CHEMISTRY OF RUTHENIUM(II) AND OSMIUM(II) AMMINES

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Abstract— Part of the motivation for the continued interest in the chemis-
try of ruthenium and osmium ammines arises from the fact that the 2+ oxida-
tion states show a very high affinity for π acid ligands, this affinity
being maximum when only one π acid ligand is present and the remaining li-
gands are saturated. The complexes provide an opportunity for the systema-
tic study in the octahedral case of the effect of the metal center on the
properties of the π acid ligand, and of the effect of the π acids on the
auxiliary ligands.

A large number of π acid ligands which are not particularly nucleophilic
toward dipositive ions of the first transition series replace H_2O from
$[Ru(NH_3)_5H_2O]^{2+}$ in water as solvent to produce the respective pentaam-
mine complexes. The list of such ligands includes N_2, N_2O, $(CH_3)_2S$,
$(CH_3)_2Te$, $(RO)_3P$. Because of the instability of $[Os(NH_3)_5H_2O]$ to
oxidation, indirect methods for preparation of the desired species are
resorted to for Os(II). Equilibrium data are presented which contrast
the affinity pattern for Ru(II) on the one hand with that shown by a
typical dipositive ion of the first transition series.

The strong electron-withdrawing effect of the π acid ligands is documented
by data showing their effect on the acidity of H_2O as an auxiliary ligand.
The electron withdrawing effect is manifested also in a much reduced
affinity for other π acids, and a much reduced rate for substitution of
H_2O as an auxiliary ligand by an incoming nucleophile. Data are also out-
lined which document the increased electron density on the π acid ligand
caused by the interaction with the pentaammine groups. These effects are
enormous for $Os(NH_3)_5^{2+}$: thus coordination of this group to pyrazinium
ion decreases the acid strength of the ligand by almost 7 powers of ten.

Some features of the chemistry of the 3+ states are also commented on.
The fact that $Ru(NH_3)_5^{3+}$ has a low spin d^5 electronic state manifests
itself in placing the ligand-to-metal charge transfer transitions for
Ru(III) complexes at energies often much lower than the d-d, and in sig-
nificant ground state stabilization by ligand-to-metal charge transfer.
The facile linkage isomerizations noted for Ru(III) may also be directly
related to the feature of electronic structure referred to.

Though there is little evidence for stabilization of the Ru(III)-π acid
combination by back bonding, this promises to be revealed as an important
feature of the chemistry of Os(III), this promise being documented by
observations cited on the chemistry of $Os(NH_3)_5N_2^{3+}$.

INTRODUCTION

A dichotomy of interests exists in the field of coordination chemistry, which has been quite
detrimental to its development. Those who were trained in the more traditional descriptive
chemistry which emphasizes saturated ligands have tended to limit their research to them.
On the other hand, the rapidly growing area of organometallic chemistry has attracted many
who began to work in this field with but little exposure to the more traditional lore.
Unfortunately, the subject matter of coordination chemistry readily lends itself to this
dichotomy. The preparative methods of organometallic chemistry owes little to the kind of
procedures which were used in elaborating the chemistry of cobaltammines, for example.
Unsaturated or π acid ligands play a central role in organometallic chemistry, but the metal
carbonyls, though known for many years, were regarded as a class apart by those exposed to
the traditional training in coordination compounds. Very little chemistry was recognized as
constituting an interface between the behavior of saturated vs unsaturated ligands, and

this situation has a natural chemical basis. Metal ions such as Co(III), Ru(III), Ir(III), Cr(III), Pt(IV), which, because they form robust complexes, provided the experimental foundation for the principles of traditional coordination chemistry, do not tend to make stable complexes with π acid ligands. Such ligands, however, stabilize low oxidation states and organometallic, in contrast to traditional coordination chemistry, involved mainly metals in low (2+ or lower) oxidation states at least in the early stages of its growth.

Historically, the chemistry of Cu(I) did provide an interface between saturated and unsaturated ligand behavior. In spite of a high effective nuclear charge, Cu(I) because of its low oxidation state, has a high affinity for π acid ligands, among them carbon monoxide. However, the complexes tend to be labile, and as a result, systematic studies of the chemistry, these presupposing detailed knowledge of structure and composition also in solution, are severely hampered. The chemistry of platinum(II) has provided and continues to provide an important and extensive interface between saturated and unsaturated ligand chemistry. Observations on formation and properties of PF_3 complexes (Refs. 1& 2) played a crucial role in generalizing the concept of back-bonding and in applying the expanded views to preparative chemistry. More recently, the results of measurements of the affinity of Pt(II) ammines with a water soluble phosphine have been reported (Ref. 3). Extensive though the overlap between saturated and unsaturated ligand chemistry is for Pt(II), the area of overlap is being greatly expanded by research on the chemistry of Ru(II) and Os(II). Since octahedral rather than planar coordination geometry is dealt with, the results complement those which have been obtained with Pt(II). Also, it should be mentioned that the effects of back-bonding are more striking for Ru(II) than for Pt(II) (note for example the formation of an N_2 complex by the direct reaction $[Ru(NH_3)_5OH_2]^{2+} + N_2$) (Ref. 4) and are more striking for Os(II) than they are for any other metal ion of the same oxidation state. These considerations provide at least in part the motivation for the effort being devoted to the new chemistry of Ru(II) and Os(II).

The reasons for back bonding being so prominent in the chemistry of Os(II) and Ru(II) have been discussed at some length elsewhere (Ref. 5). Historically, the discovery that directed so much interest to their chemistry was the preparation of the first (Ref. 6) stable combination of dinitrogen, namely $[Ru(NH_3)_5N_2]^{2+}$. Interest in the discovery was heightened by the observation that dinitrogen sources of high chemical potential are not necessary for the preparation of $[Ru(NH_3)_5N_2]^{2+}$, and that it can be formed by the direct reaction of N_2 with $[Ru(NH_3)_5H_2O]^{2+}$ in water (Ref. 4). These observations strongly suggested an important role of back bonding in the chemistry of Ru(II), and the suggestion was confirmed by the preparation and characterization of a series of *N*-heterocyclic complexes of Ru(II) (Ref.7).

A major, though not the sole theme of this article is to trace some of the consequences of back bonding in chemical behavior as they are manifested in complexes of Ru(II) and Os(II). The effects are greatest in complexes in which the auxiliary ligands do not compete for π electron density. The simplest systems then to begin with would be those in which the auxiliary ligands are saturated, and among these NH_3 is the first choice because (i) the dominant bonding mode being a σ interaction, it is the simplest ligand to understand and (ii) it tends to undergo substitution less readily than does any other saturated ligand. Ligands which are both σ donors and π donors are of course also of interest, and such ligands can in fact enhance back bonding between the central metal and a π acid ligand. Their systematic study is also under way, and some of the results obtained with them will be referred to.

COMPARISON OF $[Fe(CN)_5]^{3-}$ AND $[Ru(NH_3)_5]^{2+}$

Having fixed upon the 2+ ions of the iron group, a point of immediate interest is the comparison of the back-bonding propensity for the members of the group. Unfortunately, few comparisons can be made which encompass the whole group. A difficulty is that Fe(II) tends to make high spin complexes except with ligands of high field strength, and few studies have been carried through with such ligands which bear on the point at issue. One such study (Ref.8) in which the proton affinity of Cp_2M was measured for the group suggests that this affinity decreases in order from Fe to Os and this in turn suggests that the radial extension of πd electrons decreases in the series Fe to Os. Such a conclusion is strongly at variance with that which will be reached on the basis of numerous comparisons in the pentaammine series, at least for Ru compared to Os.

No extensive studies have been made for the purpose of comparing a ruthenium(II) species with a low spin iron(II) center in the same environment. However, the capacity $[Fe(CN)_5]^{3-}$ has for back bonding interactions has been explored especially by Toma, Malin, Giesbrecht (Ref. 9) and coworkers. To a remarkable degree, the observations parallel those which have been made for $[Ru(NH_3)_6]^{2+}$. As a case in point, in Fig. 1, the maximum in the π* ←πd absorption for the complexes of a series of N heterocyclics with $[Ru(NH_3)_5]^{2+}$ are shown plotted against those observed with $[Fe(CN)_5]^{3-}$ as the metal center [a more complete plot
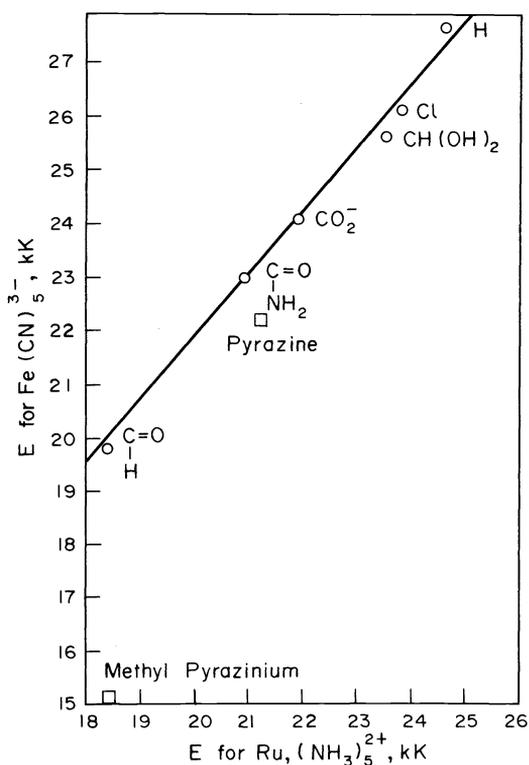
Fig. 1. The energies of the band maxima of the πd-π^* transitions for complexes of $Fe(CN)_5^{3-}$ plotted against those for complexes of $Ru(NH_3)_5^{2+}$. Circles refer to pyridine derivatives, with the substituents indicated in the 4 positions.

appears in Ref. 9(a)] . The correlation is very good except for methyl pyrazinium ion. The deviation in this case may have the same origin as the anomalous response of pyrazine on Os(II) to protonation, which arises in part from the circumstance that the π^* orbital approaches the πd orbital in energy. The effect is expected to be greater for $Ru(NH_3)_5^{2+}$ than for $[Fe(CN)_5]^{3-}$; by all indications back bonding is more important for the former than the latter.

PREPARATION OF PENTAAMMINE DERIVATIVES

The value of E° for $[Ru(NH_3)_5H_2O]^{3+/2+}$ is 0.06 (Ref. 10), which is high enough so that the 3+ ion can be reduced by H_2 over Pt, should this be the method of choice, but low enough so that preparations must be carried out with exclusion of oxygen. The half-time for the aquation of NH_3 in $[Ru(NH_3)_5H_2O]^{2+}$ is about a day in neutral solution (Ref. 11) but becomes shorter when the solution is made acidic. The lability of the coordinated water is much higher, and, as a result, the pentaammine derivatives can conveniently be prepared by reaction in water as a solvent when the affinity of the ligand for Ru(II) is high enough. This is the case for N_2 (Ref. 4(a)); $[Ru(NH_3)_5N_2]^{2+}$, (Ref. 4(b)); nitrogen heterocyclics, (Ref. 7); nitriles, (Ref. 12); H_2S, (Ref. 13); R_2Se, R_2Te, $SnCl_3^-$, (Ref. 14); SO_2, (Refs. 15 & 16) ethylene (Refs. 17 & 18) and acetylene (Refs. 17 & 18). Nitrous oxide makes a rather labile combination with $Ru(NH_3)_5^{2+}$ in water (Ref. 19) but solids containing the N_2O complex have been prepared (Refs. 20 & 21). The affinity of $P(OEt)_3$ for Ru(II) is certainly high enough so that the ligand can replace H_2O from $[Ru(NH_3)_5H_2O]^{2+}$ even in water, but because of the rapid hydrolysis of the ligand, a non-aqueous medium is preferred (Ref. 22). Acetone is suitable, and this weakly nucleophilic solvent serves also for the preparation of a trimethylsulfonium complex by direct substitution (Ref. 14). A special case is the preparation of C-bound imidazole by the rearrangement of the N bound ruthenium complex in acidic solution (Ref. 23).

By contrast to $[Ru(NH_3)_5H_2O]^{2+}$, $[Os(NH_3)_5H_2O]^{2+}$ is very strongly reducing ($E_f = -0.73$ vs. (NHE) (Ref. 24) so that its lifetime in water is very short, and the simple preparative methods which usually suffice for Ru(II) complexes are not applicable to osmiumpentaammines. Despite the rapid reduction of water by $[Os(NH_3)_5H_2O]^{2+}$ the preparation of $[Os(NH_3)_5)_2N_2]^{4+}$ by keeping a solution containing $[Os(NH_3)_5Cl]^{2+}$ and $[Os(NH_3)_5N_2]^{2+}$ over zinc amalgam has proven to be possible (Ref. 25). Surprising in this context is the fact that we have not been able to prepare $[Os(NH_3)_5N_2]^{2+}$ by a similar method using N_2 in the presence of $[Os(NH_3)_5Cl]^{2+}$, even when the former is used at a pressure so high as to make its concentration equal to that

of $[Os(NH_3)_5N_2]^{2+}$ in the procedure which leads to the successful production of the binuclear complex.

A preparative method of considerable generality was developed by Magnuson (Ref. 26). When $cis\text{-}Os(NH_3)_4(N_2)_2^{2+}$ (Ref. 27) is heated in aqueous solution, one molecule of N_2 is lost, leading to a mono aquo complex, but leaving one N_2 as ligand to stabilize osmium in the 2+ state. When the operation is carried out in the presence of a suitable ligand, L(the method proved successful for L = nitrogen heterocyclic or $[Os(NH_3)_5N_2]^{2+}$ and was by no means exhaustively investigated) the complex $[Os^{II}(NH_3)_4(N_2)L]$ forms. On oxidizing Os(II) to Os(III), non-bridging N_2 is lost, and in the absence of a better nucleophile is replaced by H_2O, thus leading to a series of complexes with all ligands but one saturated.

A method based on the oxidation of $[Os(NH_3)_5N_2]^{2+}$ using the silver salt of an indifferent anion in a poorly nucleophilic solvent, S1, has proven successful for the preparation of a number of complexes (Ref. 25). In this preparation, $[Os^{II}(NH_3)_5S1]$ is an intermediate and at least nitrogen heterocyclics convert the solvent-containing complex to the corresponding complex of the heterocyclic ligand L. When L is a π acid, the 2+ state can readily be generated by reduction.

ABSORPTION SPECTRA

A property of the $Ru^{II}(NH_3)_5Ln$ and $Os^{II}(NH_3)_5Ln$ combinations (Ln represents an unsaturated ligand) is that they feature absorption bands ascribable to transitions involving πd and π* levels (Ref. 7). For N-heterocyclic ligands, at least when these are good π acids, the absorption bands occur in the visible and have high extinction coefficients, of the order of 10^4. Data for a series of complexes are summarized in Table I.

TABLE 1. Band maxima in metal – ligand charge transfer absorption for pentaammine species ([a])

Ligand	$Ru(NH_3)_5^{2+}$	$Os(NH_3)_5^{2+}$
$CH_3\text{-}$⟨◯⟩N	398	
⟨◯⟩N	407	
$O=C$⟨◯⟩N , H_2N	479	508
N⟨◯⟩N	472	460
N⟨◯⟩NH$^+$	529	430
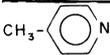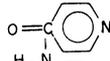
(a) λ in nm; Ru data, (Ref 7); Os data, (Ref. 25).[b]

(b) Data for $Os(NH_3)_5^{2+}$ (Ref. 25) and $Os(NH_3)_4Cl^+$(Ref. 26) are not significantly different.

It is to be noted that as the electron withdrawing power of the unsaturated ligand is increased the πd – π* absorption for the Ru(II) complexes moves to lower energies. This is to be expected if the ground state orbital is mainly metal centered, and thus the excited state is mainly ligand in character. The relatively small change observed on the protonation of pyrazine when ligated to $Ru(NH_3)_5^{2+}$ compared to that attending protonation of the same ligand on $Fe(CN)_5^{3-}$ has already been pointed out. Protonation is of course expected to increase the electron withdrawing power of the ligand, and if the metal πd orbital lies lower than the π* orbital, protonation is expected to shift the πd – π* transition to lower energies. In the light of these considerations, the fact that protonation of $[Os(NH_3)_5pz]^{2+}$ causes a shift in the opposite direction is noteworthy.

Zwickel and Creutz (Ref. 27) have treated the πd – π* absorptions shown by the N-heterocyclic complexes. For any heterocyclic, the absorptions for the pentaammines, the *cis* and *trans* tetraammines constituting a total of 4 independent data (1, 2 and 1 band(s) respectively) are correlated by two parameters: β, the exchange integral, $t_{2g}|H|π*$ and δ, the difference in energy between the unperturbed πd and π* levels. For the osmium ammines, data for the bis substituted species have not been obtained but the mono substituted ones show two absorptions (Ref. 26) which then makes it possible to extract values for the same two parameters. The results for pyrazine and pyrazinium ion as ligands are summarized in Table 2.

The increased value of β for the pyrazinium compared to the pyrazine complex and the fact that in the former complex, the πd and π* levels approach in energy can be taken to be the cause of the anomaly noted in Fig. 1. The formal analysis, as intuition would suggest, shows that on protonating the osmium complexes, the π* level lies <u>below</u> that of the πd metal level,

so that now the ground state orbital has more ligand than metal character. The large transfer of electron density from metal to pyrazine which this implies is documented by equilibrium data to be introduced presently. The situation that protonation shifts the $\pi d - \pi^*$ absorption to higher energies has been realized also for $Ru(NH_3)_5{}^{2+}$, when quinonediammine is the ligand (Ref. 29). This case is particularly interesting because of the existence of a stable 2e reduced state of the ligand, which leads to an ambiguity in how to best view

the complex in the first approximation: [Ru(II) + HN = ⟨—⟩ = $NH_2{}^+$] or [low spin Ru(IV) +

N—⟨◯⟩—NH_2]
|
H
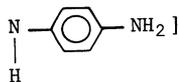
TABLE 2. Parameters derived from $\pi d - \pi^*$ absorption spectra for pyrazine and pyrazinium ion as ligands (units, cm^{-1} x 10^{-3})

Species	β	δ	Δδ
$(NH_3)_5RuN\langle◯\rangle N^{2+}$	6.6	16.7	
			12.2
$(NH_3)_5RuN\langle◯\rangle NH^{3+}$ (a)	9.2	4.5	
$(NH_3)_4ClOsN\langle◯\rangle N^{+}$	10.5	4.9	
			10.6
$(NH_3)_4ClOsN\langle◯\rangle NH^{2+}$	11.3	-5.7	

(a) The results for the tetraamminechloro complexes of Os(II) (Ref. 26), rather than for the pentaammine which have since been prepared (Ref. 25) are presented, because the analysis was first carried through for the former. In both systems protonation of pyrazine shifts the absorption to higher energies, so that both have this significant feature in common.

Two additional points relating to the Zwickel and Creutz treatment of the absorption spectra remain to be made. The values of Δδ in Table 2 represent the differences in the energies of π^* levels for pyrazine and pyrazinium ion, and if the theory were strictly applicable, Δδ for the Ru and Os systems would be the same. The agreement is close enough to be gratifying but not so close that the difference can be dismissed as experimental error. Finally, it should be noted that using the Zwickel and Creutz treatment the change in the energy for a πd orbital when it interacts with the ligand can be calculated, and thus also the contribution of back bonding to stabilizing the metal–ligand combination. The estimate thus made for pyridine as ligand, *ca.* 4 kcal/mole is in fair agreement with estimates arrived at in other ways (Ref. 28).

EQUILIBRIUM STABILITIES

In Table 3 the affinities of H^+, $Ni(H_2O)_5{}^{2+}$ and $Ru(NH_3)_5{}^{3+}$ for a series of ligands as measured by the equilibrium quotients for the replacement of coordinated water by the ligand are shown:

TABLE 3. Equilibrium quotients governing the substitution in aqueous solution

Center	$N\langle◯\rangle$	$N\langle◯\rangle N$	$N\langle◯\rangle NH^{+}$
		Ligand	
H^+	9.2	5.2	0.6	<0
$Ni(H_2O)_5{}^{2+}$	2.8[a]	1.8[b]	1.0[c]	--
$Ru(NH_3)_5{}^{2+}$	4.5[d]	7.4[d]	>8[d]	>10[e]

(a) (Ref. 30), (b) (Ref. 31), (c) (Ref. 32), (d) (Ref. 33).

(e) From the change in the acidity of pyrazinium ion when $Ru(NH_3)_5{}^{2+}$ is coordinated to it (vide infra), the affinity of pyrazinium ion for Ru(II) is known to be approximately 10^2 that of pyrazine.

The results show that Ni^{2+} (aq), which can be taken to be fairly representative of a 2+ ion of the first transition series, shows relative affinities much like H^+, but because of the lower ionic potential they change much less markedly as the σ basicity of the ligands

decrease. By contrast, the affinity of Ru(II) for the ligands increases as the base strength
decreases. The operative factor, however, is not the decrease in σ base strength along the
series, but the fact that in the series as selected the π acidity increases as the σ base
strength decreases.

The data of Table 3 put on a quantitative basis the implications of the successful prepara-
tion of complexes of $Ru(NH_3)_5^{2+}$ with π acid ligands from $[Ru(NH_3)_5H_2O]^{2+}$ in aqueous solution.
Additional data of this kind are summarized in Table 4, but in this case they contrast the
affinity patterns for Ru(II) with Ru(III). The general experience with Ru(III) is that the
stabilities of its complexes owes little to back donation, and this supposition is borne out
by the entries in Table 4.

TABLE 4. Comparisons of the equilibrium quotients[(a)] governing complex
formation with $Ru(NH_3)_5H_2O^{2+}$ and $Ru(NH_3)_5H_2O^{3+}$ in aqueous
solution

Ligand	Ru(II)	Ru(III)	Ratio
N_2	3×10^4	$<4 \times 10^{-13}$	$>10^{17}$
(thiophene, S)	~ 10	$\sim 3 \times 10^{-8}$	$\sim 3 \times 10^8$
H_2S	1.5×10^3	$\sim 2 \times 10^{-4}$	$\sim 8 \times 10^6$
(pyridine, N)	2×10^7	6×10^3	3×10^3
(pyrazine, HN, N)	3×10^6	2×10^6	1.5
NH_3	4×10^4	2×10^5	2×10^{-1}
OH^-	6×10^2	6×10^{11}	10^{-9}

(a)   Taken from (Ref. 13).

The affinities of the ligands for Ru(III) follow the σ base strengths or reasonable suppositions
of what the relative base strengths of the ligands would be. With Ru(II) having a rather weak
affinity for simple σ bases such as OH^- and NH_3, but a high affinity for weak σ bases if the
π acid strength is great enough, the ratios of the quotients governing complex formation for
the two oxidation states cover a very wide range — approximately 10^{26} for the ligands shown.
These effects are of course directly reflected in the redox potentials for the various couples
which therefore span a range of more than 1.5 V. Of specific interest is the evidence that
thiophene is a rather poor ligand for both Ru(II) and Ru(III), though better for the former
than the latter.

No work paralleling that shown in Tables 3 and 4 has thus far been done with Os(II). However
the effect on the 3+/2+ redox potential of substituting H_2O in the aquopentaammine complex
by a π acid ligand does lead to some estimate of the affinities for Os(II). When isn is the
π acid ligand, the potential of the 3+/2+ couple for $Ru(NH_3)_5$ increases by 0.38 V., but for
$Os(NH_3)_5$ the increase is 0.49 V. The affinity of isn for Os(III) can be assumed to be at
least as great as for Ru(III) (see later section) and thus the affinity of isn for Os(II)
is about 10^2 times that for Ru(II), or greater than 10^{10}.

        THE EFFECT OF THE METAL IONS ON THE LIGANDS

The principal concern in this section will be with π acid ligands, but to provide a setting
for these results, data for H_2O as a typical saturated ligand, and for its congener H_2S,
interesting in its own right, will be shown.

TABLE 5. Effect of $Ru(NH_3)_5^{2+}$ and $Ru(NH_3)_5^{3+}$ on acidity[(a)] of
coordinated H_2O and H_2S

Ligating Center	H_2O	H_2S
None	15.7	7
$Ru(NH_3)_5^{2+}$	13.1	4.0
$Ru(NH_3)_5^{3+}$	4.1	~ -10

(a) pK_a values in body of table taken from Ref. 13.

Quite remarkable is the fact that $[Ru(NH_3)_5H_2O]^{2+}$ is so weakly acidic. The comparison with
Hg^{2+} in this respect is striking $[pK_a$ for $Hg^{2+} = 2.5$ (Ref. 34)$]$; less so, but important in its
implications about electron distribution in the ions is the fact that pK_a for $[Ru(NH_3)_5H_2O]^{2+}$

is also much greater than those for 2+ aquo ions of the first transition, most of which are less than 10. While the increase in pK_a for H_2S in coordinating to $Ru(NH_3)_5^{2+}$ is slightly greater than it is for H_2O, this result must be taken in the context of the fact that S as a center is much more sensitive to an inductive effect than is H_2O. Thus replacing one H in HOH by C_2H_5, the pK_a value increases by slightly over 2 units (Ref. 35) but the same change in HSH causes an increase of 5 units (Ref. 36). The modest change in the pK_a for H_2S on being coordinated to Ru(II) probably reflects some π acid character for H_2S as ligand, so that back bonding partly counteracts the inductive effect of the 2+ change. Bearing out this supposition is the fact that there is no significant ligand deprotonation in the second stage (Ref. 13) even at a pH of 14(back bonding is expected to decrease sharply in the series H_2S, HS^-, S^{2-}). Finally attention is drawn to the enormous increase in the acidity of coordinated H_2S when Ru(II) is oxidized to Ru(III). If low spin Fe(II) and Fe(III) in a porphyrin are even approximately like Ru(II) and Ru(III) it follows that oxidation of a thiol complex of Fe(II) to the Fe(III) state is a simple way of producing a super acid in a biological setting.

Table 6 features data on the effect which coordination to Ru(II) and Os(II) has on the proton acidity of the π acid, pyrazinium ion (pzH^+).

TABLE 6. Effects of coordination on acidity of pz^+ in ground state and in charge transfer excited state

Ligand	Ground state pK_a	Excited state	Ref.
free	0.6		37
on $Ru(NH_3)_5^{3+}$	~ -1.0	$13^{(a)}$	7
on $Ru(NH_3)_5^{2+}$	2.5	7.3	7
on $Os(NH_3)_4Cl^+$	7.6	3.9	26 a,b
on $Os(NH_3)_5^{2+}$	7.4	4.6	25

(a) On oxidizing $[Ru^{II}(NH_3)_5$ N-heterocyclic$]$ to the 3^+ state, a band is observed short of where d-d transitions are expected. If this band is interpreted as $\pi^* \leftarrow \pi d$ in character, a pK_a is calculated as entered in the table. Similar values result from observations on Os(III).

Of interest in the second column of the table is the increase in pK_a registered for the ligand in coordinating the dipositive center $Ru(NH_3)_5^{2+}$ to it. Even in this case, the effect of back bonding in transferring electron density from metal to ligand more than compensates for the inductive effect of the dipositive charge. In the case of Os(II) the basicity of pyrazine is increased almost seven orders of magnitude on coordination! This large effect is in harmony with the observations on the spectra which place the π^* level for pzH^+ below that of a πd orbital on Os(II). Thus the ground state orbital in $[Os(NH_3)_5pzH]^{3+}$ has more ligand than metal character. This relation is manifested also in the pK_a values for the charge transfer excited states which can be calculated from the shifts in band maxima on protonation of the ligand and pK_a for the ground state. The entries in column 3 do not refer to equilibrated states, but rather represent what might be called Franck-Condon values and may differ from the equilibrium ones — these allow for changes in nuclear coordinates after excitation — by as much as 2 pK units. Nevertheless, they suffice to demonstrate that in the case of $Os(II)pzH^+$, because the ground state has more ligand character than the excited state, pK_a decreases on excitation while the reverse is true for Ru(II). The entry for Ru(III) measures the effect of charge transfer on acidity in the absence of back bonding, the excited state in this case being more basic than the ground state by $ca.$ 14 units in pK_a.

The results of measurements of acidity of coordinated SO_2 are summarized in Table 7.

TABLE 7. Acidity of SO_2, free and coordinated

Ligating center	pK_a	pK_2	Ref.
None	1.76	7.2	(38)
$Ru(NH_3)_5^{2+}$	2.45	5.1	(16)
$Os(NH_3)_5^{2+}$	7.0*	--	(25)
$Ru(NH_3)_5^{3+}$	<< 0	< 0	(39)

* Note added subsequently: at pH = 7.0, coordinated SO_2 is converted directly to SO_3^{2-} and thus $\frac{1}{2}$ (pK_1 + pK_2) = 7.0.

Back bonding is expected to be greatest for SO_2 and to diminish as the negative charge on the ligand increases. In accord with this, while for pK_1 back bonding to $Ru(NH_3)_5^{2+}$ more than compensates for the inductive effect of the 2+ charge, the reverse is true for pK_2. As when $pzH+$ is the ligand, the effect of Os(II) in stabilizing the strong π acid SO_2 is very great, in this case requiring the pH to be raised to 7.0 before coordinated SO_2 is converted to coordinated HSO_3^- (or SO_3^{2-}). Ruthenium in the 3+ state shows the expected inductive effect of its charge and it decreases the basicity of coordinated S(IV) to the point that the SO_3^{2-} form persists even at very high acidities.

The stabilization of SO_2 on Ru(II) extends also to the rate of hydration. This rate for the free ligand is 3.4×10^6 sec^{-1}(Ref. 40). The conversion of $trans$-[$Ru(NH_3)_5SO_2(H_2O)$]$^{2+}$ to the HSO_3^- complex at a pH just high enough to bring about the reaction has been measured (Ref. 39) as 0.32×10^2 sec^{-1} and this value must be regarded as an upper limit on the rate of the water (i.e. non-base induced) reaction. Presumably the rate for [$Os(NH_3)_5SO_2$]$^{2+}$ is even lower, but in this case the path that operates when the conversion to the OH^- containing form takes place is in all likelihood not the simple water dependent path, but involves base as reactant.

THE EFFECT OF π ACIDS ON AUXILIARY LIGANDS

The electron withdrawing power of a particular π-acid ligand can be assessed by including a molecule of H_2O in the coordination sphere, and observing the effect on its acidity of replacing an ammonia molecule, cis or $trans$, by a π acid ligand. Most of the comparisons of this kind which can be made with present data center on nitrosyl ion as the π acid. An instructive example involves the pK_a for [$Ru(NH_3)_5H_2O$]$^{2+}$ and that for $trans$-[$Tc(NH_3)_4(NO)H_2O$]$^{2+}$. It should be noted that Ru(II) and Tc(I) are isoelectronic and the systems differ in the respect that while Ru(II) has unit higher kernel charge, in the Tc(I) complex, an extra charge resides in the ligand. The values of pK_a for the species are 13 (Ref. 13) and 7.3 (Ref. 41) respectively, showing that the inductive effect of NO^+ exceeds that of increasing kernel charge by one unit. In this case NO^+ is acting on a metal in a low oxidation state and electron release by Tc(I) to NO^+ is expected to be particularly large. But the same effect can be observed also in a higher range of oxidation states. Thus the pK_a values for [$Ru(NH_3)_5H_2O$]$^{3+}$ and $trans$-[$Ru(NH_3)_4(NO)H_2O$]$^{3+}$ are 4.1 (Ref. 42) and 1.4 (Ref. 43) respectively. (The pK_a for the cis form of the nitrosyl is 4.1 (Ref. 43)). It is of interest to note that pK_a for $trans$-[$Tc(NH_3)_4(NO)H_2O$]$^{3+}$ is $ca.$ 2 (Ref. 41), that is, very close to that measured for the corresponding Ru(II) complex. Thus there is very little difference between the πd^5 and πd^6 cases for the same charge, at least when a $trans$ position is in question. There may, however, be a marked difference in comparing cis positions because the electron hole in the d^5 nitrosyl complex is expected to reside in an orbital perpendicular to the metal-NO^+ axis.

Effects of the kind documented for nitrosyl are observed also with other π acids. Thus, pK_a for cis-[$Ru(NH_3)_4(CO)H_2O$]$^{2+}$ is ~ 8 and for the $trans$ complex is 7.1 (Ref. 43). The effects on affinities have been illustrated for OH^- replacing H_2O but are of course not limited to this particular complex formation reaction. For no other nucleophiles have data as extensive as those cited been obtained and conclusions involving them depend largely on qualitative observations. Thus, though the affinity of Cl^- for [$Ru(NH_3)_5H_2O$]$^{2+}$ has been determined (Ref. 44), there seem to be no data for complexes in which NH_3 is replaced by π acid ligands. General preparative experience (Refs. 45 & 46) with complexes in which pyridine replaces ammonia at least in part, however, does suggest that the affinity for Cl^- is greatly enhanced by such replacement. Since a π acid is electron withdrawing, it favors the attachment to the metal center of OH^- over that of H_2O — hence the effect on acidities — but by the same token, it is expected to decrease the affinity of another π acid for the metal center. This kind of effect has frequently been encountered but mainly in qualitative experiments. In that category is the experience that on replacing a single NH_3 in [$Ru(NH_3)_5H_2O$]$^{2+}$ by pyridine, no trace of a dinitrogen complex is observed when the resulting species is brought into contact with N_2 at 1 atm.

There are no quantitative experiments which unambiguously bear on the issue, but a number of quantitative results have been obtained with SO_3^{2-} or $P(OEt)_3$ $trans$ to the π acid ligand. Typical of them is the following: while the equilibrium quotient governing the reaction of isn with $trans$-[$Ru(NH_3)_4(SO_3)H_2O$] is 3.8×10^3 (Ref. 16), for the reaction with aquopenta – ammine complex it is in excess of 10^8 (Ref. 33). The point that neither SO_3^{2-} nor $P(OEt)_3$ are representative of simple π acid ligands needs to be made, and will be further elaborated presently, and quantitative experiments with ligands such as pyrazine are needed.

Lacking a detailed understanding of the activation process for substitution, it would be impossible to predict from the equilibrium effects how π acid ligands affect rates of substitution. The very effects which lead to a strengthening of bonds might be enhanced in the activated complexes for reaction and thus lead to rate increases. Nor can experience with square planar complexes be a guide: there is no reason whatever why the energy differences between reactants and activated complexes need be the same for square planar and octahedral

complexes. The redetermination by Bottomley (Ref. 47) of the structure of a salt of pentaamminenitrosylruthenium(II) did much to erase misconceptions about the labilizing effect of nitrosyl, and by inference then, of other π acid ligands on the coordination sphere of hexacoordinated ruthenium(II). There is no structural basis for an abnormal lability of NH_3 *trans* to NO^+ and Bottomley suggests that the rather facile replacement of NH_3 *trans* to NO^+ by OH^- is a result of conversion of NO^+ to NO_2^- and labilization by NO_2^-. In fact it has been shown (Ref. 48) that for a large group of ligands which can be characterized as good π acceptors and moderate to indifferent σ donors, the lability of water coordinated to ruthenium(II)ammine is diminished as the π acid character increases. The latter property can be gauged at least approximately by the extent to which Ru(II) is stabilized over Ru(III) and is thus reflected on the values of the redox potentials. Figure 2 shows data on the rate of substitution of H_2O in *cis* or *trans* $Ru^{II}(NH_3)_4(L)H_2O$ by isonicotinamide as a function of E_f for the $Ru^{3+/2+}$ couple. A rather good correlation over a wide range in lability exists, with not much difference between *cis* and *trans* forms. A monotonous relationship of the kind observed is expected if bond breaking is important in the activated complex for substitution and if the mechanism does not change abruptly throughout the series. The relationship is of course not direct; both rates and values of E_f depend on the back bonding capacity of the ligands.
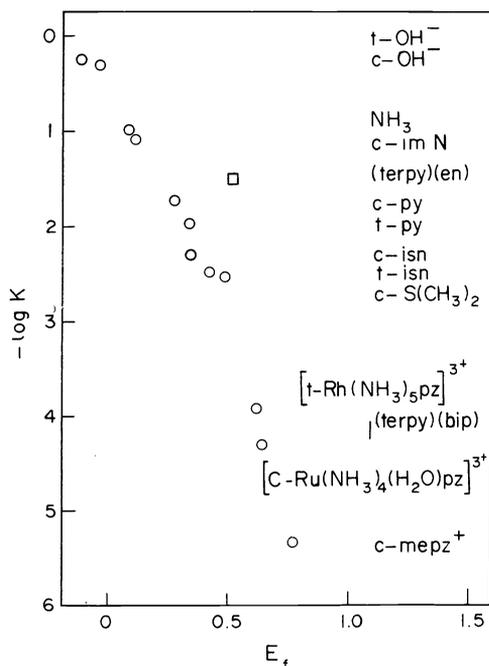
Fig. 2. The specific rate for replacement of water by isonicotinamide in tetraammineaquo complexes (circles) and in [Ru(terpy)(en)H_2O] $^{2+}$ and [Ru(terpy)(bip)H_2O] $^{2+}$ [squares] as a function of E_f for the Ru(III)-Ru(II) couples. Units of k, $M^{-1}sec^{-1}$, at 25°.

Much more difficult to understand are groups which are strongly *trans* labilizing. These include SO_3^{2-}(Ref. 16), CN^-(Ref. 49), carbon-bound imidazole (Refs. 23 & 48), and recently $P(OR)_3$ (Ref. 22) has been added to the roster. Not merely do they labilize *trans*, but for SO_3^{2-} it has been shown that when it replaces NH_3, a water molecule *cis* to it is in fact delabilized (Ref. 16). The *trans* labilizing effect of SO_3^{2-} has a great deal of preparative utility. A *trans* position is opened up for substitution and once the product is formed by ligand substitution, it can be "fixed" by using H_2O_2 as an oxidant. This converts SO_3^{2-} to SO_4^{2-}, which usually remains trapped in the coordination sphere of the metal. On reduction, sulfate ion is readily lost and thus a second position is opened up for substitution. In attempts (Ref. 22) to prepare [Ru(NH)P(OEt)$_3$] $^{2+}$ by direct substitution, the product obtained is always *trans*-[Ru(NH$_3$)$_4$(P(OEt)$_3$)$_2$] $^{2+}$, owing to the labilization of the *trans* position by a phosphite ligand once it has been added. On being kept in solution, one of the phosphite groups is lost by being hydrolyzed to the diester, and the resulting *trans*-[Ru(NH$_3$)$_4$P(OEt)$_3$(H_2O)] $^{2+}$ has made possible the systematic study of P(OEt)$_3$ in affecting the position *trans* to is on Ru(II) (Ref. 22).

Comments on the 3+ States
A number of the observations relating to the 3+ state of ruthenium have been included in the foregoing, mainly to illustrate the point that back bonding is a relatively unimportant effect

for it. But there are some consequences of the electronic structure of Ru(III), low
spin d^5, which call for special comment. Though in an equilibrium sense, $[Ru(NH_3)_5H_2O]^{3+}$
is a weaker oxidizing agent than $[Co(NH_3)_5H_2O]^{3+}$, the $Ru(NH_3)_5^{3+}$ unit is more strongly
electron withdrawing than is $Co(NH_3)_5^{3+}$. The equilibrium oxidizing effect of Co(III) is
achieved only after strong distortion of its coordination sphere and, because the electron
hole in Co(III) resides in a higher energy antibonding orbital, the charge transfer from
ligand to Co(III) in the ground state is small. By contrast, the electron hole in Ru(III)
resides in a low energy orbital. This difference manifests itself directly in the fact
that while for Co(III), ligand to metal charge transfer absorption usually occurs in regions
of the spectrum where d-d or pure ligand transitions interfere, on Ru(III), for many ligands
of interest absorption having this origin occurs at wavelengths longer than and well separated
from absorptions involving different electronic processes. A systematic exploration of ligand
to metal absorption is facilitated for Ru(III) (Ref. 50) and in our laboratories is in progress
on thioethers (Ref. 14). Ground state ligand to metal charge transfer is likely the reason
that $[Ru(NH_3)_5H_2O]^{3+}$ (pK = 4.1) is so much more acidic than $[Co(NH_3)_5H_2O]^{3+}$(pK_a = 6.4)(Ref. 51)
An obvious and important direction for future research is to discover whether such effects
are enhanced when the oxidizing power of Ru(III) is increased by suitable substitution. It
is by no means certain, however, that the ground state electron transfer will follow the
oxidizing power. A direct and simple relation is expected only if the dimensions of the
molecules in the two oxidation states are the same.

Linkage isomerization occurs with great facility on Ru(III) (N-bound to C-bound imidazole
has already been mentioned as an example). That this is the result largely of the electron
hole in the πd levels rather than being attributable to the general tendency for substitution
at 3+ ions of the 2nd and 3rd transition series to involve some bond making in the activated
complexes is shown by the fact that the nitrito-nitro conversion on $Rh(NH_3)_5^{3+}$ is only a
factor of about 20 greater than on $Co(NH_3)_5^{3+}$(Ref. 52). This ratio is to be contrasted with
the result that N → O rearrangement for glycine on $Co(NH_3)_5^{3+}$ has never been reported; in
$[Ru(NH_3)_5NH_2CH_3CO_2]^{2+}$ the rearrangement takes place with a half-life of 21 sec at 25°, and
though it is slower for the protonated form, even here the half-life is only 350 sec (Ref. 53).
Thioacetamide on Ru(III) provides another example, low pH favoring S bound and high pH the
N bound form (Ref. 54). In this case the change is even more facile than it is for glycine.
Thus lability to linkage isomerization becomes an important factor in attempts to extend to
Ru(III) the definitive investigations of nucleophilic substitutions on coordinated ligands
which have been done for ligands on Co(II) (Ref. 55 and earlier).

Though back bonding between the π acid ligands which have been considered and Ru(III), as has
repeatedly been asserted, appears not to be an important interaction, it seems to be signi-
ficant for Os(III). Back bonding on Os(III) has thus far been investigated only for N_2 as
the π acid, and some of the evidence accumulated on the issue will now be outlined (Ref. 56).

In attempting to apply to osmium ammines the remarkable Pell and Armor (Ref. 57) reaction

$$Ru(NH_3)_6^{3+} + NO + OH^- = (NH_3)_5RuN_2^{2+} + 2H_2O$$
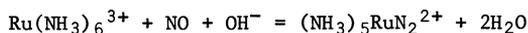
we found that once a single NH_3 in $Os(NH_3)_6^{3+}$(Ref. 58) is replaced by halide ions, the
concentration of alkali required to bring about the necessary deprotonation of a coordinated
ammonia is impractically high. But to our surprise, the diazotization is found to proceed
in acidic solution with HNO_2, producing dinitrogen complexes of Os(III) which can be isolated
as solids. The reaction has been shown to proceed stepwise, the first step being oxidation of
Os(III) to Os(IV):

$$. \quad Os(NH_3)_4Cl_2^+ + HNO_2 + H^+ = Os(NH_3)_4Cl_2^{2+} + NO + H_2O$$
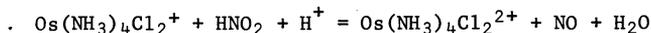
Osmium(IV) is quite acidic, and deprotonates adequately even in acid solution for the
diazotization by the NO which is produced to succeed. The two stages can be uncoupled, by
first producing Os(IV) using any suitable oxidizing agent, and then treating the Os(IV)
product with NO. Application of this reaction to a variety of starting complexes and in
succession to some of them, has led to a number of new osmium species of which the dinitrogen
complexes of Os(III) only are germane to present purposes.

In the absence of back-bonding, Os (III) would be expected to increased the N = N stretching
frequency; an effect of this kind has been observed for $Ru(NH_3)_5^{3+}$ coordinated to a nitrile
(Ref. 12). The substantial decrease in the N=N stretching frequencies caused by $Os(NH_3)_5^{3+}$
suggests that back bonding is quite significant for it. Continued replacement of NH_3 by
halide ion lowers the N_2 stretching frequency still further, the decrease pointing to an
influence of π electron donors on the back bonding capacity of the metal center. Iodide ion,
it should be noted, is more effective in this respect than is chloride ion.

Stabilization of the Os(III)-N_2 combination by halide ion is indicated by some other observa-
tions. The values of E_f for the 3+/2+ couples for $Os(NH_3)_5N_2$, $Os(NH_3)_4(N_2)I$,
$trans$-$Os(NH_3)_3(N_2)I_2$ are 0.58, 0.36 and 0.26 V. respectively. In addition, the rate of N_2
loss from the Os(III) complexes by aquation decreases markedly in the series when NH_3 is

replaced by I^- : $k = 2 \times 10^{-2} sec^{-1}$ for $[Os(NH_3)_5N_2]^{3+}$ (Ref. 59) and $1.75 \times 10^{-3} sec^{-1}$ for $[Os(NH_3)_4N_2I]^{2+}$ (Ref. 55).

In Table 8 are summarized results on the N≡N stretching frequencies for a series of dinitrogen species which afford some instructive comparisons:

TABLE 8. Vibration frequencies for dinitrogen species

N_2	2331
$[Ru(NH_3)_5N_2]Cl_2$	2114
$[Os(NH_3)_5N_2]Cl_2$	2037
$[Os(NH_3)_5N_2]Cl_3$	2212
$[Os(NH_3)_4(N_2)I]Br_2$	2200
$trans$-$[Os(NH_3)_3(N_2)I_2]Br$	2174
$trans$-$[Os(NH_3)_3(N_2)Cl_2]Br$	2205

A back-bonding interaction between N_2 and Os(III) is expected to increase the positive charge on Os(III). That there is an effect of this kind is demonstrated by the fact that pK_a for a coordinated NH_3 on $[Os(NH_3)_5N_2]^{3+}$ is *ca*. 6-7 (Ref. 58), while for $Os(NH_3)_6^{3+}$ it appears to be in excess of 15. The recent observations explain the puzzling conversion (Ref. 27) by HNO_2 in acid of $[Os(NH_3)_5N_2]^{2+}$ to $[Os(NH_3)_4(N_2)_2]^{2+}$. In all likelihood, HNO_2 oxidizes the osmium complex to the 3+ state, which then is acidic enough to make reactions of NO with coordinated NH_2^- possible.

CONCLUSION

Only a little has been said in the foregoing on the subject of the effect of coordination on the ease of transforming the ligands themselves. The systematic control of such reactions is the long range goal of the kind of studies which have been outlined. This is not to say that the effects which have been dealt with — for example, the influence of the metal ion on equilibrium properties of the ligands, and of the ligands on each other — are not important and interesting in their own right. But the research should not stop with these issues. The control of kinetic reactivity is central to a chemist's concern and coordination chemistry has an important role to play in this art, which it is hoped can be developed into a science. The effects which have been dealt with involve largely ground state properties but are unquestionably important also in affecting stabilities of activated complexes. A large number of observations dealing with the transformation of the ligands, only a few of which have been mentioned, have already been encountered. This phase of the subject will undoubtedly increasingly be emphasized and increasingly will undergo systematic development as the questions basic to understanding it are being settled.

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