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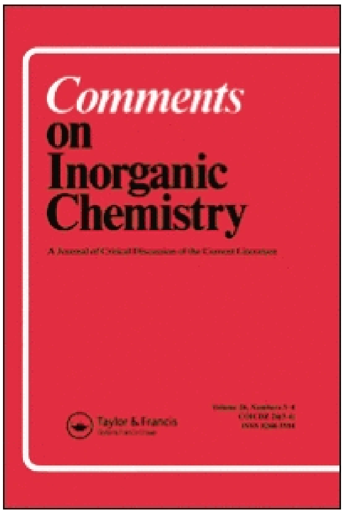

Comments on Inorganic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Substitution Reactions of Ruthenium Ammines

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To cite this Article Taube, Henry(1981) 'Substitution Reactions of Ruthenium Ammines', Comments on Inorganic Chemistry, 1: 1, 17 — 31

To link to this Article: DOI: 10.1080/02603598108078077

URL: http://dx.doi.org/10.1080/02603598108078077

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Substitution Reactions of Ruthenium Ammines

Several metal ions of oxidation state 3+ form substitution-inert octahedral complexes: the d^3 species Cr(III) and Mo(III); the low spin d^5 species Ru(III) and Os(III); the low spin d^6 species Co(III), Rh(III), Ir(III). Because of the advantages which slow substitution reactions offer in being amenable to searching tests of mechanism, these 3+ centers have been the subject of much study. Metal ions in the 2+ oxidation state which form substitution-inert octahedral complexes are much less common, and in fact Ru(II) is unique in being the only one which forms a series that is both abundant and convenient for study. It is for this reason in part that the Ru(II) complexes provide the main focus for this article. There are other important reasons as well.

Back-bonding is much more prominent in Ru(II) than it is in any of the 3+ ions which have been mentioned.[1] Thus in addition to the saturated ligands implied by the title, unsaturated ligands in great variety can be co-ligands in the ammine series, and the effect of their electron-withdrawing capacities, as well as of idiosyncracies of individual ligands, can be studied. Discussions of mechanism becomes more productive when affinities are known and these can fairly readily be determined for Ru(II) complexes. Though in the past most such determinations have been done by the kinetic method, which is competent to yield answers only for the less stable complexes, a few measurements of ΔH^0 have been made,[2,3] and recently a systematic program devoted to measuring the enthalpies of complex formation has been initiated.[4] The entropies of reaction can be sufficiently well estimated so that reasonably good values of ΔG° can be gotten in this way.

The stability data for the Ru(II) species make it possible to get data on rates of substitution on Ru(III), even for systems in which the direct reaction cannot be observed. This is particularly important for neutral ligands in water, where often the equilibrium militates against observing complex formation, and few data on the reactions of metals in oxidation state 3+ with neutral ligands exist. The difficulty with the 3+ species can be illustrated by some examples taken

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0260-3594/81/0101-0017$06.50/0

from the chemistry of $Co(NH_3)_5H_2O^{3+}$. The rate of formation in water of the acetonitrile or the dimethyl sulfide complex cannot be measured directly because the affinity in either case is too low. Even with a good nucleophile, such as NH_3, there is difficulty; at a pH where NH_3 exists, the Co(III) complex is converted to $Co(NH_3)_5OH^{2+}$ and even though in 1 M NH_3 at a pH of 9, the complex is stable [K_{eq} for $Co(NH_3)_5OH^{2+} + NH_3 = Co(NH_3)_6^{3+} + OH^-$ is ca. $10^{-2.8}$ at 30°)[5] the rate of complex formation will be very slow owing to the low concentration of the aquopentaammine species at the high pH. The Ru(III)–Ru(II) states are connected by very facile electron transfer and thus the stability of the Ru(III) complex can be determined electrochemically when the stability of the Ru(II) complex is known. The rates of aquation of the complex of the 3+ state can usually be measured and, since the equilibrium quotient for the reaction is known, the rate of substitution can be calculated.

Little has been done along the lines just described, but there are substantial reasons for extending the work in this direction. The comparisons possible for the closely related Ru(II), Ru(III), and Rh(III) species provide an unusual — in fact unique — opportunity for tracing the effect of oxidation state and of electronic structure on the dynamics of the systems, both rates and equilibria.

Finally we draw attention to the fact that interest in the interaction of ruthenium complexes with constituents of living cells is growing.[6] To best exploit the complexation effects, a high degree of specificity in ligation is needed. Though progress can be made by a purely empirical approach, an understanding of the mechanism of substitution and of the factors which affect specificity will ensure more rapid progress to successful practical applications and ensure that applications, as yet unforeseen, are not overlooked. In the work that has been done thus far, loading takes place in the Ru(II) state, and the metal ion then is usually oxidized to the 3+ state, if for no other reason than that a species such as $Ru(NH_3)_5^{2+}$ in combination with any of the polar groups abundant in biological systems — namely NH_2–, imidazole, thiol, thioether, carboxylate — reacts with O_2.

Inviting though these prospects are, the investigations which they imply have for the most part not been pursued systematically, and there are important gaps in the evidence. Our understanding of the subject is for this reason at least of necessity quite limited. It is the purpose of this article to summarize and examine the evidence, and to draw attention particularly to areas where further work is called for.

Ruthenium(II) Ammines

Much of the preparative chemistry of ammine complexes depends on the fact that water in the coordination sphere is more labile than ammonia. In Table 1

TABLE I
Labilities of metal–H_2O and metal–NH_3 bonds[a]

	Cr(III)	Ru(III)	Ru(II)	Ni(II)[d]
$M(NH_3)_5H_2O + H_2O$	6.8×10^{-5} (9)	5×10^{-4}[b]	3[c]	3×10^4 (15)
$M(NH_3)_6 + H_2O$	2.5×10^{-8} (10)	1.4×10^{-10} (13)	1.5×10^{-6} (14)	6.6 (16)

[a] At 25°; units, sec^{-1}. Values for hexaammine corrected for the statistical factor by dividing the specific rate of conversion to aquopentaammine by 6. References in parenthesis.

[b] Estimated from the rate of formation of the chlorocomplex,[11] using for comparison data on water exchange and rate of anation for $Co(NH_3)_5H_2O^{3+}$ [12] and $Cr(NH_3)_5H_2O^{3+}$.[9]

[c] Estimated by rate comparison.[14]

[d] Based on rate of water exchange for $Ni(H_2O)_6^{2+}$ and rate of aquation of $Ni(H_2O)_5NH_3^{2+}$.

are summarized the few data available for substitution-inert species which provide a comparison of the labilities of the two ligands; data for Ni^{2+} as a representative of the substitution-labile centers are included. Astonishingly, a comparison cannot be made for cobaltammines, which have been the most thoroughly studied of all metal ammine complexes. The specific rate of water exchange between the pentaammine and solvent, which is used as a measure of the lability of the metal–water bond, is known[7] but not for the rate of aquation of the hexaammine. The measurement[8] of the rate of exchange between $Co(NH_3)_6^{3+}$ provides only a lower limit on the desired quantity, because in the exchange work undoubtedly the reaction catalyzed by OH^- was being followed.

The lower lability of the M–NH_3 compared to the M–H_2O bond is expected because for all the systems featured, reaction of NH_3 with the aquo ion is exothermic. In this connection, enthalpy data would be particularly revealing. Is the difference in lability accounted for fully by the enthalpy difference? Ascribing the difference in rates to differences in stability is of course not an explanation of the rate behavior. Undoubtedly ligand field effects contribute to producing the pattern observed but there appears to be no simple explanation of the fact that despite the greater lability of Ru(II) compared to Cr(III) and Ru(III) the rate contrast for it is much greater than for Cr(III) and is in fact almost as great as that shown by Ru(III). This large rate difference for substitution on Ru(II) is established only for the acid-independent path. Ruthenium(II) ammines, in contrast to any others studied, show[17] a marked increase in lability with acidity. Whether increasing the acidity also enhances the rate of water exchange is not known. Regardless of what happens to the Ru(II)–NH_3 vs. Ru(II)–H_2O rate, as a practical matter high acidities must be avoided if the Ru(II) ammine unit is to remain intact.

The concern over the large contrast in the labilities of NH_3 and H_2O on Ru(II) may be misplaced because the estimates of the rate of water exchange may be in error. Direct measurements of the rate of water exchange need to be

TABLE II
Affinities of acids for amines[a,b]

Base	Acid				
	H^{+c}	Cd^{2+}	$Ru(NH_3)^{3+}$	$Ru(NH_3)_5^{2+}$	
NH_3	7.6×10^9 (18)	5.5×10^2 (21)	$7 \times 10^{4\,c*}$	3.5×10^{4c} (14)	5.5^d (14)
NH_2CH_3	1.4×10^{11} (19)	5.6×10^2 (21)	3.5×10^3 (20)	3.5×10^3	3.8 ± 0.2^d (20)
$NH_2CH_2CO_2Et$	1.9×10^8 (20)		5.5×10^2 (20)	3.2×10^3	10.0 ± 0.8^d (20)
$NH(CH_3)CH_2CO_2Me$	1.3×10^8 (20)		2.0 (20)	50 ± 10	2.1 ± 0.4^d (20)

[a] At 25°.
[b] References in parentheses.
[c] Statistical factors applied.
[d] Specific rate for ligation, $k_1 \times 10^2$ M^{-1} sec^{-1}.
* *Note added in proof*: This value differs from that reported in reference 14 but is preferable because the two values of E_f needed were determined under the same conditions by the same authors. [T. Matsubara and P. C. Ford, Inorg. Chem. **15**, 1107 (1976)].

made both for Ru(II) and Ru(III), and the measurements of rate of replacement of NH_3 by H_2O for the latter need to be refined.

The effect of alkyl substitution in ammonia on the dynamics of the substitution reaction is of interest in its own right, but takes on added importance in biological systems where the interaction of a metal with primary and secondary amines must be considered. In Table II are summarized data on stabilities for Ru(II) and Ru(III), and related systems, and data on the rate of complex formation for Ru(II) with a series of amines.

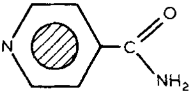
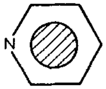
The affinity of the proton for methylamine is much greater than for ammonia but the metal ions do not behave in like fashion. In fact, the ruthenium ammines show a marked decrease in affinity for the ammine on methylation, which continues also into the second stage (see last two entries). This decrease in affinity is probably steric in origin. One component of the steric effect is the direct interaction between the substituents on the ligand and those in the coordination sphere of the metal, the repulsions being greater for the pentaammine residue than for the proton. The second results from solvent interactions, methyl groups causing desolvation of the metal complex. The effect of desolvation is expected to be much greater for Ru(III) than Ru(II), and in fact the decrease in affinity is much greater for the former. Because the dimensions of Ru(II) and Ru(III) ammines are nearly the same,[22] this observation supports the idea that desolvation effects are important.

The insensitivity of the rate of complex formation to ligand identity and thus to the stability of the complex being formed, shown by the data of Table II, is even more strikingly illustrated by those in Table III.

Over at least a 10^7 variation in the value of the equilibrium constant for ligand association, the rate of formation is almost constant and such variations in k_1 as are observed do not correlate at all with K_{eq}. The data summarized in the table are limited to systems for which reasonably good values of K_{eq} have been determined. The affinity of Ru(II) for a nitrile is probably greater than for isonicotinamide, and for CO is certainly greater, but

TABLE III

Specific rates of ligation, k_1, in $[Ru(NH_3)_5H_2O]^{2+}$ as a function of stability[a]

L	K_{eq}	k_1, M^{-1} sec^{-1}
	2×10^9 (23)[b]	0.105 (14)
	2×10^7 (14)	0.093 (14)
NH_3	3.5×10^4 (14)	0.055 (14)
N_2	3.3×10^4 (24)	0.073 (24)
$Ru(NH_3)_5N_2^{2+}$[c]	7×10^3 (24)	0.013 (24)
H_2S	1.5×10^3 (25)	0.10 (25)
$NH(CH_3)CH_2CO_2Et$	50 ± 10 (20)	0.021 (20)
Cl^-[d]	1.6 (26)	7 (26)

[a] At 25°.

[b] References in parentheses.

[c] $\mu = 0.10$.

[d] $\mu = 0.20$.

the rates of formation of the corresponding complexes are in the same range as those shown in Table III.

Since the rate of complex formation does not reflect the stability of the complex, we can conclude that there is very little bond formation in the activated complexes for the reactions. It is of course not proven that an intermediate is formed which lasts long enough so that its properties are independent of how it is produced. Changes in configuration — *cis* to *trans*, for example — have not been observed in the course of studying a series of tetraammines,[27] but this of itself does not settle the question of whether an equilibrated intermediate is formed. Even though it is not proven that an intermediate of reduced coordination number is formed, for the sake of simplicity, in the following the mechanism of substitution will be discussed in terms of an intermediate being formed.

The charge on the entering ligand is seen from the data in Table III to be much more important than the stability of the product in affecting k_1. The effects observed [a marked increase in rate for Cl^- compared to neutral ligands and a moderate decrease for $Ru(NH_3)_5N_2^{2+}$] can be understood as arising from electrostatic influences on encounter frequency and support the conclusion that the activated complex for reaction is strongly dissociative in character.

Of great interest is the question of how auxiliary ligands affect the lability of the metal–water bond. The effect of replacing NH_3 by H_2O on the lability of the water molecule being replaced as it applies to Ru(II) and other species has

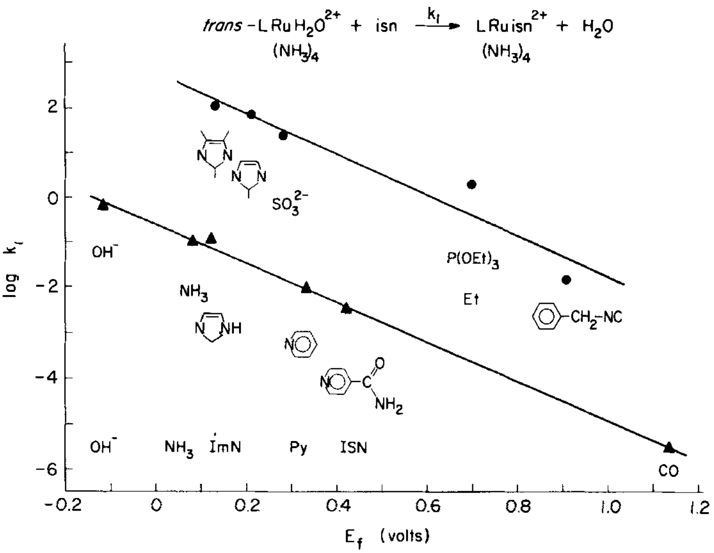


FIGURE 1 Effects of auxiliary ligands on the substitution lability of H_2O in ruthenium(II) ammines. Points identified by triangles from Isied and Taube.[27] Circles are data for ligands which are specifically *trans*-labilizing.

been considered in some detail elsewhere.[1,28] Although H_2O and NH_3 are isoelectronic, the response can become quite large after several stages of replacement and is especially so for the much studied but atypical case of Co(III). Here we will consider auxiliary ligands differing widely in character. The reaction which has been used as a gauge of the lability of the Ru(II)–H_2O bond is represented by Eq. (1)

$$\mathrm{Ru^{II}(NH_3)_4L(H_2O) + isn = Ru(NH_3)_4L(isn) + H_2O} \qquad (1)$$

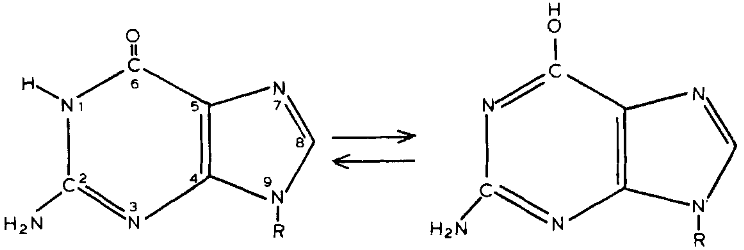
Many of the data which have been accumulated on the rate of this reaction are summarized in Figure 1, where the specific rate of formation of the complex (k_1) with isonicotinamide (isn), is plotted against the potential of the $3+/2+$ couple (E_f). The justification for making such a plot is this: π acids stabilize Ru(II) more than Ru(III), thus increasing E_f; if there is a monotonous change in the stability of the Ru(III) complex as π-acid character increases, then a monotonous relationship between E_f and specific rate of substitution on Ru(II) is expected. The stronger the π acid, the more is electron density withdrawn from ruthenium and the slower the rate of substitution is expected to be. The points in the lower part of Figure 1, taken from a paper by Isied and Taube,[27] reflect this expectation. There is a large decrease in rate within the series, starting with a group such as OH^- in the coordination sphere, and ending with the strongest π acid studied. Isied and Taube recognized that certain groups, specifically those which are *trans*-labilizing, did not fit this correlation. Following Tweedle,[29] also the data for ligands of this kind are included in the figure. The data at present suggest that the *trans*-labilizing groups themselves constitute a series, showing a correlation of k_1 with E_f. The separation into two different classes will undoubtedly become blurred as more data are accumulated but the results at present indicate that two distinct mechanisms for substituion operate. For ligands L which are not *trans*-labilizing, activation may involve simple loss of H_2O from the coordination sphere, without significant rearrangement of the intermediate. The *trans*-labilizing groups at first sight appear to be a motley collection. However, it is likely that they have in common the property that they are good π donors as well as π acceptors, and it is expected that here, as in the case of σ donation and π acceptance, a synergistic effect will operate. For species such as SO_3^{2-} and $P(OR)_3$, the π donation is from unshared electrons on oxygen, rather than from the sulfur or phosphorus atoms. For the class of *trans*-labilizing ligands, the intermediate may be a trigonal bipyramid with the group L occupying an equatorial position. For low spin d^6 in this geometry one orbital, say d_{xy}, would be occupied by an electron pair while the second, say $d_{x^2-y^2}$, is in position to accept electron density from L. When L is quite different in character from NH_3, as in the case under consideration, there is no reason to expect configuration changes accompanying substitution, even with a bipyramidal intermediate; it is not unreasonable to suppose that the entering and leaving groups are constrained to be *trans* to the activating group.

It is important to note that the delabilizing effect illustrated by the data points clustering about the lower line in Figure 1 is limited to saturated ligands as leaving groups. A good π acid decreases the affinity for another of its kind, and as a consequence, two such groups are mutually labilizing. Just how these effects compare in *cis* and *trans* positions has not been investigated.

We turn now to a consideration of specificity in attachment. It is immediately clear, in view of the insensitivity in the pentaammine series of the rate of complex formation to ligand variation, that when product composition is under kinetic control, the level of discrimination is very low. Thus in a mixture of NH_2CH_3 and isn, each at some moderate concentration, say 0.10 M, and with ligand in excess, consumption of $Ru(NH_3)_5H_2O^{2+}$ will take place with a half-life of the order of a minute and with ca. 30% of the aquo complex being converted to $Ru(NH_3)_5NH_2CH_3^{2+}$. This early reaction phase then is followed by a longer one in which the methylamine complex is reorganized to the more stable isonicotinamide complex. If there is no direct — i.e. S_N2 — reaction of isn with $Ru(NH_3)_5NH_2CH_3^{2+}$, then reorganization to the isonicotinamide complex will occur at a specific rate of $[0.11/(0.04+0.11)]1.1 \times 10^{-5}$ sec^{-1}. As to the important issue of whether there is direct replacement of

NH_2CH_3 by isn, it should be noted that in many systems, the rate of aquation of a complex such as $Ru(NH_3)_5NH_2CH_3^{2+}$ has been studied by following the conversion to the isn complex, with isn at a high concentration relative to the ligand being lost, and in no case has an activated complex of composition $[Ru(NH_3)_5L^{2+} \cdot isn]$ been encountered. If S_N2 paths operate, they involve the solvent water as the leaving or entering group.

In most real cases in complex systems, a mix of kinetic and equilibrium control governs the distribution of products at the end of a convenient interval for reaction. To illustrate this we consider the reaction of $Ru(NH_3)_5H_2O^{2+}$ with guanosine (R = ribose):



Reorganization after Ru(II) settles on N-7, a preferred site, is extremely slow. However, the complex with Ru(II) on N-4 is very unstable and at ordinary concentrations of Ru(II) does not form to a significant extent.[30] Assuming pseudo-first-order conditions with ligand in excess, the approach to equilibrium for each site is governed by $(k_1[L] + k_a)$ when k_a represents the rate of aquation. For an unstable complex, $k_a > k_1[L]$, and if k_1 for the sites is about the same, the complex at an unstable site will always be labile, and reorganization of whatever amount forms will be rapid. Now if the complex at site N-1 (see tautomeric form at right) were about as stable as it is at N-7, when aquo Ru(II) has largely been consumed the two stable complexes would be at ratios governed by kinetic control, but the unstable one would have reached a maximum in concentration and then declined. Just what the situation is with respect to the N-1 vs. the N-7 complex is not known quantitatively in this system. The work referred to[30] was done with 1-methylguanine, precluding the formation of the tautomeric form.

Whenever the activated complex for substitution is dissociative in nature, site discrimination under kinetic control will be poor. In this respect, square planar complexes have an advantage because they usually react by mechanisms in which bond-making is also important. To achieve equilibrium product control and yet retain the advantages of substitution inertia, it is obviously necessary to labilize for substitution, and then freeze the equilibrium state. Two different strategies for achieving this will be outlined.

As illustrated below for a reaction in which the effect was first observed,[32] Ru(II) can serve as a catalyst for substitution on Ru(III).

$$Ru(NH_3)_5H_2O^{2+} + Cl^- \rightarrow Ru(NH_3)_5Cl^+ + H_2O \quad (2)$$

$$Ru(NH_3)_5Cl^+ + Ru(NH_3)_5H_2O^{3+} \rightarrow Ru(NH_3)_5Cl^{2+} + Ru(NH_3)_5H_2O^{2+} \quad (3)$$

The equilibrium in this case is easily frozen by oxidizing Ru(II) to Ru(III). The scope of this approach has not been explored, but it has been applied successfully in attaching Ru(III) in systems of biological interest.[33,34] There are limits to its usefulness. If the entering ligand stabilizes Ru(II) much more than Ru(III) — this is the case for example with isn — equilibrium in Eq. (3) will be far to the left, and the catalyst would be sequested in the form $Ru(NH_3)_5isn^{2+}$, i.e., the concentration of $Ru(NH_3)_5H_2O^{2+}$ would be very low and the reaction corresponding to Eq. (2) would take place very slowly.

In a second approach, which combines the advantages of equilibrium ligation and substitution inertia, a ruthenium(II) complex containing a *trans*-labilizing group is used for ligation, and the equilibrium is frozen by altering the *trans*-labilizing group. This strategy has thus far been applied only to SO_3^{2-} as a *trans*-labilizing group; oxidation of $Ru(NH_3)_4(SO_3)L$ by H_2O_2 in acidic solution produces $Ru^{III}(NH_3)_4SO_4L$. Sulfate ion being a saturated ligand is not strongly labilizing, and in any case is easily replaced by H_2O, when the complex is reduced to Ru(II) and reoxidized. It should be pointed out that SO_3^{2-} is also very strongly labilizing on Ru(III) [as it is on Co(III)] so that simple oxidation to $Ru^{III}(NH_3)_4(SO_3)L$ does not accomplish the desired end. It is likely that all the groups in the upper region of Figure 1 also labilize Ru(III), thus altering the *trans*-labilizing group is a necessity if the final product is to be kinetically stable. This important step has not been studied systematically but it is known that $P(OR)_3$ in $Ru^{II}(NH_3)_4[P(OR)_3]H_2O$ is not at all readily oxidized, or otherwise altered to convert it to a non-labilizing group. Unless some new ingenious chemistry is discovered, the scope of this approach, so attractive in important respects, will be very limited.

The site discrimination achieved in this approach is that characteristic of the Ru(II) state. In Table 4 are summarized the data on the rate of complex formation and affinities for a variety of ligands.

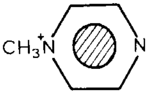
Of specific interest is the large equilibrium discrimination between binding to guanine and to adenosine, which is much greater than is to be expected under kinetic control with $Ru(NH_3)_5H_2O^{2+}$ as reactant. Of general interest from the standpoint of understanding rates of substitution in a basic way is the fact that the rates of complex formation are much more sensitive to the nature of the incoming group than is the case for $Ru(NH_3)_5H_2O^{2+}$, suggesting that in substitution on $Ru(NH_3)_4(SO_3)H_2O$ bond-making by the incoming group is significant. This, in turn, suggests that it might be instructive to study rates for substitution on a species such as *cis*- and *trans*-$Ru(NH_3)_4(NCR)H_2O^{2+}$; a

TABLE IV
Dynamics of the interaction of $Ru(NH_3)_4(SO_3)H_2O$ with various ligands

Ligand	K_{eq}	k_f, M^{-1} sec^{-1}	References
Imidazole	11.8×10^3	43.3	36
1,9-Dimethylguanine	1.38×10^3	58	36
1-Histidine	1.1×10^3	4.4	36
Isonicotinamide	3.8×10^3	24	36
Adenosine	8 ± 7	1.0 ± 0.5	36
Ethylglycine	4.7×10^2	19.8	37
Methylsarcosine	3.1	2.9	37
Methionine methyl ester		1.7	37

nitrile is selected because it is a good π acid, but an indifferent π donor. Bond-making in the activated complex may be very prominent in these cases owing to the electron-withdrawing effect of the π acid.

Finally, a feature of the substitution reactions of Ru(II) will be mentioned which has been encountered only sporadically but is remarkable enough to deserve special mention. Complications in the kinetics of substitution of tripositive ions attributable to outer-sphere association are by now commonplace, and are particularly prominent for an entering group such as SO_4^{2-} which carries a high charge.[38] For ammine complexes of ruthenium(II), it is a complication also for entering groups which are neutral,[14,35] and more remarkably even for a cationic ligand, such as



($K_{ass} = 16$; 30°, $\mu = 1.00$).[39] The complexes are presumably stabilized by metal-to-ligand charge transfer. The interesting question, which has not really been examined thoroughly or critically, is the extent to which charge transfer occurs in the activated complex and how it affects reaction rates. It has been invoked,[40] but now ligand to metal, in explaining the origin of a term of the form

$$k[\mathrm{Ru(III)}][\mathrm{I}^-]^2$$

in the rate law for substitution by I^- into *trans*-$Ru(NH_3)_4(isn)H_2O^{2+}$.

Ruthenium(III) Ammines

The observations on the substitution reactions of cobalt ammines, and the insight into the mechanisms of substitution which they have provided, constitute a convenient back-drop for viewing the work — still quite limited — which has been done on the ruthenium(III) ammines. Comparisons with rhodium(III) ammines would be especially instructive, but these species also have not been studied extensively.

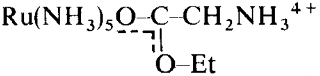
The reaction paths inversing OH^- and involving the conversion of NH_3 to NH_2^- prior to forming the activated complexes for substitution are particularly prominent for both Co(III)[41] and Ru(III) ammines.[42] In both cases, there is undoubtedly a considerable amount of charge transfer from NH_2^- to the metal center in the activated complex, but there is an important difference between the two cases. Because there is an electron hole in the πd subset, charge transfer is important also in the ground state for Ru(III), and is much less important for Co(III) which has a πd^6 configuration. This likely accounts for the higher acidity of $Ru(NH_3)_5H_2O^{3+}$ ($pK_a = 4.1$; 25°, $\mu = 1.0$)[25] compared to $Co(NH_3)_5H_2O^{3+}$ ($pK_a = 6.22$; 25°, $\mu = 0.30$)[42] despite the larger size of Ru(III) [M to N distances in $M(NH_3)_6^{3+}$, 1.936 Å for Co[43] and 2.104 Å for Ru[22]].The effects of charge transfer, important as they are in the ground state, can become even more pronounced in the activated complexes. For Co(III), the stabilization of the activated complex relative to the ground state will be particularly great if a trigonal bipyramidal intermediate, with NH_2^- in a equatorial position, is adopted. In this configuration, an orbital is available to accept electron density from NH_2^-, thus stabilizing the intermediate relative to the ground state. This net stabilization is less for Ru(III), which as already mentioned, is significantly stabilized in the ground state by charge transfer. Configuration changes are more likely for a trigonal bipyramidal than for square pyramidal intermediate, and thus charge transfer effects probably account, at least partly, for the fact that Co(III) ammines are particularly prone to undergo changes in configuration, much more so than Ru(III) ammines.[44] Configuration changes are especially facile when the intermediate retains a ligand, such as NH_2^-, OH^-, or X^-, which can readily donate electron density to the metal.

The opportunity mentioned in the introduction, for determining rates of substitution for Ru(III) complexes which are not accessible by direct measurement, has by no means been systematically exploited. A single example can be offered. Making allowance for the statistical factor, the value for the rate of aquation of $Ru(NH_3)_6^{3+}$, (see Table I, based, it should be noted, on a single experiment) together with the value for the equilibrium constant for complex formation leads to a value of 1.0×10^{-5} M^{-1} sec^{-1} for the specific rate of the reaction

$$Ru(NH_3)_5H_2O^{3+} + NH_3 = Ru(NH_3)_6^{3+} + H_2O.$$

This seems fairly reasonable in relation to the estimated specific rate for water exchange. If the value in Table I is divided by 55.5, the second order specific rate for water exchange becomes ca. 1×10^{-5} M^{-1} sec^{-1}.

Certain linkage isomerization reactions are much more facile for Ru(III) than for Co(III) ammines. Though little work has been done, it suffices to show that the chemistry of nucleophilic substitutions on ligands coordinated to Ru(III) will not be a simple extension of that which has been described for the Co(III) assisted reactions.[45] The molecule $Ru(NH_3)_5NH_2CH_2CO_2^{2+}$ in acidic solution rearranges to $Ru(NH_3)_5O_2CCH_2NH_3^{3+}$ by a first order process. The limiting specific rate at high acid concentration and at 25° is 2×10^{-3} sec^{-1}. Though Ru(II) is ordinarily more labile than Ru(III), the isomerization is less facile in the Ru(II) ammine. This particular kind of reaction has not been reported for Co(III), though of course it must also occur there at a finite rate. The linkage isomerization is undoubtedly intramolecular — the ligand once lost to acid solution would never re-enter the coordination sphere at the high yield characteristic of the reaction — and surely has a great deal of S_N2 character. The difference in the Ru(III), a πd^5 case, and Ru(II) and Co(III), both πd^6, may reside in the fact that in the former, a single electron is antibonding for a seven-coordinate intermediate, while in the πd^6 systems, two electrons become antibonding.

An analogous facile rearrangement is observed[47] also for $Ru(NH_3)_5NH_2CH_2CO_2Et^{3+}$, but in this case it has rather more interesting consequences. The limiting specific rate at high acidity governing the disappearance of the ester complex is 1.14×10^{-3} sec^{-1}, only a little slower than it is for the acid ligand, and two sets of products are formed: $[Ru(NH_3)_5O_2CCH_2NH_3^{3+} + EtOH]$ (ca. 70%); $[Ru(NH_3)_5H_2O^{3+} + NH_3CH_2CO_2Et^{+}]$ (30%). In the presence of Cl^-, some of the aquo product, but none of the carboxyl-bound product, is diverted to $Ru(NH_3)_5Cl^{2+}$. A trace of Ru(II) changes the stoichiometry so that virtually no ester hydrolysis ensues. Neither of the changes in composition mentioned affects the limiting rate of disappearnce of the reactant. There seems little doubt that the reaction involves  $Ru(NH_3)_5O{-}\underset{\underset{\displaystyle O{-}Et}{\|}}{C}{-}CH_2NH_3^{4+}$ as an intermediate, its fate then depending on the chemical environment. The point needs perhaps to be emphasized that analogous chemistry has not been reported for the corresponding cobalt(III) complexes. It is likely that the higher lability to linkage isomerization of Ru(III) compared to Co(III) is quite general. An additional, especially interesting case of labile salt isomerization has been described by Clarke[48] involving migration of Ru(III) from a ring to an exocyclic nitrogen in adenosine.

A remarkable inversion of lability for Ru(III) vs. Ru(II) has been reported by Matsubara and Creutz.[49] Whereas in the pentaammine series the lability of

H_2O on Ru(II) is 10^4-fold greater than on Ru(III), for the EDTA complexes the labilities are reversed so that Ru(III) can now act as a catalyst for the formation of the Ru(II) complex. The Ru(III)–EDTA complex reacts readily with a variety of ligands producing Ru(III)–EDTA.L species and there is a strong dependence of the rate of formation of the Ru(III) complexes on the stability of the product, indicating that bond-making is important in the activated complexes. This may be characteristic of Ru(III) complexes as a consequence of the πd set being incompletely occupied. More work on substitution reactions of Ru(III) ammines, particularly with neutral ligands, and for comparison, on Rh(III) ammines would be very instructive. Extensive data for Rh(III) will, however, be difficult to obtain because the indirect approach involving an adjacent oxidation state, as described for Ru(III), is not applicable to Rh(III).

Finally, we turn to what may be the most remarkable manifestation in reactivity of the vacancy in the πd sub-shell of Ru(III), namely reductive substitution by NO.[50]

$$NO + Ru(NH_3)_6^{3+} + H^+ = Ru(NH_3)_5NO^{3+} + NH_4^+.$$

The specific rate for this reaction at 25° is 1.9×10^{-1} M^{-1} sec^{-1}, to be compared to 1.6×10^{-9} M^{-1} sec^{-1} for the aquation (the latter figure is arrived at by multiplying the specific rate in Table I by six, the statistical factor, and dividing by the molality of water). Remarkably, Br^-, which is ordinarily much more labile than ammonia, is replaced at a rate competitive with that of ammonia replacement. The selectivity in replacement is a matter of interest and has been investigated to some extent.[51] The reductive substitution by NO is not limited to Ru(III) complexes but is observed also for Os(III) and also in $Fe(CN)_6^{3-}$, though in the last case reaction is very slow.[50] There is, in principle, no reason why the reaction should not be observed for a πd^4 system. The only ammine complexes with this electronic structure known are those of Os(IV),[52,53] and when these react with NO, reductive diazotization[54] takes precedence:[53]

$$Os^{IV}(NH_2^-) + NO \rightarrow Os^{III}N_2 + H_2O.$$

The expected substitution might occur with $OsCl_6^{2-}$ as reactant, but this possibility has not been examined.

Epilogue

In the interests of keeping this article within reasonable bounds, its descriptive content has been severely restricted. Even with this limitation, a number of significant issues have been exposed which have been incompletely investigated and as a result are poorly understood. Their number and significance are enhanced if account is taken of related work which has been done or is in progress —for example the striking modification of the reactivity of the ruthenium centers when ammonia is replaced by bipyridine and similar ligands.[55] Closely related too is parallel work with osmium species — it is already quite clear that back donation is much more prominent for Os(II) than Ru(II), and that it is a factor also in the chemistry of Os(III). Though chemistry of the kind which has been described, comprising as it does an extension of traditional or classical coordination chemistry, may lack the glamour of newly emerging areas, it nevertheless features basic and important problems which challenge our experimental ingenuity and our capacity to understand

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