinetic behavior of $[M(NH_3)_5X]^{n+}$ compounds ($X = OH_2, Cl^-$) (Table IV). Softer metal ions such as Rh(III) and Ru(III) lose or gain soft chloride ions slower or faster, respectively, than harder Co(III) and Cr(III). The $CF_3SO_3{}^-$ is invariably an O-donor (*179*), and thus, like OH_2, is a harder ligand than Cl^-. The trends in its rate of displacement follow more closely the variation in water exchange with metal ion; for example, the ratio of aqua exchange rate constants for Co : Rh : Ir is 93 : 140 : 1 compared with a ratio of 117 : 82 : 1 for triflate aquation. The subtle interplay of metal ion and ligand makes the role of one difficult to isolate and can lead to misconceptions. For example, the view that Ru(III) amines are more substitution inert than cobalt(III) analogs derives largely from the relatively slow aquation rates observed for halopentaammineruthenium(III) ions, but has no general validity (*99*). In fact, aqua, carbonyl, and phosphine complexes of the second transition series metals are generally more labile than related complexes of

TABLE IV

WATER EXCHANGE, CHLORIDE AQUATION AND CHLORIDE ANATION RATES FOR $[M(NH_3)_5X]^{n+}$ COMPOUNDS[a]

	$X = OH_2$		$X = Cl$		$X = OH_2$	
M	k_{ex} (sec^{-1})	Ref.	k_{aq} (sec^{-1})	Ref.	k_{an} (sec^{-1})	Ref.
Cr	6.1×10^{-5}	*88*	7.3×10^{-6}	*212*	3.5×10^{-6}	*88*
Ru	2.3×10^{-4}	*80*	8.8×10^{-7}	*36*	1.2×10^{-4}	*38*
Co	5.7×10^{-6}	*127*	1.7×10^{-6}	*3*	2.8×10^{-6}	*157*
Rh	8.6×10^{-6}	*270*	3.8×10^{-8}	*231*	6.8×10^{-6}	*231*
Ir	6.1×10^{-8}	*30*	1.1×10^{-9}	*249*	$\sim 4 \times 10^{-7}$[b]	*80*

[a] At 25°C.

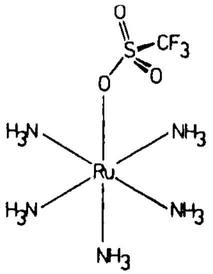
[b] Extrapolated value.

the first and third series (*14, 80*). What has been established is that accessible labile leaving groups on inert metal complexes play this role generally, irrespective of the metal ion. The fact that all the accessible good leaving groups are O-donor molecules conveniently contributes since the heavier and traditionally more-inert metal ions also have a diminished preference for O-donor ligands.

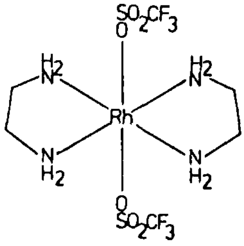
C. SYNTHETICALLY ACCESSIBLE COMPLEXES WITH LABILE SITES

Convenient access to complexes with one or more labile sites on reasonable scales is not necessarily possible in all cases. Compounds with neutral ligands such as sulfolane or acetone can be difficult to isolate and store, as in the former case (*129*), or may not be stable in the solid state, as in the latter case (*82*). Other compounds, such as perchlorato complexes, may be stable in the solid state (*121*), but their use on large scales must be balanced against the oxidizing properties of perchlorate, which can introduce dangers best avoided. Some good leaving groups can undergo rapid decomposition reactions in which the products can interfere in the preferred chemistry, as occurs with fluorosulfate (*145*).

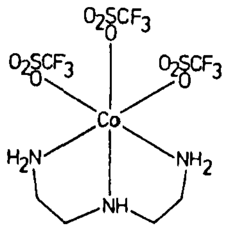
Of available good leaving groups, $CF_3SO_3^-$ provides the best range of accessible and stable complexes. Examples of these compounds have also been included in Section II,A. Applications in synthesis appear in Section V. The range of stable, isolable compounds is extensive, covering coordination and organometallic chemistry. Some examples of compounds appear in Structures **1–6** (*82, 84, 164, 165, 263*).



1



2



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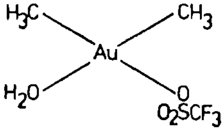

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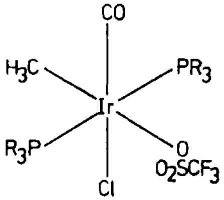
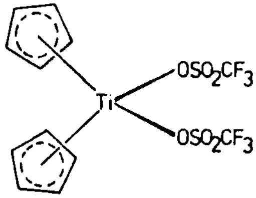


5



6

From such structures it is clear that $CF_3SO_3^-$ is generally bound as an O-donor unidentate ligand; limited examples of other bonding modes, such as bidentate chelate, have been reported (*179*). However, given the poor nucleophilicity of the ion, there are no compelling reasons nor strong evidence for triflate occupying more than one coordination site in solution generally. At least up to three triflato ligands can be introduced conveniently without affecting overall stability of the inert complex. Further, a range of coordination geometries, particularly octahedral and square planar, but also tetrahedral and more complex structures, can exist.

Synthesis may involve simple displacement reactions, Eq. (3), one of the most common approaches. Reaction with the anhydride of triflic acid [as in Eq. (4), for example, where M = Cr, Mo, and W (*276*)] or with the acid ester [as in Eq. (5), for example, which is an oxidative addition reaction (*263*)] also provides access to labile triflato complexes:

$$[ML_mX_y]^{n+} + yCF_3SO_3H \longrightarrow [ML_m(OSO_2CF_3)_y]^{n+} + yHX \tag{3}$$

$$MO_2X_4 + 2(CF_3SO_2)_2O \longrightarrow [MO_2(OSO_2CF_3)_4]^{2-} \tag{4}$$

$$\textit{trans}\text{-}[Ir(CO)Cl(PR_3)_2] + CF_3SO_3CH_3 \longrightarrow [Ir(CO)Cl(PR_3)_2(CH_3)(OSO_2CF_3)] \tag{5}$$

Such compounds should continue to be prominent amongst the most synthetically accessible and practical when seeking good leaving-group properties at one or even several sites of a complex.

D. Labile Sites Produced by Chemical Reaction on a Ligand

An alternative to introducing a good leaving group such as $CF_3SO_3^-$ directly into an isolable complex is to generate a good leaving group *in situ* by a selective chemical reaction on a usually stable ligand. Haim and Taube showed that reaction of NO^+ and cobalt(III)-coordinated azide ion in water is a rapid process and forms N_2 and N_2O as products of the NO^+-N_3^- reaction (*118*). The immediate product of reaction, $[Co(NH_3)_5(NNNNO)]^{3+}$, can be considered to decay in several ways. If N_2O is lost rapidly, an intermediate $[Co(NH_3)_5(N_2)]^{3+}$ may exist; if formed, this does not persist for longer than several seconds (*161*), that is, coordinated dinitrogen is an excellent leaving group in this case [although, of course, it may be stable when ligated to heavy transition metal ions such as osmium(III)]. Several other reports of this reaction have appeared (*40, 151*). Further, nitrozation of the cyanatopentaamminecobalt(III) ion has been reported (*45*). In this case the hydrated cyanate (i.e., N-deprotonated carbamate) adds NO^+ at the coordinated nitrogen to produce an intermediate, Eq. (6), which decays with release of nitrogen and carbon dioxide:

$$\begin{array}{lll} [(NH_3)_5CoNHCOOH]^{2+} + NO^+ & \longrightarrow & [(NH_3)_5CoNH(NO)COOH]^{3+} \\ & & \quad \text{fast} \downarrow \\ & & [(NH_3)_5Co^{3+}]^* + N_2 + CO_2 + H_2O \end{array} \tag{6}$$

Conversion of a coordinated acid to a coordinated ester can be anticipated to generate a good leaving group since the ester CH_3COOCH_3 is known to depart rapidly from cobalt(III) (*129*). Reaction of acetatopentaamminecobalt(III) with acetyl perchlorate in dimethylformamide (DMF) was observed to undergo very rapid solvolytic replacement, presumed to arise from attack of the electrophile on the acetato ligand to form the much less nucleophilic ester (*143*). The chemistry (a deacetoxylation reaction) occurs with both acetyl perchlorate and methyl triflate, with ^{18}O-labeling showing [Eq. (7)] that attack by the electrophile occurs exclusively at the carbonyl oxygen atom of the acetato ligand (*142*):

$$\begin{aligned}&[(NH_3)_5Co{-}{}^{18}O{-}CO{-}CH_3]^{2+} + CH_3{-}OSO_2CF_3 \longrightarrow\\ &\qquad [(NH_3)_5Co{-}{}^{18}O{=}C(OCH_3)CH_3]^{3+} + CF_3SO_3^-\\ &\qquad\quad \text{fast}\downarrow\\ &\qquad [(NH_3)_5Co^{3+}]^{\neq} + H_3CC^{18}OOCH_3\end{aligned} \tag{7}$$

Oxidation of a coordinated ligand in a variety of ways can also generate a good leaving group. Hypohalite and halide oxidations of cobalt(III)-coordinated ligands such as iodide, bromide (*117*), dimethylsulfoxide (*121, 154*), urea (*178*), formate ion (*197, 246*), and azide (*181*) have been reported. With dimethylsulfoxide, for example, the poor nucleophile dimethylsulfone is formed and rapidly departs the coordination shell (*154*). The effective oxidation of metal-bound ligands by Cl_2 and HOCl has been well demonstrated though reaction usually proceeds faster with the former. A study of *cis*- and *trans*-$[Co(en)_2BrX]^{n+}$ complexes with Cl_2 and HOCl showed that the action of the two oxidants may be somewhat different since different product distributions were observed in each case (*239*); indeed, even the original study of $[Co(NH_3)_5I]^{2+}$ or $[Co(NH_3)_5Br]^{2+}$ with Cl_2 and HOCl identified differences (*117*). The silver(II) oxidation of coordinated formate ion has also been investigated recently (*175*), and formation of a labile complex of carbon dioxide is implicated in the reaction.

Essentially all the examples cited involve cobalt(III) compounds, but the chemical generation of a good leaving group should generally be independent of the metal ion unless some metal-centered redox chemistry is initiated. Most examples reported involve generation of short-lived complexes in which a labile ligand has been formed (such as an acid ester or neutral gaseous molecule); subsequently, it is reasonable to include this section under the banner of inherent lability. At the same time, if viewed from the perspective of the precursor compound, we are dealing with cases of induced lability; this section then forms a bridge into the next major topic.

III. Induced Lability

A. EFFECTS OF THE NONLEAVING GROUPS

It is apparent that, in some cases, variation of the nonleaving groups has no marked effect on the rate of displacement of leaving groups. For example, aquation reactions of $[Cr(NH_3)_5X]^{n+}$ and $[Cr(OH_2)_5X]^{n+}$ ions occur with quite similar rate constants (Table III), whereas aquation of the cation $[Co(NH_3)_5NCS]^{2+}$ and the anion $[Co(CN)_5(NCS)]^{3-}$ also proceeds at comparable rates (*4, 119*). Nevertheless, apparently subtle changes can cause marked effects; the rate constant for aquation of *trans*—$[Co(tn)_2Cl_2]^+$ (tn = propane-1,3-diamine) (*156*) is 1500 times greater than that of *trans*—$[Co(en)_2Cl_2]^+$ (*57*) as a result of changing from a six-membered to a five-membered chelate ring, for example. In general, solvolytic reactions of octahedral complexes are modestly sensitive to the type and relative position of other ligands in the complex. Although enhanced lability of a complex as a result of influences of nonleaving groups is often serendipitous in the sense that these ligands are often fixed in a particular reaction by other considerations, it may be useful to catalog briefly some of the effects. In certain cases, usually inert metal-ion systems can show high lability as a consequence of the ligand donor set. For example, porphinato, Schiff-base, and ethylenediaminetetraaacetic acid complexes of chromium(III) (*12, 110, 211, 236, 264*) and ruthenium(III) (*194*) are relatively labile. This behavior arises from the presence of amido-type nitrogen donors in porphyrins, distortions imposed by the ligands, and/or internal activation by pendant groups such as carboxylates. Largely, the following discussion is restricted to saturated ligand systems.

1. *Octahedral Polyamine Complexes*

A great deal of information exists about pentaamine complexes with one leaving group, particularly for cobalt(III) but also for chromium(III) and other metal ions. The amine ligands can comprise any assembly of mono-, bi- or multidentate ligands occupying five sites, and much of the data has been comprehensively reviewed (*126*). An extensive range of cis- and trans-octahedral tetraamine complexes are also known. A selection of aquation rate constants for chloro complexes appears in Table V. The influence of steric effects of ligands is most clear for the series of pentakis-(alkylamine) complexes of cobalt(III) and chromium(III); steric acceleration is observed for the former (*44, 223*) and steric retardation for the latter (*224*), the variation apparently reflecting the different mechanisms operating (*182*). Steric influences can be seen also for the variation from en to tn chelates in *trans*-dichlorocobalt(III) complexes, where the 1500-fold increase is assigned to the extra inter- and intraligand strain in the six-membered ring tn complex (*64*). Variation of geometry can have a larger influence than simply changing the type of nitrogen donor, as exemplified with data for the ruthenium(III) complexes in Table V (*37, 232*). Overall, effects

TABLE V

INFLUENCE OF AMINE NONLEAVING GROUPS ON CHLORIDE AQUATION RATE CONSTANTS[a,b]

Complex	k_{aq} (sec^{-1})	Reference	Complex	k_{aq} (sec^{-1})	Reference
$[Co(NH_3)_5Cl]^{2+}$	1.7×10^{-6}	*3*	$[Cr(NH_3)_5Cl]^{2+}$	8.7×10^{-6}	*224*
$[Co(NH_2CH_3)_5Cl]^{2+}$	3.9×10^{-5}	*223*	$[Cr(NH_2CH_3)_5Cl]^{2+}$	2.6×10^{-7}	*224*
$[Co(NH_2iPr)_5Cl]^{2+}$	1.8×10^{-4}	*44*	*trans*-$[Ru(NH_3)_4Cl_2]^+$	1.7×10^{-6}	*232*
trans-$[Co(en)_2(NH_3)Cl]^{2+}$	3.4×10^{-7}	*107*	*trans*-$[Ru(en)_2Cl_2]^+$	4.2×10^{-6}	*232*
fac-$[Co(dien)(en)Cl]^{2+}$	9.4×10^{-8}	*87*	*cis*-$[Ru(en)_2Cl_2]^+$	3.7×10^{-4}	*37*
trans-$[Co(cyclam)(NH_3)Cl]^{2+}$	7.3×10^{-8}	*187*	*trans*-$[Co(en)_2Cl_2]^+$	3.5×10^{-5}	*57*
			trans-$[Co(tn)_2Cl_2]^+$	5.3×10^{-2}	*156*

[a] Data for selected $[MN_5Cl]^{2+}$ and $[MN_4Cl_2]^+$ compounds measured at 25°C.

[b] Ligand abbreviations: NH_2iPr = $NH_2CH_2CH(CH_3)_2$; en = ethane-1,2-diamine; dien = 1,5-diamino-3-azapentane; cyclam = 1,4,8,11-tetraazacyclotetradecane.

on the leaving group resulting from variations in saturated ligands are often not strong compared with variations as a result of changing the leaving group itself. One can anticipate that the variations of the type seen (Table V) would be largely paralleled when a good leaving group is involved. For example, $CF_3SO_3^-$ would be expected to aquate from $[Co(NH_2CH_3)_5(OSO_2CF_3)]^{2+}$ faster than from $[Co(NH_3)_5(OSO_2CF_3)]^{2+}$ by analogy to the behavior of the chloro analogs, and this is observed (*84*). Likewise, the retardation seen in the alkylaminechromium(III) system with Cl^- as the leaving group is also observed for $CF_3SO_3^-$ as leaving group (*84*).

2. *Trans Effects*

One of the more recognizable effects of nonleaving groups relates to the specific influence of groups trans to the leaving group. The effect, normally documented in terms of labilization of the leaving group opposite, is observed in both octahedral and square-planar inert complexes (*18, 19*). For simple aqua ions CrX_{aq}^{2+} ($X = Cl^-, Br^-$, NCS, I^-), rates of water exchange are such that k_{trans}/k_{cis} lies in the range 5–84, and k_{cis} is essentially constant for the series (*33, 205*). The variation in the ratio with trans group can then be related to variation in electronic influence as the X-group varies. Extreme effects have been noted in molecules such as $VO(OH_2)_5^{2+}$, where bonds trans to the O^{2-} ligand are invariably elongated; exchange of cis water molecules occurs with a rate constant of 5×10^2 sec^{-1}, whereas the water trans to the yl-oxygen has a residence time of only about 10^{-11} sec (*240, 290*). For square-planar platinum(II) compounds, the effect can be substantial, with rate of displacement increasing about 10^5-fold between extremes of trans influence (*277*).

The kinetic trans effect is influenced by both ground state and transition state effects. Ground-state effects, largely seen as significant lengthening, with concominant weakening, of the metal-leaving group bond, can be identified by physical methods. At least for a dissociative mechanism (where bond breaking dominates in forming the transition state), it is reasonable to equate a longer than usual bond with an increase in reactivity; for an associative (bond making) process, the argument is less facile, but sustainable if one views the elongation as facilitating approach of the entering group in forming the transition state. Transition-state influences of the labilizing group are less accessible, since they can only be seen in the rate of reaction. Stabilization of the transition state may arise if the labilizing ligand has the capacity to accept electron redistribution from the metal ion in empty antibonding or nonbonding orbitals. Clear examples of ground-state trans effects have arisen from X-ray crystallography. For example, in $[Co(NH_3)_5(OSO_2)]^+$, the ammonia trans to the $SO_3{}^{2-}$ ligand shows an elongated Co—N distance of 2.055 Å compared with cis Co—N distance ranging from 1.962 → 1.972 Å (*92*). This complex rapidly loses the trans ammonia in the presence of excess $SO_3{}^{2-}$ to form *trans*-$[Co(NH_3)_4(SO_3)_2]^-$ (*256*), and with thiocyanate it readily forms *trans*-$[Co(NH_3)_4(OSO_2)(NCS)]$ (*92*). The kinetic trans effect of $SO_3{}^{2-}$ in the latter reaction is two orders of magnitude greater than the effect of $RSO_2{}^-$ (R = *p*-toluene, benzene), and this is reflected in the X-ray structure of the *p*-toluenesulfinato complex, where the trans Co—N bond (2.023 Å) is shorter than for the $SO_3{}^{2-}$ analog (*92*). Labilization of trans ligands by $SO_3{}^{2-}$ has been reviewed earlier (*53*). The trans-labilizing influence of organic R-groups in $[RCr(OH_2)_5]^{2+}$ compounds with chromium(III)–carbon bonds has also been well described (*95, 254*). There is an effect of cis ligands, but their influence is relatively weak compared with trans influences.

It is clear that lability can be significantly enhanced with the appropriate choice of a trans nonleaving group. For the series of complexes *trans*-$[Co(cyclam)(X)Cl]^{n+}$ and *trans*-$[Co([14]diene)(X)Cl]^{n+}$, for example (Table VI), if the macromonocyclic ligands act to maintain the geometry during the reaction, the variation in aquation rate with variation in trans group is clearly defined. Even though the trans effect of the X-group is obvious in both systems, it cannot be divorced from other influences; steric and electronic influences from the six methyl substituents and the two coordinated imine groups in [14]diene

TABLE VI

INFLUENCE OF *trans* NONLEAVING GROUPS ON CHLORIDE AQUATION RATE CONSTANTS

trans-[Co(cyclam)(X)Cl]$^+$			*trans*-[Co([14]diene)(X)Cl]$^+$		
X-group	k_{aq} (sec^{-1})^a	Reference	X-group	k_{aq} (sec^{-1})^a	Reference
Cl^-	1.1×10^{-6}	*233*	Cl^-	3.6×10^{-2}	*163*
N_3^-	2.6×10^{-6}	*234*	N_3^-	2.1×10^{-2}	*188*
NCS^-	3.2×10^{-8}	*199*	NCS^-	1.4×10^{-6}	*188*
CN^-	4.8×10^{-7}	*198*	CN^-	2.4×10^{-3}	*235*
OH^-	1.2×10^{-2}	*233*	—	—	—
NO_2^-	4.3×10^{-5}	*198*	NO_2^-	4.4×10^{-4}	*122*

[a] At 25°C; cyclam = 1,4,8,11-tetraazacyclotetradecane; [14]diene = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene.

(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) also influence leaving-group displacement compared with the unsubstituted and saturated cyclam macrocycle. From a synthetic viewpoint, tailoring lability by the introduction of good trans-labilizing groups may be more difficult than simply introducing a leaving group that is a poor nucleophile.

B. EFFECTS OF EXTERNAL REAGENTS

The formation of a good leaving group by chemical reaction on a good bound nucleophile has been addressed (Section II,D). This can be considered as a case of a significant effect of an external reagent, and a range of such effects addressed here. Perhaps the best known effect, catalysis by hydroxide ion, is dealt with first, albeit briefly. Other influences on lability are also addressed in this and the next section, often without any attempt at exhaustive reviewing.

1. *Rate Enhancement by Hydroxide Ion*

Significant acceleration of leaving-group displacement has been observed for particularly inert octahedral complexes with ammine or amine nonleaving groups. This area of chemistry has been extensively reviewed (*19, 90, 126, 258, 278, 289*). The currently accepted mechanism for this acceleration involves the hydroxide ion acting as a base rather than a nucleophile to remove a proton from an amine ligand and form a substitutionally labile amido species. The amido conjugate base that is formed loses the leaving group to form a short-lived intermediate (commonly viewed as of lower coordination number) that reacts rapidly with water or other nucleophiles, Eq. (8).

$$\begin{array}{lcl} [\mathrm{ML_4(NHR_2)X}]^{n+} + \mathrm{OH}^- & \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} & [\mathrm{ML_4(NR_2)X}]^{(n-1)+} + \mathrm{H_2O} \\ & & \qquad\downarrow \\ [\mathrm{ML_4(NHR_2)(OH)}]^{n+} & \xleftarrow[\mathrm{OH_2}]{\text{fast}} & [\mathrm{ML_4(NR_2)}]^{n+} + \mathrm{X}^- \end{array} \tag{8}$$

The amido group in the conjugate base apparently exerts a considerable labilizing effect, particularly with cobalt(III) (*278*); the ability of this group to act as a π-donor and facilitate the formation of a 5-coordinate intermediate may be important (*225*).

The rate enhancements observed in amine complexes of metal ions such as cobalt(III) and ruthenium(III) are not universally observed. Water exchange on $[\mathrm{Fe(OH_2)_6}]^{3+}$ is more rapid in base (~750-fold) (*112*), enhanced but less so for $[\mathrm{Cr(OH_2)_6}]^{3+}$ (~60-fold) (*266*), and absent in $[\mathrm{V(OH_2)_6}]^{3+}$ (*227*). The trend reflects expectations of increasing associative character in reactions of these metal ions from Fe^{3+} to Cr^{3+} to V^{3+}; eventually, the conjugate base may play no significant role in the exchange mechanism. For the type of complexes generally covered in this review, however, hydroxide ion causes a significant increase in lability.

Given the extensive reviews of this area of chemistry, it would be unreasonable to do more than document the order of the enhancement for simple systems. A comparison of the rate constants for the base hydrolysis and uncatalyzed aquation of some simple $[\mathrm{Co(NH_3)_5X}]^{n+}$ complexes appears in Table VII. It is notable that the trend in lability mentioned earlier for spontaneous aquation of such complexes with a variety of ligands is largely preserved. Thus, a good leaving group departs even faster in aqueous base. The relative constancy of $k_{\mathrm{OH}}/k_{\mathrm{aq}}$ (Table VII) reflects this point. The acceleration in 1-M base compared with neutral solution is of the order of 10^5 for cobalt(III) amines. Acceleration can be even higher if macrocyclic and unsaturated ligand systems are present; for example, $k_{\mathrm{OH}}/k_{\mathrm{aq}} \sim 10^{10}\ \mathrm{M}^{-1}$ for hydrolysis of the first chloride in *trans*-$[\mathrm{Co(L)Cl_2}]^+$, where L = 5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (*123*). For other inert octahedral amine metal complexes, accelerations are also substantial. Chromium(III) complexes are generally less sensitive to base hydrolysis than their cobalt(III) analogs, but rate differences of as little as 10-fold exist (*278*). Rhodium(III) analogs are notably less sensitive though $k_{\mathrm{OH}}/k_{\mathrm{aq}}$ is still of the order of $10^3\ \mathrm{M}^{-1}$ provided that a trans amine

TABLE VII

COMPARATIVE RATE CONSTANTS FOR AQUATION AND BASE HYDROLYSIS OF $[Co(NH_3)_5X]^{n+}$[a]

X-group	k_{aq} (sec^{-1})	k_{OH} (M^{-1} sec^{-1})	$10^{-5}k_{OH}/k_{aq}$	Reference
NH_3	5.8×10^{-12}	7.1×10^{-7}	1.2	*209, 271*
N_3^-	2.1×10^{-9}	3.0×10^{-4}	1.4	*173*
$HCOO^-$	2.6×10^{-9}	5.8×10^{-4}	2.2	*160*
CH_3COO^-	2.7×10^{-8}	9.6×10^{-4}	0.35	*54, 202*
CF_3COO^-	1.7×10^{-7}	2.2×10^{-2}	1.3	*162, 202*
SO_4^{2-}	8.9×10^{-7}	4.9×10^{-2}	0.55	*201, 230*
Cl^-	1.8×10^{-6}	2.3×10^{-1}	1.3	*3, 41*
$OS(CH_3)_2$	2.2×10^{-5}	5.4	2.5	*83, 241*
NO_3^-	2.7×19^{-5}	5.5	2.0	*35, 41*
$CH_3SO_3^-$	2.0×10^{-4}	55.0	2.8	*42*
$OP(OCH_3)_3$	2.5×10^{-4}	79.0	3.2	*83, 251*
p-$NO_2C_6H_4SO_3^-$	6.3×10^{-4}	270.0	4.3	*42*
$CF_3SO_3^-$	2.7×10^{-2}	10,000.0	3.7	*71, 82*

[a] At 25°C

proton is available for conjugate base formation (*278*). Ruthenium(III) amine complexes are at least as sensitive to base as cobalt(III) analogs; k_{OH}/k_{aq} values of the order of 10^7 have been observed for simple pentaamines (*36, 37*).

An excellent and recent review of base hydrolysis of transition metal complexes has been written by Tobe (*278*), and readers can obtain detailed information from that source. The major point is that for many complexes lability is substantially enhanced in basic solution. Importantly, the order of lability observed for leaving groups in spontaneous aquation reactions is largely preserved in aqueous base. Exceptions are with ligands such as $NH_2SO_2NH_2$, for which deprotonation of the potential leaving group (to form, for example, $^-NHSO_2NH_2$) substantially diminishes its capacity as a leaving group (*168*). Largely, however, hydrolyses that are rapid in the absence of base are accelerated further in basic solution.

2. *Rate Enhancement by Protons*

We have already dealt with the case of the sulfamido ($NH_2SO_2NH^-$) ligand, for which aquation is enhanced much more than 10^3-fold by protonation (*168*). When complete or significant protonation of the donor atom can occur in aqueous acid, it is clear that a substantial effect is possible. The cobalt(III) complex of the *N*-bonded urea

Me_2NCONH^-, though it does not aquate, is protonated and isomerizes rapidly to the relatively stable *O*-bonded form in acidic solution (*81*). The high basicity of many ligands makes them amenable to protonation; almost invariably, protonation causes an increase in lability.

An acid-promoted path for aquation is frequently observed for a range of metal-ion complexes containing basic ligands and is generally explained in terms of a protonation equilibrium followed by dissociation of the conjugate acid produced, Eq. (9).

$$\begin{tikzcd}[MN_5L]^{x+} + H^+ \arrow[r, shift left, "K"] \arrow[d, "k_{aq}"] & {[MN_5(HL)]^{(x+1)+}} \arrow[l, shift left] \arrow[d, "k_H"] \\ {[MN_5(OH_2)]^{(x+1)+} + L^-} & {[MN_5(OH_2)]^{(x+1)+} + HL}\end{tikzcd} \tag{9}$$

An extensive range of reports exists for both $[Cr(NH_3)_5L]^{n+}$ (*159, 196, 245, 257, 292*) and $[Cr(OH)_2)_5L]^{n+}$ (*24, 78, 96, 103, 268, 284*) complexes undergoing acid-catalyzed aquation, with L basic ligands such as CN^-, F^-, N_3^-, ONO^-, CH_3COO^-, and $H_2PO_2^-$. The ratio k_H/k_{aq} can vary markedly with leaving group. Where $X = CN^-$ or ONO^-, the acid-dependent path predominates completely for the pentaammine complexes; k_H/k_{aq} is $>10^5$ M^{-1} for the CN^- system (*245*). With $[Cr(NH_3)_5CN]^{2+}$ in acid, the association constant is sufficiently large for a considerable amount of the complex to be protonated at high acidities (e.g., ~25% at pH 0). The observed rate constant fits an expression of the form in Eq. (10), as expected for the reaction described in Eq. (9).

$$k_{obs} = \frac{k_{aq} + k_H K[H^+]}{1 + K[H^+]} \tag{10}$$

At 25°C, the components terms are $k_{aq} < 10^{-7}$ sec^{-1}, $k_H = 3.3 \times 10^{-4}$ sec^{-1} and $K = 0.079$ M^{-1}. More commonly $K[H^+] \ll 1$, and then $k_{obs} = k_{aq} + k_H K[H^+]$, which does not permit separate determination of k_H and K. This is the case for the nitritopentaamminechromium(III) ion (*196*), for example.

Acid-catalyzed paths are, of course, known with other central metal ions such as cobalt(III) (*201*) and ruthenium(III) (*213, 214*), but again, enhancements are quite variable. When protonation of the leaving ligand can occur at an atom that is not the donor atom, as with unidentate-bound oxalate, for example, acid-promoted rates are only slightly greater than those in the absence of acid (*1*). Compared with base catalysis, acid catalysis is more dependent on the leaving group, consistent with the mechanism operating; the constancy observed for $k_{OH}/$

k_{aq} does not occur for k_H/k_{aq}. Nevertheless, increased lability is a fairly general phenomenon for reactions performed in acidic media.

3. *Rate Enhancement by Metal Ions*

Since the proton can enhance lability markedly for ligands of high basicity, it is not surprising that metal ions can also play a similar role. Metal-ion assisted aquation reactions of metal complexes have been reviewed recently (*17*). These reactions can be termed as electrophilic substitution reactions since they appear to involve displacement of one electron-deficient species by another. Ligands with the capacity to bridge between two metal ions (such as Cl^- or NCS^-) generally show considerably enhanced rate constants for aquation from metal complexes in the presence of added aqua metal ions. This is usually interpreted in terms of an adduct or tight ion pair in which the dissocation of the adduct is faster than that of the precursor, Eq. (11), and the leaving group is the ligand–metal-ion adduct.

$$\begin{array}{lcl} [M'L_5X]^{m+} + M^{n+} & \overset{K}{\rightleftharpoons} & [M'L_5XM]^{(m+n)+} \\ \quad\downarrow k_{aq} & & \quad\downarrow k_M \\ [M'L_5(OH_2)]^{(m+y)+} + X^{y-} & & [M'L_5(OH_2)]^{(m+y)+} + XM^{(n-y)+} \end{array} \tag{11}$$

As usual, the observed rate constant fits the form in Eq. (12) for Eq. (11).

$$k_{obs} = \frac{k_{aq} + k_M K[M^{n+}]}{1 + K[M^{n+}]} \tag{12}$$

Substantial accelerations have been observed for aquation of halo-, thiocyanato-, azido-, and diacido-metal complexes, particularly in the presence of aqua metal ions such as Hg^{2+} and Ag^+ (*17, 20, 56, 77, 221, 286*). Both the leaving groups themselves and their complexes form strong associations with such added metal ions. For associations such as that in Eq. (13), the equilibrium constant can be readily measured spectrophotometrically (*171*).

$$[L_5M - NCS]^{2+} + Ag^+ \overset{K}{\rightleftharpoons} [L_5M - NCS - Ag]^{3+} \tag{13}$$

Under favorable conditions, all of the terms k_{aq}, k_M, and K in Eq. (12) can be determined. Selected data appear in Table VIII.

The affinity of soft metal ions such as Hg^{2+} and Ag^+ for soft donors in ligands such as NCS^- is high; for example, formation constants for

TABLE VIII

RATE AND EQUILIBRIUM CONSTANTS FOR METAL-ASSISTED AQUATION REACTIONS[a,b]

Complex ion	M_{aq}^{n+c}	k_0 (sec^{-1})	k_M (sec^{-1})	K (M^{-1})	k_MK (M^{-1} sec^{-1})	k_MK/k_0 (M^{-1})	Reference
$[Co(NH_3)_5(NCS)]^{2+}$	Hg^{2+}	4.0×10^{-10}	$\leq 3 \times 10^{-6}$	9.8×10^4	0.30	7.5×10^8	*5*
$[Cr(NH_3)_5(NCS)]^{2+}$[d]	Ag^+	2.8×10^{-5}	5.6×10^{-4}	60	0.033	1.2×10^3	*172*
$[Cr(OH_2)_5(NCS)]^{2+}$	Hg^{2+}	9.1×10^{-9}	8.5×10^{-5}	1.7×10^4	1.4	1.5×10^8	*116*
$[Co(NH_3)_5Cl]^{2+}$	Hg^{2+}	1.7×10^{-6}	—	—	0.12	7.0×10^4	*43*
$[Cr(OH_2)_5Cl]^{2+}$	Hg^{2+}	2.8×10^{-7}	—	—	0.13	4.6×10^5	*97*
cis-$[Co(en)_2(NH_3)Cl]^{2+}$	Hg^{2+}	3.5×10^{-7}	—	—	0.014	4.0×10^4	*43*
$[Co(NH_3)_5I]^{2+}$	Ag^+	1.1×10^{-4}	—	—	0.8	7.3×10^3	*174*
$[Rh(NH_3)_5Br]^{2+}$[e]	Hg^{2+}	1.2×10^{-7}	—	—	4.9	4.1×10^7	*283*
$[Co(NH_3)_5(N_3)]^{2+}$	Hg^{2+}	2.1×10^{-9}	1.0×10^{-5}	7.3	7.3×10^{-5}	3.5×10^4	*52*

[a] At 25°C unless indicated; k_0 and k_M refer to first-order rate constants for spontaneous and metal-assisted aquation paths, respectively.

[b] Separate k_M and K values entered only where accessible.

[c] Added assisting ion.

[d] At 76.4°C.

[e] At 29.5°C.

$Ag(SCN)$ and $Hg(SCN)^+$ are 1.55×10^5 and 1.2×10^9, respectively (*171, 220*). Therefore, it is not surprising to find that even for isothiocyanato complexes, in which the S donor is not coordinated, ions can bind strongly to Ag^+ and Hg^{2+}; the $[Co(NH_3)_5(NCS)]^{2+}$ complex displays $K = 2.4 \times 10^3$ and $K = 9.8 \times 10^4$ for complexation with Ag^+ and Hg^{2+}, respectively (*100, 171*). A dimunition in K is expected from free to complexed thiocyanate as a result of coordination to the cobalt(III) cation and concomitant destabilization of the assembly, yet the binuclear species are quite stable. In fact, the two bridged binuclear species $[Co(NH_3)_5NCSAg](ClO_4)_3$ and $[Co(NH_3)_5NCSHg](ClO_4)_4$ have been isolated (*170*). The stable association observed for isothiocyanato complexes, in which the soft sulfur atom can bind the soft Ag^+ or Hg^{2+}, is not typical. The K values are very much higher than those found with the corresponding thiocyanato (in which $K = 1.3$, almost 10^4-fold smaller), since the S is now cobalt-bound, or with cyano or azido analogs (*5, 52*).

For simple pentaammine compounds, the formation constant for the binuclear species is not markedly influenced by the complex metal ion; log K values for $[M(NH_3)_5NCSAg]^{3+}$ are 2.97 (Cr), 3.38 (Co), and 3.38 (Rh), with only a small difference from the d^3 to the d^6 ions. Possibly the size and charge of the complex ion is more important than bonding influences resulting from variation in *d*-electron character. Certainly, significant metal-assisted aquation is observed generally for octahedral metal amine complexes with at least one potentially bridging leaving group. Influences of the complex metal ion on observed rate constants are seen; for example, Hg^{2+} activation of $[M(NH_3)_5Cl]^{2+}$ aquation increases in the order Ru < Rh < Co (*272*), but this correlates as well with ionic radius as with any more subtle parameters.

Certain reactions do not fit the expression in Eq. (12). Where $K[M^{n+}] \ll 1$, the simpler relationship Eq. (14) applies.

$$k_{obs} = k_{aq} + k_M K[M^{n+}] = k_{aq} + K_M' [M^{n+}] \qquad (14)$$

Given that K is often not large, a limiting rate (as expected for Eq. (12)) is often not seen, and Eq. (14) operates. Separation of k_M and K is then not accessible from the kinetics. Rarely, the pseudo first-order rate constants have been reported to be a relatively complicated function of $[M^{n+}]$. This is the case for $[Co(NH_3)_5I]^{2+}$ and $[Rh(NH_3)_5I]^{2+}$ with Ag^+ (*32, 174*), in which the complications are reported to result from the existence of species such as $[((NH_3)_5MI)_2Ag]^{5+}$ in addition to $[(NH_3)_5MIAg]^{3+}$. In the presence of excess chloride ion, Hg^{2+}-promoted aquation can be complicated by separate pathways involving Hg^{2+},

$HgCl^+$, $HgCl_2$, and even $HgCl_3^-$, with at least the first two leading to significant accelerations (*97*).

Rate acceleration is also observed with a range of other metal ions. Thallium(III) has been employed, but generally k_M/k_{aq} for Tl^{3+} is smaller than for Hg^{2+} (*105, 106*). The higher charge on Tl^{3+} may be important since highly charged ions should form less stable assemblies purely on electrostatic arguments; the general observation that the k_M/k_{aq} is slightly greater for $HgCl^+$ than for Hg^{2+} supports this view. Ferric ion accelerates aquation in complexes with leaving groups in which dangling O-donors are present, such as substituted salicylates (*76*), malonate (*74*), and oxalate (*75*). Assemblies such as $[(NH_3)_5CoOOCCOOFe]^{4+}$ are presumed. In general, unidentate coordinated diacids such as malonate and oxalate aquate faster in the presence of divalent and trivalent metal ions (*1, 74*). Association constants of oxalatopentaamminecobalt(III) with a range of M^{2+} lie between 10 and 400 M^{-1}, with observed accelerations roughly increasing with increasing association (*1*). Aquation of $[Co(NH_3)_5F]^{2+}$ is assisted by Al^{3+} (*131, 132*) since F^- has an affinity for Al^{3+}; aquation of other ligands, such as dimethylformamide, are unaffected by added aluminum(III) (*111*). Substitution of platinum(IV) complexes is catalyzed by platinum(II), but a redox ligand-transfer reaction path is important in those cases (*193*).

Because metal-promoted aquation invariably results from specific association between the leaving group and the accelerating metal ion, it is not anticipated that significant effects will be seen for complexes of poor nucleophiles such as $CF_3SO_3^-$, which are unlikely to associate further with added metal ions. Whereas further acceleration in the presence of added base is a fairly general phenomenon, further acceleration in the presence of added metal ions depends strongly on both the type of leaving group and the added metal ion.

4. *Other Methods of Rate Enhancement*

One notable area of chemistry that can offer some prospects for enhanced displacement of ligands is photochemistry. The photochemistry of metal complexes has been extensively studied and reviewed (*16, 282*), and it is not proposed to cover this area in any detail. One of the complications in photochemistry of metal complexes is the marked change in reactivity even within a triad of the d block. For example, the reaction modes of the simple $[M(NH_3)_5N_3]^{2+}$ ions for the cobalt triad vary clearly. For cobalt(III), the photochemistry is dominated by an intramolecular redox reaction (*93*) whereas for iridium(III), reaction proceeds exclusively via a coordinated nitrene $[(NH_3)_5IrN]^{2+}$, which can be trapped in the presence of HCl to form the stable complex $[(NH_3)_5IrNH_2Cl]^{3+}$ (*237*). The rhodium(III) analogs show both photoredox and nitrene paths (*237*). In some circumstances, photoaquation can produce a significantly different outcome when compared with normal aquation, and this may prove of synthetic value although only modest interest has been shown to date. For example, aquation of $[Cr(NH_3)_5OCH{\cdot}N(CH_3)_2]^{3+}$ proceeds with 100% Cr—O bond cleavage to form only the $[Cr(NH_3)_5(OH_2)]^{3+}$ compound; however, photoaquation of this compound forms only 16% of the aquapentaammine, the major product being the *cis*-$[Cr(NH_3)_4(OH_2)(OCH{\cdot}N(CH_3)_2)]^{3+}$ compound (*244*). The order of preferred bond rupture for photoaquation of chromium(III) compounds is $Cl^- < NCS^- < OCH{\cdot}N(CH_3)_2 < H_2O < NH_3$, which parallels decreasing participation of π-donor bonding. This order differs for spontaneous aquation; variations of this type may have utility in synthesis.

The generation of ligand radicals in most circumstances can be achieved for metal complexes by reaction with other chemically or radiolytically generated radicals in solution when the latter are good oxidants or reductants. Unfortunately, for most cases the ligand radical does not adopt a role as an efficient leaving group but initiates an intramolecular redox reaction that reduces the central metal ion to usually a labile oxidation state (*31*). There are a few exceptions for which, in effect, a redox-catalyzed aquation reaction occurs. For example, reaction of the ruthenium(II) complex $[Ru(NH_3)_5(NO)]^{3+}$ with the radicals CO_2^- or $(CH_3)_2COH$ first forms the reduced species $[Ru(NH_3)_5(NO^{\cdot})]^{2+}$, which then undergoes rapid aquation of the trans ammine ($k = 1.8 \times 10^{-2}$ sec) (*58*), prior to other chemistry. Extensive application of this type of reaction seems unlikely.

C. EFFECTS OF THE SOLUTION ENVIRONMENT

1. *Influence of Simple Salts and Solvents*

Numerous studies have appeared of the effect of added salts on the rates of reaction in solution, and the area has been reviewed (*228*). The key concept of the activity coefficient of the activated complex affecting the reaction rate was introduced by Brønsted (*34*), which led to an expression of the type in Eq. (15), though variations exist.

$$\log k = \log k_0 + 2Az_Pz_QI^{1/2} \tag{15}$$

The charges of the ions P and Q and the ionic strength I are involved, with A a constant. Overall, salt effects on aquation rates in aqueous solution are not particularly significant, at least for simple salts. More significant effects occur with polyelectrolytes (Section III,C,2). Added anions can specifically assist dissociation by stabilizing the usually higher-charged complex cation formed in the activated step whereas cations can assist by electrostatic interactions the departure of particularly anionic ligands. The latter prospect, in its extreme case, has been discussed (Section III,B,3).

The effect of added salts is commonly viewed in terms of ion pairing since it is clear that reactivity of an ion pair need not be identical to that of the unpaired complex and has been anticipated to be different (*285*). Whereas the effect of ion pairing on the rates of aquation reactions is usually acceleration (*54*), retardation can be observed (*287*). Ion-pairing constants in the high dielectric solvent water are generally low, and salt effects are small. The type of added anion significantly influences the strength of the ion pair. For example $K_{IP} \sim 1000$ for $Cr(DMF)_6^{3+}$, Cl^- in dimethylformamide (DMF), but falls to $K_{IP} \sim 30$ only for $Cr(DMF)_6^{3+}$, ClO_4^-, and is not measurable for $Cr(DMF)_6^{3+}$, $B(C_6H_5)_4^-$ (*190*). Small, nucleophilic ions such as Cl^- clearly pair more strongly than large ions of poor nucleophilicity. The significance of ion pairing on the intrinsic reactivity of a complex cation is still contentious, and one current view is that it is small (*190*).

Of factors that affect reaction rates, the role of the solvent has received only modest attention (*90, 169, 176, 189*), and many studies have employed mixed aqueous–organic solvent systems, in part as a consequence of the solubility properties of ionic complexes. Extensive studies of relationships between the physical properties of solvents and rate constants for solvolysis exist in organic systems (*238*), and correlations with solvent physical properties (*113*) such as dipole moment, dielectric constant, viscosity, and polarizability have also been sought in inorganic systems. Although there are inorganic reactions in which no notable solvent participation occurs, such as the solvent-independent ligand dissociation of $[Rh(P(OCH_3)_3)_5]^+$ (*94*), most reactions exhibit some dependence of rate constant on choice of solvent (*50*).

Bulk solvent properties such as dielectric constant (ε) may sometimes correlate with solvolysis rate constants, but microscopic dielectric constants in the vicinity of ions can be very different from bulk values. For water within 1.5 Å of an ion, ε has been estimated to fall to ~5, rising to ~80 for a water 4 Å from the ion (*252*). One notable effect of the lowering of the dielectric constant of a solvent, however, is to encourage ion-pair formation (*222, 285*). Correlations that employ a range of empirical parameters that apparently reflect microscopic solvent polarity have been reported. The Dimroth–Reichardt parameter (E_T) (*79*), a composite measure of polarity and hydrogen-bond donor acidity, and the Gutmann donor number (D_N) (*115*), which reflects hydrogen-bond acceptor basicity, are two of a range of solvent parameters employed. A multiparameter approach, employing Eq. (16), has been used for simple pentaamminecobalt(III) complexes reacting in various solvents with modest success (*150, 177*).

$$\log k = \log k_o + aE_T + bD_N \tag{16}$$

Results for solvolysis of $CF_3SO_3^-$ indicated that solvent basicity is as important as polarity and hydrogen-bond donor acidity, consistent with some association of solvent as a base with the metal ion in the transition state.

For solvolysis of the labile ligand $CF_3SO_3^-$ in $[M(NH_3)_5(OSO_2CF_3)]^{2+}$ compounds (*177*), it was observed that the relative ratio of rate constants Co : Rh : Ir of approximately 90 : 40 : 1 is maintained irrespective of solvent. However, solvolysis rate constants for any one metal complex varied with solvent, though the greatest difference in the range of solvent employed was only ~60-fold. At least for the polar solvents in which most ionic metal complexes dissolve, solvent effects are obviously not greatly significant. Ligands that are good leaving groups in water usually maintain that property in other solvents.

2. *Influence of Polyelectrolytes and Micelles*

Spectacular increases in spontaneous and base-catalyzed or metal-assisted aquation rate constants of particularly pentaamminecobalt(III) complexes have been observed in the presence of polyelectrolytes and micelles. Polyelectrolytes are known to cause marked acceleration of reactions, though decelerations can be observed, and the effects are very large compared with those produced by equivalent amounts of corresponding low molecular weight substances; similar effects are observed in solutions containing charged micelles. This area of research has been extensively reviewed (*63, 101, 133, 139, 195, 206, 207*), so discussion will be selective.

In a polyelectrolyte, a chain of linked, closely spaced charged groups can exist. The accelerating factor may be related to the charge spacing, the concentration, or the radius of rodlike polyions (*141*), with variation in activation entropy usually responsible for the rate change. The influences can be explained by electrostatic interactions between the reactants and the macroions using Brönsted–Bjerrum–Manning theory (*140*), though desolvation of reactants and/or the activated complex by the macroions may be important (*137, 215*). Several observations have been made regarding these reactions (*228*). First, the effects produced by polyions are quantitatively much greater than those by simple ions. Second, addition of an additional simple salt to a polyion-catalyzed reaction can markedly reduce the effect of the polyion, presumably as a result of saturation of the polyion domain with the added counterions. Cation inhibition increases in the order $Li^+ < Na^+ < Cs^+$, with divalent cations even more efficient inhibitors in the order $Mg^{2+} < Sr^{2+} < Ba^{2+}$. Even 0.1 *M* of a M^+ ion can reduce acceleration by $\geq 10^2$-fold. Third, the acceleration effect is dependent on polyion concentration and passes through a maximum usually around 10^{-3} equivalents/liter. It is argued that the decrease at higher concentrations arises because once the concentration of dissociated sites on the polyelectrolyte becomes very much larger than the total concentration of the reactants, these latter species can be distributed over widely separated sites, thus reducing the probability of reaction. Obviously, as a consequence of this argument, acceleration is also markedly dependent on the concentrations of the reacting species. Last, product inhibition may be important for very low polyion concentrations as a result of the products being attracted to and occupying the polyion domain.

Many of the examples with simple octahedral complexes involve metal-assisted reactions of $[Co(NH_3)_5X]^{2+}$ (*134–141, 208, 215, 216*), with salts of polyethylenesulfonate, polystyrenesulfonate, polymethacryloxyethylsulfonate, polyvinylsulfonate, or polyphosphates. Enhanced rates are also observed for base hydrolysis reactions of these complexes in the presence of polyions (*136*), and further acceleration of the Hg^{2+}-assisted aquation of cobalt(III) complexes is reported in the presence of mucopolysaccharides (*29*). Whereas catalysis of the reaction of $[Co(NH_3)_5Cl]^{2+}$ with Hg^{2+} in the presence of polyvinylsulfonate is observed even at extreme dilution of the polyion (*208*), catalysis by sodium dodecyl, tetradecyl, and hexadecyl sulfate is limited to a concentration range where stable micelles can be formed (*59*) (Fig. 1). Strong accelerations are then observed, although at high detergent concentrations, the effect decreases since the reagent ions are distributed over a larger number of micelles. Acceleration factors as large as 10^5 have been reported, which compares favorably with acceleration factors observed in the presence of polyelectrolytes.

The observed effects are particularly dependent on the central metal ion. For example, the rate-enhancing effect of polyethylenesulfonate on spontaneous aquation of $[Cr(NH_3)_5Br]^{2+}$ is very small compared with the effect on the cobalt(III) analog (*140*). Given the apparent

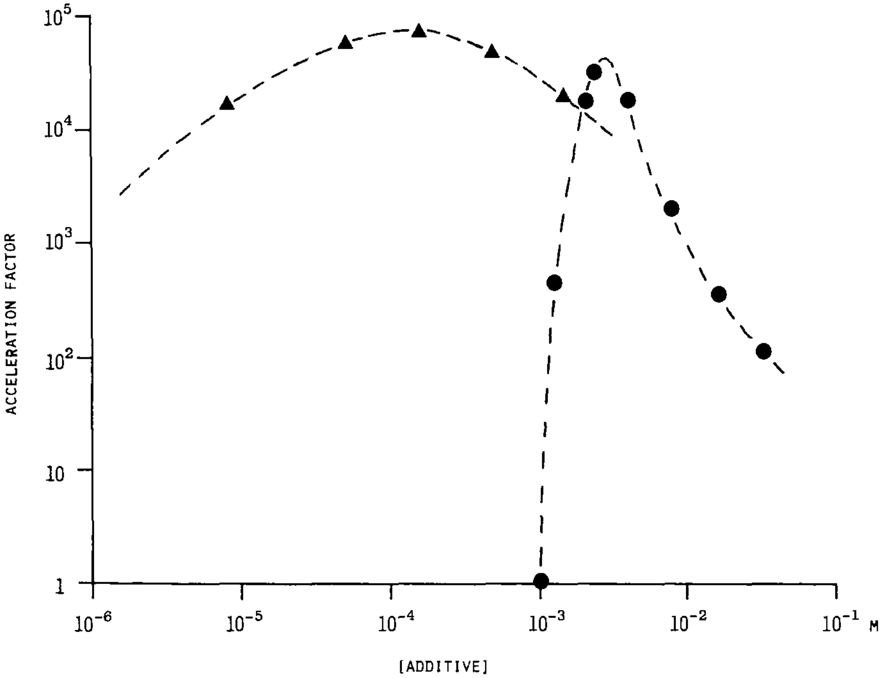


FIG. 1. Acceleration of the Hg^{2+}-assisted aquation of $[Co(NH_3)_5Cl]^{2+}$ in the presence of (▲) a polyelectrolyte (polyvinylsulfonate) and (●) a micelle (formed by sodium dodecyl sulfate) (*59, 208*). (Adapted with permission from the American Chemical Society.)

preferences of chromium(III) and cobalt(III) complexes for dissociative and associative reactions, respectively, it is presumed that the polyion enhances dissociative-type mechanisms. Effects of the leaving group are apparently less important though not tested for a reasonable range of leaving groups. There is no information on how polyelectrolytes or micelles effect the dissociation of the better leaving groups, but it is presumed that the behavior follows the trend observed largely for halogen ions as leaving group.

IV. Probing Mechanistic Detail

A. REACTIONS INVOLVING INHERENTLY LABILE LIGANDS

An understanding of the general variation in rates of substitution in octahedral complexes has been sought in terms of properties of the metal ion, notably charge and electronic configuration. Calculations of differences in crystal field stabilization energy from octahedral to specifically 5-coordinate geometries have been reported, where the crystal field activation energy determined represents the loss of stabilization energy (*62, 130*). These lead to the conclusion that metal ions with certain electronic configurations should react more slowly than others of similar charge. The ions of d^3, low-spin d^4, d^5, and d^6, and d^8 configurations are predicted to be inherently inert, and this accords fairly well with observations. The actual mechanism by which the reaction proceeds, as distinct from the rate of reaction, has usually concerned acquiring information on the form of the transition state or intermediate, with reaction mechanisms described in terms of the perceived intermediate.

The detection of a reaction intermediate is usually not possible in coordination chemistry because lifetimes of intermediates are commonly extremely short. The simple mechanisms of reaction are commonly designated as an associative mechanism (A, with an intermediate of expanded coordination number formed) or a dissociative mechanism (D, with an intermediate of reduced coordination number formed). Intermediates of expanded coordination number are important in ligand substitution in square-planar complexes and in a few cases can actually be detected. For example, $Ni(CN)_5^{3-}$ is known from exchange reaction of $Ni(CN)_4^{2-}$ with CN^- (*288*). Even in octahedral complexes, some evidence for associative processes exists indirectly. The $[Ru(NH_3)_6]^{3+}$ ion reacts with NO in acid to form $[Ru(NH_3)_5NO]^{3+}$ and NH_4^+ much more rapidly than can be explained by aquation of the hexaamine as the initial step, and a bimolecular mechanism with a 7-coordinate intermediate has been proposed (*11, 226*).

Evidence for intermediates of reduced coordination number is exclusively of an indirect nature. The observation of limiting rates in plots of k_{obs} versus nucleophile concentration provides good evidence for a limiting D mechanism in a few cases, such as reaction of CN^- with *trans*-$[Co(CN)_4(SO_3)(OH_2)]^{3-}$ (*275*). Strong labilizing groups such as SO_3^{2-}, CN^-, or CH_3^- appear to promote dissociative mechanisms. In aqueous base, steric acceleration of hydrolysis of $[Co(NH_2R)_5Cl]^{2+}$ is $\sim10^5$-fold over $[Co(NH_3)_5Cl]^{2+}$, and this has been interpreted in terms of a 5-coordinate transition state in which steric crowding is relieved (*44*). Largely, however, few reactions are thought to process by pure D or A mechanisms, and adequate labels for reactions mechanisms are still in dispute (*267*). Currently, intermediate reactions are usually assigned to an interchange mechanism with dissociative (I_d) or associative (I_a) character.

A dissociative-type mechanism has for several decades been accepted as most reasonable for cobalt(III) complexes, and experiments to identify a transient of reduced coordination number not based on kinetic data have been devised (*151, 247*). These are essentially competition experiments, in which the outcome may imply transition-state information. Largely, the process has involved induced aquation reactions of $[Co(NH_3)_5X]^{n+}$ in the presence of a nucleophilic coordinating anion Y^-, the ratios of the products $[Co(NH_3)_5Y]^{n+}/[Co(NH_3)_5(OH_2)]^{3+}$ being employed to infer the presence (or otherwise) of an intermediate of reduced coordination number (*40, 111, 118, 146–155, 242, 243*). One of the bases for employing the induced reactions was the belief that the leaving group should be more likely to depart without assistance from the entering group as a consequence of its lability. Spontaneous aquation reactions have usually been too slow to permit accurate determinations in any case since anation of the aqua complex formed can occur during reaction, giving a false and higher amount of $[Co(NH_3)_5Y]^{n+}$. Availability of labile ligands in recent years has permitted competition experiments to be performed more accurately for spontaneous aquation reactions; for example, capture of NCS^- over the range 3–13% in 1-*M* SCN^- has been observed; it is leaving-group dependent (*152*) (Table IX).

Capture of azide ion has been determined for $[M(NH_2R)_5(OSO_2CF_3)]^{2+}$ compounds (M = Co, Rh, Cr; R = H or CH_3) in dilute base (*71*) and also for a range of $[Co(NH_3)_5L]^{n+}$ compounds in aqueous base (*41, 42, 46, 83*) (Table IX). Base has been employed not merely to labilize the complex, which is not strictly required with the labile leaving groups such as $CF_3SO_3^-$, but largely to probe the existence and lifetime of a pentacoordinate conjugate base intermediate, $[Co(NH_3)_4(NH_2)]^{2+}$. Results span complexes with reactivities that differ by at least 10^6-fold; for the cobalt(III) series in base, competition is dependent on the formal charge of the complex before the substituent has left but only slightly dependent on leaving group. These results have been interpreted in terms of a common, short-lived, reduced coordination number amido intermediate (*42*). Related experiments in aqueous base with $S_2O_3^{2-}$, NO_2^-, or SCN^- as entering nucleophile (*147, 148, 153*) have been interpreted in the same way. The lifetime of the supposed intermediate must be very short if different competition results occur with variation in precursor charge since this implies that the intermediate operates in the inherited solvation shell of its precursor without sufficient time to equilibrate. It is only with the possibly sterically congested $[Co(NH_2CH_3)_5X]^{2+}$ ions that competition by azide ion is both large and possibly independent of leaving-group influences

TABLE IX

COMPETITION BY ANIONS IN SPONTANEOUS AND BASE-CATALYZED REACTIONS OF PENTAAMMINEMETAL(III) COMPLEXES

Precursor	Y^{-a}	%(CoY)	Reference	Precursor	Y^-	%(CoY)	Reference
$[Co(NH_3)_5Cl]^{2+}$	N_3^-	8.5	*46*	$[Co(NH_3)_5OClO_3]^{2+}$	SCN^{-b}	5.1	*152*
$[Co(NH_3)_5Br]^{2+}$	N_3^-	8.7	*46*	$[Co(NH_3)_5OSO_2CF_3]^{2+}$	SCN^{-b}	4.6	*152*
$[Co(NH_3)_5I]^{2+}$	N_3^-	9.9	*46*	$[Co(NH_3)_5OSO_2CH_3]^{2+}$	SCN^{-b}	3.1	*152*
$[Co(NH_3)_5SCN]^{2+}$	N_3^-	9.5	*41*	$[Co(NH_3)_5OS(CH_3)_2]^{3+}$	SCN^{-b}	5.1	*152*
$[Co(NH_3)_5OClO_3]^{2+}$	N_3^-	10.3	*42*	$[Co(NH_3)_5OP(OCH_3)_3]^{3+}$	SCN^{-b}	6.6	*152*
$[Co(NH_3)_5OSO_2CF_3]^{2+}$	N_3^-	10.1	*42*	$[Co(NH_3)_5NH_2SO_2NH_2]^{3+}$	SCN^{-b}	10.4	*152*
$[Co(NH_3)_5OSO_2CH_2]^{2+}$	N_3^-	9.7	*42*	$[Co(NH_3)_5NH_2SO_2C_6H_4CH_3]^{3+}$	SCN^{-b}	11.3	*152*
$[Co(NH_2CH_3)_5OSO_2CF_3]^{2+}$	N_3^-	36.0	*71*	$[Co(NH_3)_5NH_2COCH_2F]^{3+}$	SCN^{-b}	8.2	*152*
$[Rh(NH_3)_5OSO_2CF_3)^{2+}$	N_3^-	2.0	*71*	$[Co(NH_3)_5(NH_2CONHC_6H_5]^{3+}$	SCN^{-b}	6.3	*152*
$[Rh(NH_2CH_3)_5OSO_2CF_3]^{2+}$	N_3^-	3.3	*71*	$[Co(NH_3)_5OS(CH_3)_2]^{3+}$	N_3^{-a}	12.3	*83*
$[Cr(NH_3)_5OSO_2CF_3]^{2+}$	N_3^-	9.4	*71*	$[Co(NH_3)_5OP(OCH_3)_3]^{3+}$	N_3^{-a}	12.5	*83*
$[Cr(NH_2CH_3)_5OSO_2CF_3]^{2+}$	N_3^-	12.0	*71*	$[Co(NH_3)_5OC(NH_2)_2]^{3+}$	N_3^{-a}	12.0	*83*

[a] In basic solution; 25°C and 1.0-M competitor (Y^-) leading to $[Co(NH_3)_5Y]^{2+}$ and $[Co(NH_3)_5OH_2]^{3+}$.

[b] In neutral or acidic solution, 25°C and 1.0-M competitor (Y^-).

(*71*), suggesting a much longer-lived 5-coordinate intermediate. With such an argument, notably lower competition for the chromium(III) analog implies a shorter lifetime for any intermediate. The much lower competition observed for the rhodium(III) amines may reflect the stronger ligand field strength of Rh(III) and a concomitant greater demand for 6-coordination (*71*); this would act to limit the lifetime of an intermediate, its selectivity for a nucleophile in solution, and the rearrangement of remaining ligands.

The much more marked leaving-group dependence for competition data in neutral or acid solution (Table IX) implies that the intermediate decays more rapidly than the time required for the leaving group to diffuse to the bulk solution (*49*). This is consistent with a long-held view that lifetimes of 5-coordinate intermediates in base are longer than those in acid due to stabilization by the amido group in base (though it would appear we are likely to be dealing with timescales in the pico- or even nanosecond regime generally). If the intermediate is so short-lived in acid solution, it is difficult to envisage how a nucleophile diffusing to the vacant site from the bulk solvent can effectively compete, and it suggests that anion competition must arise from ion-pair preassociation. Yet there is no apparent correlation of competition with ion-pairing constants. Certainly, the role of the ion pair is almost that of a "spectator" in base hydrolysis of $[Co(NH_3)_5L]^{n+}$ compounds since anions that form measurable ion pairs (CO_3^{2-}, PO_4^{3-}, and SO_4^{2-}) show little or no competition and do not seriously alter competition by azide ion (*149*). More extended studies of competition in spontaneous aquation reactions employing various metal complexes with good leaving groups would seem warranted. The approximate linear relationship between log of hydrolysis rate in acid or base and percentage competition suggests that an intermediate of reduced coordination number is more accessible when the unassisted departure of the leaving group is rapid.

Traditionally, the details of mechanism have been probed by comparisons of series of related compounds and by activation parameters, particularly employing activation entropy (ΔS^*) (*19, 90*) and activation volume (ΔV^*) (*183, 281*). Although complexes of labile leaving groups have permitted facile syntheses of a wide range of complexes (Section V), many employed in new mechanistic studies, the mechanistic study of these labile compounds themselves has generated only modest interest and results. The fact that most isolable compounds with labile sites involve ionic leaving groups complicate mechanistic interpretations based on activation parameters (*183*). Nor is there any inherent reason why a ligand like $CF_3SO_3^-$, departing some 10^4-fold faster than Cl^- from a common metal ion, should initiate a marked change in mechanism. These labile ligands do offer promise in studies of the very inert metal ions such as iridium(III), in which traditional ligands depart so slowly that accurate determination of activation parameters can be a major task. For example, the $[M(NH_3)_5(OSO_2CF_3)]^{2+}$ solvolysis reactions have been followed, and negative ΔS^* values vary in the order Co(III) < Rh(III) < Ir(III), suggesting increasing associative character down the triad (*177*). There may be further opportunities for these compounds in traditional mechanistic studies in the future.

B. REACTIONS INVOLVING INDUCED LABILITY

Although it has been convenient to discuss spontaneous and base-catalyzed reactions together in the previous subsection, it must be recognized that lability in the latter is induced. Separate approaches to induced lability involving metal-ion catalysis or nitrozation reactions have also been applied to characterization of an intermediate by competition experiments. One of the first studies of nitrozation involved reaction of $[Co(NH_3)_5N_3]^{2+}$ with HONO in aqueous acid in the presence of nucleophilic anions Cl^-, Br^-, NO_3^-, or NCS^- (*118*). Following what is presumed to be rapid, unassisted loss of the bound N_2 formed, the presumed $[Co(NH_3)_5]^{3+}$ intermediate acquires X^- or OH_2, with the product ratio related to the relative rates for uptake of ligand. Nitrozation of pentaamminecobalt(III) complexes of N_3^- and NH_2COO^-, in which different leaving groups N_2 and CO_2 are involved, gave essentially identical competition by Cl^-, Br^-, and NO_3^- (*45*), supporting the concept of a common intermediate. Experience has shown that it is the more poorly solvated anions (such as NO_3^-) that appear to be the best competitors; strongly solvated ions such as F^- and OH^- are poor competitors, as are neutral ligand such as ammonia.

Detail relating to the intermediate geometry has been sought also with induced labile systems. Reaction of *trans*-$[Co(NH_3)_4(ND_3)X]^{2+}$ ($X = N_3^-$ or NH_2COO^-) with HONO and *trans*-$[Co(NH_3)_4(ND_3)X]^{2+}$ ($X = Cl^-$ or Br^-) with Hg^{2+} give the common *trans*-$[Co(NH_3)_4(ND_3)(OH_2)]^{3+}$ product, suggesting a common square-pyramidal intermediate (*47*). However, a trigonal-bipyramidal intermediate has been inferred from reactions of *cis*-$[Co(en)_2Cl_2]^+$ with Hg^{2+} and *cis*-$[Co(en)_2Cl(N_3)]^+$ with HONO from a common isomer distribution of the product (*48*). The lifetime and existence of a common intermediate in such reactions are still open to question; for example, HONO and Hg^{2+} aquation of *t*-$[Co(tren)(NH_3)N_3]^{2+}$ and *t*-$[Co(tren)(NH_3)Cl]^{2+}$, respectively, follow different pathways with different levels of saturated entry of nitrate ion (*39*).

The most recent view regarding both spontaneous and induced aquation reactions is that a discrete intermediate $[Co(NH_3)_5]^{3+}$ is not involved (*152*). For base-catalyzed hydrolysis, the case for a genuine intermediate $[Co(NH_3)_4(NH_2)]^{2+}$ is far stronger. Even for this one metal-ion system the debate is probably not complete, and data with other metal ion complexes are particularly sparse. There are still opportunities for telling mechanistic studies of simple systems, particularly involving labile ligands. Properties demonstrated and mechanisms defined for such simple systems can probably be transferred or adapted to more complicated systems, including biological metal complexes.

V. Synthetic Applications

A. Introduction of New Ligands

The synthetically accessible and isolable complexes of coordinated triflate, in particular, represent a resource for chemical synthesis. Not only is the labile $CF_3SO_3^-$ ligand readily substituted by ligands of even modest nucelophilicity, but also the cationic complexes with $CF_3SO_3^-$ as the counterion display extended solubilities in a wide range of polar solvents compared with many other common anions. Although syntheses of new compounds can be approached *in situ* by generating a labile leaving group by chemical reaction of a coordinated ligand (Section II,D) or by catalysis by external reagents (Section III,B), the option of employing a stable, solid precursor is compelling and will form the basis of this discussion.

Essentially all the simple $[(M(NH_2R)_5(OSO_2CF_3)]^{2+}$ ($R = H$ or CH_3) ions undergo simple solvolysis reactions in potentially coordinating solvents (*65, 68, 70, 82, 84, 85*). For example, pentaamminecobalt(III) complexes of the unidentate neutral coordinating solvents OH_2, NH_3, $OHCH_3$, $OHCH_2CH_3$, $OHCH(CH_3)_2$, $NCCH_3$, $OP(OCH_3)_3$, $OCH{\cdot}N(CH_3)_2$, and $OS(CH_3)_2$ can be prepared in essentially quantitative yield simply by dissolution of $[Co(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ in the pure solvent (*82*). The technique offers a way of introducing isotopically labeled water without dilution since no solvent exchange is involved. The anions acetate and dichloroacetate have also been introduced to cobalt(III) by reaction in the acid in the presence of a trace of the salt (*82*). Further, if the reaction is carried out in dry, poorly coordinating solvents such as sulfolane or acetone, neutral solids also dissolved in the solvent can be introduced into the coordination sphere. This has permitted synthesis of cobalt(III), rhodium(III), and chromium(III) complexes with coordinated urea (*65, 68, 72, 82*), a cobalt(III) cyanamide complex (*82*), and ruthenium(II) or chromium(III) complexes of the nitrogen heterocycles pyrazine or imidazole, respectively (*68, 180*). The diquaternary viologen analog 1,1′-(1,3-propanediyl)-bis(4,4′-bipyridinium) has been coordinated to ruthenium(II) as a unidentate ligand (*13*).

Some of these syntheses of simple triflato pentaamines produce in a facile manner compounds that were previously inaccessible or obtained only by lengthy and often low-yielding routes. For example, the first synthesis of $[Co(NH_3)_5(urea)]^{3+}$ employed severe conditions and extensive recrystallizations (*15*), which could not be extended readily to the chromium(III) analogs. Synthesis of the latter had to await the availability of the labile triflato precursor (*68*). From the $[Cr(NH_3)_5(OSO_2CF_3)]^{2+}$ precursor also came the first syntheses of imidazole, trimethylphosphate, methanol, dimethylacetamide, urea, acetonitrile, and formamide pentaamminechromium(III) complexes (*68, 72, 84*). Syntheses of $[M(NH_3)_6]^{3+}$ ions (M = Rh or Ir) based on $[M(NH_3)_5(OSO_2CF_3)]^{2+}$ are more facile and higher yielding than conventional techniques (*84*). The osmium(III) analog is also accessible by this route (*184*), in addition to other solvent complexes.

Complexes with several bound triflates permit coordination of several more nucleophilic molecules in place of $CF_3SO_3^-$. The complexes *cis*-$[Co(en)_2L_2]^{3+}$ [L = $OHCH_3$, $OS(CH_3)_2$, or $NCCH_3$] are readily prepared (*82*), as are the *cis*-$[Co(tren)L_2]^{3+}$ series [L = $OS(CH_3)_2$, $OP(OCH_3)_3$, $NCCH_3$, or $OCH{\cdot}N(CH_3)_2$] (*67*) and *cis*-$[Co(cyclen)(OCH{\cdot}N(CH_3)_2)_2]^{3+}$ (*66*). The *trans*-$[Co(cyclam)L_2]^{3+}$ ions [L = $NCCH_3$ or $OCH{\cdot}N(CH_3)_2$] have been recently prepared from the bis(triflato) precursor (*22*). The ion *cis*-$[Ru(en)_2(OH_2)Cl]^{2+}$ has also been prepared by a chloro(triflato) precursor (*120*). Further, *cis*-$[Rh(en)_2(NH_3)_2]^{3+}$ ion is also readily prepared, as are the $[Rh(en)_3]^{3+}$ and $[Ir(en)_3]^{3+}$ ions, from reactions of bis(triflato) compounds with ammonia or ethane-1,2-diamine (*84*). For the latter two ions, this represents the most convenient route for synthesis. With *cis*-$[Ir(bpy)_2(OSO_2CF_3)_2]^+$, a third bpy ligand can be introduced in high yield when reaction is performed in ethylene glycol (*265*), or alternatively, two triphenylphosphine ligands can be coordinated. The $[Ru(phen)(CO)_2(OSO_2CF_3)_2]$ compound or its bpy analog can react in acetonitrile to form the $[Ru(phen)(CO)_2(NCCH_3)_2]$ compound or, in the presence of excess bpy or phen, can produce $[Ru(diim)_2(CO)_2]^{2+}$ ions, in which $(diim)_2$ may be $(phen)_2$,

$(bpy)_2$, or even (phen)(bpy) (*26–28*). Several other substitution reactions involving triflato oganometallic compound are known (*179*).

Examples of synthetic reactions involving square-planar complexes have also appeared. The $[Pt(PR_3)_2Cl(OSO_2CF_3)]$ compound reacts with glycine to produce eventually $[Pt(PR_3)_2(NH_2CH_2COO)]^+$, a reaction that presumably involves initially facile unidentate coordination of glycine (*219*). Compounds such as $[Pt(en)Cl(OP(OCH_3)_3)]^+$ were characterized after dissolution of $[Pt(en)Cl(OSO_2CF_3)]$ in trimethylphosphate but were not usually isolated (*86*); some solvent-palladium(II) compounds were also observed in similar reactions. The gold(III) compound $[Au(CH_3)_2(PR_3)(OSO_2CF_3)]$ readily reacts with added $P(C_6H_5)_3$ to form $[Au(CH_3)_2(PR_3)_2]^+$ (*166*). Clear opportunities remain for extension of the type of chemistry described. Examples of types of reactions performed are included in Table X.

B. COMPOUNDS OF SPECIFIC GEOMETRY

Syntheses to obtain a complex of a specific geometry represent one of the more challenging types. Use of a trans-labilizing group may permit some geometric control, as can coordination of a multidentate ligand that can attach in only one relatively rigid geometry. The relatively mild conditions of many of the substitution reactions commencing with triflato compounds can limit geometric rearrangement and provide products of essentially one stereochemistry; several examples appear in the previous subsection. Moreover, initial substitutions of a ligand by triflate occur in highly acidic conditions, in which rearrangements may be diminished. For example, *trans*-$[Co(en)_2Cl_2]Cl$ reacts with CF_3SO_3H at low temperature to form exclusively *trans*-$[Co(en)_2Cl(OSO_2CF_3)]^+$ (*61*). At temperatures above room temperature, it is only with in-plane macrocyclic tetraamines that stereoretention and compounds such as *trans*-$[Co(cyclam)Cl(OSO_2CF_3)]^+$ can result (*22*), though compounds of this type are also known with the more stereoretentive Ir(III) and Rh(III) ions (*84*).

Compounds such as *trans*-$[Co(cyclam)Cl(OSO_2CF_3)]^+$ and *trans*-$[Rh(en)_2Cl(OSO_2CF_3)]^+$ can be readily substituted to produce a series of compounds of trans geometry. This has been exemplified by syntheses of *trans*-$[Co(cyclam)Cl(OCH\cdot N(CH_3)_2)]^{2+}$ and *trans*-$[Rh(en)_2(NH_3)Cl]^{2+}$, respectively (*22, 84*). Recently, reaction of *trans*-$[Co(en)_2(py)(NO_2)]^{2+}$ in CF_3SO_3H at 0°C has produced the *trans*-$[Co(en)_2(py)(OSO_2CF_3)]^{2+}$ ion, which in aqueous HCl produces the previously elusive *trans*-$[Co(en)_2(py)Cl]^{2+}$ compound (*144*). Reactions of *cis*-$[Co(en)_2(OSO_2CF_3)_2]^+$ in various solvents appear to form exclusively

TABLE X

EXAMPLES OF SYNTHESES BASED ON TRIFLUOROMETHANESULFONATO PRECURSORS

Precursor	Entering group	Solvent	Reaction (time/temp)[a]	Yield[b] (%)	Product	Reference
$[Co(NH_3)_5(OSO_2CF_3)]^{2+}$	$OHCH_3$	CH_3OH	3 min/~50°C	81	$[Co(NH_3)_5(OHCH_3)]^{3+}$	*82*
$[Rh(NH_3)_5(OSO_2CF_3)]^{2+}$	$OC(NH_2)_2$	Sulfolane	$2\frac{1}{2}$ hr/R.T.	57	$[Rh(NH_3)_5(OC(NH_2)_2)]^{3+}$	*65*
$[Ir(NH_3)_5(OSO_2CF_3)]^{2+}$	NH_3	Liquid NH_3	14 hr/−30°C	95	$[Ir(NH_3)_6]^{3+}$	*84*
$[Cr(NH_3)_5(OSO_2CF_3)]^{2+}$	Imidazole	Sulfolane	10 min/~50°C	35	$[Cr(NH_3)_5(\text{imidazole})]^{3+}$	*68*
cis-$[Co(\text{tren})(OSO_2CF_3)_2]^{+}$	$NCCH_3$	CH_3CN	10 min/~70°C	90	*cis*-$[Co(\text{tren})(NCCH_3)_2]^{3+}$	*67*
tr-$[Co(\text{cyclam})Cl(OSO_2CF_3)]^{+}$	$OCH{\cdot}N(CH_3)_2$	$OCH{\cdot}N(CH_3)_2$	2 hr/R.T.	60	*tr*-$[Co(\text{cyclam})(OCH{\cdot}N(CH_3)_2)Cl]^{2+}$	*22*
tr-$[Rh(\text{en})_2Cl(OSO_2CF_3)]^{+}$	NH_3	Liquid NH_3	30 min/−30°C	100	*tr*-$[Rh(\text{en})_2(NH_3)Cl]^{2+}$	*84*
cis-$[Ru(\text{phen})(CO)_2(OSO_2CF_3)_2]$	bpy	CH_3CH_2OH	15 min/~80°C	53	*cis*-$[Ru(\text{phen})(\text{bpy})(CO)_2]^{2+}$	*27*
cis-$(Ir(\text{bpy})_2(OSO_2CF_3)_2]^{+}$	bpy	Ethylene glycol	5 hr/heat	80	$[Ir(\text{bpy})_3]^{3+}$	*265*
$[Au(CH_3)_2(OSO_2CF_3)]_2$	$P(C_6H_5)_3$	Benzene	minutes/R.T.	100	$[Au(CH_3)_2(P(C_6H_5)_3)_2]^{+}$	*23*
$[Pt(\text{en})Cl(OSO_2CF_3)]$	$OP(OCH_3)_3$	$OP(OCH_3)_3$	1 hr/R.T.	100	$[Pt(\text{en})(OP(OCH_3)_3)Cl]^{+}$	*86*
$[Ru(NH_3)_5(OSO_2CF_3)]^{2+}$	Pyrazine	Acetone	1 hr/R.T.[c]	95	$[(NH_3)_5Ru\text{-pyrazine-}Ru(NH_3)_5]^{5+}$	*180*
$[Os(NH_3)_5(OSO_2CF_3)]^{2+}$	Pyrazine	Acetone	hours/R.T.	High	$[(NH_3)_5Os\text{-pyrazine-}Os(NH_3)_5]^{6+}$	*192*

[a] R.T., Room temperature.

[b] Yield of isolated (and often recrystallized solid); reactions often essentially quantitative prior to workup.

[c] Includes Zn reduction and subsequent air oxidation steps to mixed valence dimer.

cis-bis(solvent) species (*82*). To date, the number of examples in which a specific geometry has been sought employing triflato compounds is not large, and there appears to be scope for further applications in this area.

C. POLYNUCLEAR COMPOUNDS

The formation of binuclear compounds by reaction of a triflato complex and a complex of a potentially bridging ligand in a noncoordinating solvent has been explored in a limited way. In general, these reactions proceed by Eq. (17).

$$[\mathrm{ML_5X}]^{n+} + [\mathrm{M'L'_5(OSO_2CF_3)}]^{m+} \longrightarrow [\mathrm{L_5M{-}X{-}M'L'_5}]^{(m+n+1)+} \tag{17}$$

The process has been established for a series of pentaamminemetal(III) compounds (of Co, Rh, or Ir) with bridging imidazolate (*21*). The μ-pyrazine mixed decaammine diruthenium(II)/(III) dimer has also been prepared (*180*), in addition to a diruthenium compound with a 1,4-dicyanobicyclo[2.2.2]octane bridging ligand and a mixed ruthenium(III)/cobalt(III) compound with the same bridging ligand (*8*). Osmium(III) dimers have also been reported (*192*).

Apart from simple decaammine dimers, the macrobicyclic complex cation (1-amino-8-methyl-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane)cobalt(III) reacts with $[\mathrm{Co(NH_3)_5(OSO_2CF_3)}](\mathrm{CF_3SO_3})_2$ to form a binuclear molecule in which the 1-amino group of the macrobicycle acts as the donor to the pentaamminecobalt(III) unit (*191*). Higher polymers may be accessible; for example, we have some preliminary evidence for formation of a trimer with a Co—X—Co—X—Co center from reaction of *trans*-$[\mathrm{Co(cyclam)(OSO_2CF_3)_2}]^+$ with $[\mathrm{Co(NH_3)_5X}]^{n+}$ species (*23*).

VI. Conclusion

Lability for at least one coordination site has been adequately demonstrated in the traditionally inert metal complexes in recent decades. Induction of lability by chemical reactions on a normally poor leaving group, by metal ions, protons, and base and by polyelectrolytes and micelles, offer opportunities in specific circumstances. Largely during the last decade, however, a number of ligands have appeared that are poor nucleophiles and inherently labile. Such molecules, of which trifluoromethanesulfonate is the most extensively studied, are "universal" good leaving groups, apparently departing the coordination sphere of all common metal ions more rapidly than most common ligands. Since trifluoromethanesulfonate complexes in particular are generally readily prepared as stable isolable solids and are soluble in a range of polar solvents, they are important in facile syntheses of new complex molecules. Evidence of their potential has been demonstrated already in organometallic and coordination chemistry.

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