Chemistry of Ruthenium(II) and Osmium(II) Ammines

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Abstract—Part of the motivation for the continued interest in the chemistry of ruthenium and osmium ammines arises from the fact that the 2+ oxidation 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 ligands are saturated. The complexes provide an opportunity for the systematic 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 \( \text{H}_2\text{O} \) from \([\text{Ru(NH}_3)_5\text{H}_2\text{O}]^{2+}\) in water as solvent to produce the respective pentaamine complexes. The list of such ligands includes \( \text{N}_2 \), \( \text{N}_2\text{O} \), \( (\text{CH}_3)_2\text{S} \), \( (\text{CH}_3)_2\text{Te} \), \( (\text{RO})_3\text{P} \). Because of the instability of \([\text{Os(NH}_3)_5\text{H}_2\text{O}]^{2+}\) 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 \( \text{H}_2\text{O} \) 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 \( \text{H}_2\text{O} \) as an auxiliary ligand by an incoming nucleophile. Data are also outlined which document the increased electron density on the π-acid ligand caused by the interaction with the pentaamine groups. These effects are enormous for \([\text{Os(NH}_3)_5\text{N}_2]^{3+}\): 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 \( \text{Ru(NH}_3)_5^{3+} \) 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 significant 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 \([\text{Os(NH}_3)_5\text{N}_2]^{3+}\).

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 owe 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
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 $\pi$ acid ligands, among them carbon monoxide. However, the complexes tend to be labile, and as a result, systematic studies of the chemistry, that presuppose detailed knowledge of structure and composition and also interaction, 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 $[\text{Ru(NH}_3\text{)}_5\text{H}_2\text{O}]^2+ + N_2$ (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 $[\text{Ru(NH}_3\text{)}_5\text{N}_2]^+$.

Interest in the discovery was heightened by the observation that dinitrogen sources of high chemical potential are not necessary for the preparation of $[\text{Ru(NH}_3\text{)}_5\text{N}_2]^+$, and that it can be formed by the direct reaction of $N_2$ with $[\text{Ru(NH}_3\text{)}_2\text{H}_2\text{O}]^2+$ 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 $\pi$ 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 $\sigma$ interaction, it is the simplest ligand to understand and (ii) it tends to undergo substitution less readily than do any other saturated ligand. Ligands which are both $\sigma$ donors and $\pi$ donors are of course also of interest, and such ligands can in fact enhance back bonding between the central metal and a $\pi$ acid ligand. Their systematic study is also under way, and some of the results obtained with them will be referred to.

**COMPARISON OF $[\text{Fe(CN)}_5]^3-$ AND $[\text{Ru(NH}_3\text{)}_5]^2+$**

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$_2$M 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 $\pi d$ 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 of $[\text{Fe(CN)}_5]^3-$ 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 $[\text{Ru(NH}_3\text{)}_5]^2+$. As a case in point, in Fig. 1, the maximum in the $\pi^* + \pi d$ absorption for the complexes of a series of $N$ heterocycles with $[\text{Ru(NH}_3\text{)}_5]^2+$ are shown plotted against those observed with $[\text{Fe(CN)}_5]^3-$ as the metal center (a more complete plot
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Fig. 1. The energies of the band maxima of the \( \pi d^*-\pi^* \) transitions for complexes of \( \text{Fe(CN)}_5^3- \) plotted against those for complexes of \( \text{Ru(NH}_3)_5^2+ \). 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 \( \pi^* \) orbital approaches the \( \pi d^* \) orbital in energy. The effect is expected to be greater for \( \text{Ru(NH}_3)_5^2+ \) than for \( \text{[Fe(CN)}_5^3] \) \(^3\); by all indications back bonding is more important for the former than the latter.

PREPARATION OF PENTAAMINES DERIVATIVES

The value of \( E^0 \) for \( \text{[Ru(NH}_3)_5\text{H}_2\text{O}]^3+ \) is 0.06 (Ref. 10), which is high enough so that the \( 3^+ \) ion can be reduced by \( \text{H}_2 \) over \( \text{Pt} \), should this be the method of choice, but low enough so that preparations must be carried out with exclusion of oxygen. The half-life for the aquation of \( \text{NH}_3 \) in \( \text{[Ru(NH}_3)_5\text{H}_2\text{O}]^2+ \) 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 pentaamine 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 \( \text{N}_2 \) (Ref. 4(a)); \( \text{[Ru(NH}_3)_5\text{N}_2]^2+ \) (Ref. 4(b)); nitrogen heterocycles, (Ref. 7); nitriles, (Ref. 12); \( \text{H}_2\text{S} \), (Ref. 13); \( \text{R}_2\text{S} \), (Ref. 13); \( \text{R}_2\text{Se}, \text{R}_2\text{Te}, \text{SnCl}_3 \), (Ref. 14); \( \text{SO}_2 \), (Refs. 15 & 16) ethylene (Refs. 17 & 18) and acetylene (Refs. 17 & 18). Nitrous oxide makes a rather labile combination with \( \text{Ru(NH}_3)_5^2+ \) in water (Ref. 19) but solids containing the \( \text{N}_2\text{O} \) complex have been prepared (Refs. 20 & 21). The affinity of \( \text{P(OEt)}_3 \) for Ru(II) is certainly high enough so that the ligand can replace \( \text{H}_2\text{O} \) from \( \text{[Ru(NH}_3)_5\text{H}_2\text{O}]^2+ \) 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 trimethylsulphonium 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 \( \text{[Ru(NH}_3)_5\text{H}_2\text{O}]^2+ \), \( \text{[Os(NH}_3)_5\text{H}_2\text{O}]^2+ \) is very strongly reducing (\( E^0 = -0.73 \) 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 osmium pentaamines. Despite the rapid reduction of water by \( \text{[Os(NH}_3)_5\text{H}_2\text{O}]^2+ \) the preparation of \( \text{[Os(NH}_3)_5\text{N}_2]^2+ \) by keeping a solution containing \( \text{[Os(NH}_3)_5\text{Cl}]^2+ \) and \( \text{[Os(NH}_3)_5\text{N}_2]^2+ \) 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 \( \text{[Os(NH}_3)_5\text{N}_2]^2+ \) by a similar method using \( \text{N}_2 \) in the presence of \( \text{[Os(NH}_3)_5\text{Cl}]^2+ \), even when the former is used at a pressure so high as to make its concentration equal to that.
of \([\text{Os(NH}_3\text{)}_5\text{N}_2\text{]}^{2+}\) 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 \(\text{cis-}\text{Os(NH}_3\text{)}_4(\text{N}_2\text{)}^{2+}\) (Ref. 27) is heated in aqueous solution, one molecule of \(\text{N}_2\) is lost, leading to a mono aquo complex, but leaving one \(\text{N}_2\) as ligand to stabilize osmium in the \(2^+\) state. When the operation is carried out in the presence of a suitable ligand, \(\text{L}\) (the method proved successful for \(\text{L} = \text{nitrogen heterocyclic or [Os(NH}_3\text{)}_5\text{N}_2\text{]}^{2+}\) and was by no means exhaustively investigated) the complex \([\text{Os(NH}_3\text{)}_5\text{N}_2\text{]}^{2+}\) forms. On oxidizing \(\text{Os(II)}\) to \(\text{Os(III)}\), non-bridging \(\text{N}_2\) is lost, and in the absence of a better nucleophile is replaced by \(\text{H}_2\text{O}\), thus leading to a series of complexes with all ligands but one saturated.

A method based on the oxidation of \([\text{Os(NH}_3\text{)}_5\text{N}_2\text{]}^{2+}\) using the silver salt of an indifferent anion in a poorly nucleophilic solvent, \(\text{Sl}\), has proven successful for the preparation of a number of complexes (Ref. 25). In this preparation, \([\text{Os(NH}_3\text{)}_5\text{Sl}]^{2+}\) is an intermediate and at least nitrogen heterocyclics convert the solvent-containing complex to the corresponding complex of the heterocyclic ligand \(\text{L}\). When \(\text{L}\) is a \(\pi\) acid, the \(2^+\) state can readily be generated by reduction.

**ABSORPTION SPECTRA**

A property of the \(\text{Ru}^{II}(\text{NH}_3\text{)}_5\text{Ln}\) and \(\text{Os}^{II}(\text{NH}_3\text{)}_5\text{Ln}\) combinations (\(\text{Ln}\) represents an unsaturated ligand) is that they feature absorption bands ascribable to transitions involving \(\pi d\) and \(\pi^*\) levels (Ref. 7). For \(\text{N}-\text{heterocyclic ligands, at least when these are good }\pi\text{ acids, the absorption bands occur in the visible and have high extinction coefficients, of the order of }10^4\). Data for a series of complexes are summarized in Table 1.

**TABLE 1.** Band maxima in metal—ligand charge transfer absorption for pentaaaminine species (a)

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Ru(\text{NH}_3\text{)}_5^{2+}</th>
<th>Os(\text{NH}_3\text{)}_5^{2+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)</td>
<td>398</td>
<td>407</td>
</tr>
<tr>
<td>O=</td>
<td>479</td>
<td>508</td>
</tr>
<tr>
<td>N(_3)</td>
<td>472</td>
<td>460</td>
</tr>
<tr>
<td>N(_2)</td>
<td>529</td>
<td>430</td>
</tr>
</tbody>
</table>

(a) \(\lambda\) in nm; Ru data, (Ref. 7); Os data, (Ref. 25).
(b) Data for Os(\text{NH}_3\text{)}_5^{2+} (Ref. 25) and Os(\text{NH}_3\text{)}_5\text{Cl}^{2+}(Ref. 26) are not significantly different.

It is to be noted that as the electron withdrawing power of the unsaturated ligand is increased the \(\pi d - \pi^*\) absorption for the \(\text{Ru(II)}\) 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(\text{NH}_3\text{)}_5^{2+} compared to that attending protonation of the same ligand on Fe(\text{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 \(\pi d\) orbital lies lower than the \(\pi^*\) orbital, protonation is expected to shift the \(\pi d - \pi^*\) transition to lower energies. In the light of these considerations, the fact that protonation of \([\text{Os(NH}_3\text{)}_5\text{pz}]^{2+}\) causes a shift in the opposite direction is noteworthy.

Zwickel and Creutz (Ref. 27) have treated the \(\pi d - \pi^*\) absorptions shown by the \(\text{N}-\text{heterocyclic complexes} for any heterocyclic, the absorptions for the pentaaaminine, the \(cis\) and \(trans\) tetraaaminines constituting a total of 4 independent data (1, 2 and 1 band(s) respectively) are correlated by two parameters: \(\beta\), the exchange integral, \(t_{2g}[\text{H}]\pi^*\) and \(\delta\), the difference in energy between the unperturbed \(\pi d\) and \(\pi^*\) levels. For the osmium amines, 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 \(\beta\) for the pyrazinium compared to the pyrazine complex and the fact that in the former complex, the \(\pi d\) and \(\pi^*\) 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 \(\pi^*\) level lies below that of the \(\pi d\) 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: \([\text{Ru(II)} + \text{HN}}\rightleftharpoons\text{N=NH_2}]\) or \([\text{low spin Ru(IV)} + \text{HN}}\rightleftharpoons\text{N=NH_2}]\).

### TABLE 2. Parameters derived from \( \pi d - \pi^* \) absorption spectra for pyrazine and pyrazinium ion as ligands (units, cm \(^{-1}\) \(\times 10^{-3}\))

<table>
<thead>
<tr>
<th>Species</th>
<th>(\beta)</th>
<th>(\delta)</th>
<th>(\Delta\delta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH(_3))(_4)RuN(_2)N(_2)N(_2) (\leftarrow) N(^{2+})</td>
<td>6.6</td>
<td>16.7</td>
<td>12.2</td>
</tr>
<tr>
<td>(NH(_3))(_4)RuN(_2)NH(_3) (\leftarrow) N(^{3+}) (a)</td>
<td>9.2</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>(NH(_3))(_4)OsN(_2)NH(_2)N(_2) (\leftarrow) N(^{7})</td>
<td>10.5</td>
<td>4.9</td>
<td>10.6</td>
</tr>
<tr>
<td>(NH(_3))(_4)OsN(_2)N(_2)N(_2) (\leftarrow) N(^{1+})</td>
<td>11.3</td>
<td>-5.7</td>
<td></td>
</tr>
</tbody>
</table>

(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 \(\Delta\delta\) in Table 2 represent the differences in the energies of \(\pi^*\) levels for pyrazine and pyrazinium ion, and if the theory were strictly applicable, \(\Delta\delta\) 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 \(\pi d\) 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, \(\approx 4\) 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\(_2\)O)\(_5\)\(^{2+}\) 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

<table>
<thead>
<tr>
<th>Center</th>
<th>(\text{N} \leftarrow \text{N} \leftarrow \text{N} \leftarrow \text{N} \leftarrow \text{NH}^+)</th>
<th>Ligand</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(^+)</td>
<td>9.2</td>
<td>5.2</td>
</tr>
<tr>
<td>Ni(H(_2)O)(_5)(^{2+})</td>
<td>2.8(^a)</td>
<td>1.8(^b)</td>
</tr>
<tr>
<td>Ru(NH(_3))(_5)(^{2+})</td>
<td>4.5(^d)</td>
<td>7.4(^d)</td>
</tr>
</tbody>
</table>

(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 \(\sigma\) 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 a 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 preparation of complexes of Ru(NH₃)₅⁺ with π acid ligands from [Ru(NH₃)₅H₂O]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 owe 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(NH₃)₅H₂O²⁺ and Ru(NH₃)₅H₂O³⁺ in aqueous solution

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Ru(II)</th>
<th>Ru(III)</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>3 x 10⁶</td>
<td>&lt;4 x 10⁻¹³</td>
<td>&gt;10¹⁷</td>
</tr>
<tr>
<td>H₂S</td>
<td>1.5 x 10³</td>
<td>&lt;2 x 10⁻⁴</td>
<td>&lt;8 x 10⁶</td>
</tr>
<tr>
<td>H₂O</td>
<td>2 x 10⁷</td>
<td>6 x 10³</td>
<td>3 x 10³</td>
</tr>
<tr>
<td>NH₃</td>
<td>3 x 10⁶</td>
<td>2 x 10⁶</td>
<td>1.5</td>
</tr>
<tr>
<td>OH⁻</td>
<td>4 x 10⁶</td>
<td>2 x 10⁵</td>
<td>2 x 10⁻¹</td>
</tr>
<tr>
<td></td>
<td>6 x 10²</td>
<td>6 x 10¹¹</td>
<td>10⁻⁹</td>
</tr>
</tbody>
</table>

(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 NH₃, 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 10²⁶ 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 H₂O in the aquopentaammine complex by a σ acid ligand does lead to some estimate of the affinities for Os(III). When ison is the π acid ligand, the potential of the 3+/2+ couple for Ru(NH₃)₅ increases by 0.38 V., but for Os(NH₃)₅ the increase is 0.49 V. The affinity of ison for Os(III) can be assumed to be at least as great as for Ru(III) (see later section) and thus the affinity of ison for Os(II) is about 10² times that for Ru(II), or greater than 10¹⁰.

### 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 H₂O as a typical saturated ligand, and for its congeners H₂S, interesting in its own right, will be shown.

### Table 5. Effect of Ru(NH₃)₅²⁺ and Ru(NH₃)₅³⁺ on acidity (a) of coordinated H₂O and H₂S

<table>
<thead>
<tr>
<th>Ligating Center</th>
<th>H₂O</th>
<th>H₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>15.7</td>
<td>7</td>
</tr>
<tr>
<td>Ru(NH₃)₅²⁺</td>
<td>13.1</td>
<td>4.0</td>
</tr>
<tr>
<td>Ru(NH₃)₅³⁺</td>
<td>4.1</td>
<td>≈-10</td>
</tr>
</tbody>
</table>

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

Quite remarkable is the fact that [Ru(NH₃)₅H₂O]²⁺ is so weakly acidic. The comparison with Hg²⁺ in this respect is striking [pKₐ for Hg²⁺ = 2.5 (Ref. 34)]; less so, but important in its implications about electron distribution in the ions is the fact that pKₐ for [Ru(NH₃)₅H₂O]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$_2$S in coordinating to Ru(NH$_3$)$_5^{2+}$ is slightly greater than it is for H$_2$O, 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$_2$O. Thus replacing one H in HOH by C$_2$H$_5$, the $pK_a$ value increases by slightly over 2 units (Ref. 35) but the same change in HSR causes an increase of 5 units (Ref. 36). The modest change in the $pK_a$ for H$_2$S on being coordinated to Ru(II) probably reflects some $\pi$ acid character for H$_2$S 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$_2$S, HS$^-$, S$^{2-}$). Finally attention is drawn to the enormous increase in the acidity of coordinated H$_2$S 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 $\pi$ acid, pyrazinium ion (pzH).

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Ground state $pK_a$</th>
<th>Excited state $pK_a$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>free</td>
<td>0.6</td>
<td></td>
<td>37</td>
</tr>
<tr>
<td>on Ru(NH$_3$)$_5^{3+}$</td>
<td>$\sim$ 1.0</td>
<td>13(a)</td>
<td>7</td>
</tr>
<tr>
<td>on Ru(NH$_3$)$_5^{2+}$</td>
<td>2.5</td>
<td>7.3</td>
<td>7</td>
</tr>
<tr>
<td>on Os(NH$_3$)$_5^{2+}$</td>
<td>7.6</td>
<td>3.9</td>
<td>26 a,b</td>
</tr>
<tr>
<td>on Os(NH$_3$)$_5^{2+}$</td>
<td>7.4</td>
<td>4.6</td>
<td>25</td>
</tr>
</tbody>
</table>

(a) On oxidizing [Ru$^\text{II}$(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 $\pi^*$ $\rightarrow$ $\pi$ 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 $\pi^*$ level for pH$^+$ below that of a $\pi$d orbital on Os(II). Thus the ground state orbital in [Os(NH$_3$)$_5$pzH]$^+$ 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>
<thead>
<tr>
<th>Ligating center</th>
<th>$pK_a$</th>
<th>$pK_2$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>1.76</td>
<td>7.2</td>
<td>(38)</td>
</tr>
<tr>
<td>Ru(NH$_3$)$_5^{2+}$</td>
<td>2.45</td>
<td>5.1</td>
<td>(16)</td>
</tr>
<tr>
<td>Os(NH$_3$)$_5^{2+}$</td>
<td>7.0*</td>
<td>--</td>
<td>(25)</td>
</tr>
<tr>
<td>Ru(NH$_3$)$_5^{3+}$</td>
<td>$&lt; 0$</td>
<td>$&lt; 0$</td>
<td>(39)</td>
</tr>
</tbody>
</table>

* Note added subsequently: at pH = 7.0, coordinated SO$_2$ is converted directly to SO$_3^{2-}$ and thus $\frac{1}{2}(pK_1 + pK_2) = 7.0$. 

Ruthenium (II) and osmium (II) amines
Back bonding is expected to be greatest for SO\textsubscript{2} and to diminish as the negative charge on the ligand increases. In accord with this, while for pK\textsubscript{1} back bonding to Ru(NH\textsubscript{3})\textsubscript{5}SO\textsubscript{2} more than compensates for the inductive effect of the 2+ charge, the reverse is true for pK\textsubscript{2}. As when pH\textsuperscript{+} is the ligand, the effect of Os(II) in stabilizing the strong \pi acid SO\textsubscript{2} is very great, in this case requiring the pH to be raised to 7.0 before coordinated SO\textsubscript{2} is converted to coordinated HS0\textsubscript{3} (or SO\textsubscript{2}\textsuperscript{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\textsubscript{2}\textsuperscript{2-} form persists even at very high acidities.

The stabilization of SO\textsubscript{2} on Ru(II) extends also to the rate of hydration. This rate for the free ligand is 3.4 \times 10\textsuperscript{6} sec\textsuperscript{-1}(Ref. 40). The conversion of trans-[Ru(NH\textsubscript{3})\textsubscript{5}SO\textsubscript{2}(H\textsubscript{2}O)]\textsuperscript{2+} to the HS0\textsubscript{3} complex at a pH just high enough to bring about the reaction has been measured (Ref. 39) as 0.32 \times 10\textsuperscript{6}sec\textsuperscript{-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\textsubscript{3})\textsubscript{2}SO\textsubscript{4}]\textsuperscript{2+} is even lower, but in this case the path that operates when the conversion to the OH\textsuperscript{-} containing form takes place is in all likelihood not the simple water dependent path, but involves base as reactant.

**The Effect of \pi Acids on Auxiliary Ligands**

The electron withdrawing power of a particular \pi–acid ligand can be assessed by including a molecule of H\textsubscript{2}O in the coordination sphere, and observing the effect on its acidity of replacing an ammonia molecule, cis or trans, by a \pi–acid ligand. Most of the comparisons of this kind which can be made with present data center on nitrosyl ion as the \pi acid. An instructive example involves the pK\textsubscript{a} for [Ru(NH\textsubscript{3})\textsubscript{4}H\textsubscript{2}O]\textsuperscript{2+} and that for trans-[Tc(NH\textsubscript{3})\textsubscript{4}(NO)H\textsubscript{2}O]\textsuperscript{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\textsubscript{a} for the species are 13 (Ref. 19) and 7.3 (Ref. 41) respectively, showing that the inductive effect of NO\textsuperscript{2-} exceeds that of increasing ion charge by one unit. In this case NO\textsuperscript{2-} is acting on a metal in a low oxidation state and electron release by Tc(I) to NO\textsuperscript{-} is expected to be particularly large. But the same effect can be observed also in a higher range of oxidation states. Thus the pK\textsubscript{a} values for [Ru(NH\textsubscript{3})\textsubscript{5}H\textsubscript{2}O]\textsuperscript{3+} and trans-[Ru(NH\textsubscript{3})\textsubscript{4}(NO)H\textsubscript{2}O]\textsuperscript{3+} are 4.1 (Ref. 42) and 1.4 (Ref. 43) respectively. (The pK\textsubscript{a} for the cis form of the nitrosyl is 4.1 (Ref. 43)). It is of interest to note that pK\textsubscript{a} for trans-[Tc(NH\textsubscript{3})\textsubscript{4}(NO)H\textsubscript{2}O]\textsuperscript{3+} is ca. 2 (Ref. 41), that is, very close to that measured for the corresponding Ru(II) complex. There is thus very little difference between the nd\textsuperscript{5} and nd\textsuperscript{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\textsuperscript{5} nitrosyl complex is expected to reside in an orbital perpendicular to the metal-NO\superscript{+} axis.

Effects of the kind documented for nitrosyl are observed also with other \pi acids. Thus, pK\textsubscript{a} for cis-[Ru(NH\textsubscript{3})\textsubscript{4}(CO)H\textsubscript{2}O]\textsuperscript{2+} is ~8 and for the trans complex is 7.1 (Ref. 43). The effects on affinities have been illustrated for OH\textsuperscript{-} replacing H\textsubscript{2}O but are of course not limited to this. For a number of reactions 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\textsuperscript{-} for [Ru(NH\textsubscript{3})\textsubscript{3}H\textsubscript{2}O]\textsuperscript{2+} has been determined (Ref. 44), there seem to be no data for complexes in which NH\textsubscript{3} is replaced by \pi 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\textsuperscript{-} is greatly enhanced by such replacement. Since a \pi acid is electron withdrawing, it favors the attachment to the metal center of OH\textsuperscript{-} over that of H\textsubscript{2}O — hence the effect on acidities — but by the same token, it is expected to decrease the affinity of another \pi 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\textsubscript{3} in [Ru(NH\textsubscript{3})\textsubscript{3}H\textsubscript{2}O]\textsuperscript{2+} by pyridine, no trace of a dinitrogen complex is observed when the resulting species is brought into contact with N\textsubscript{2} at 1 atm.

There are no quantitative experiments which unambiguously bear on the issue, but a number of qualitative results have been obtained with SO\textsubscript{2}\textsuperscript{2-} or P(OEt)\textsubscript{3} trans to the \pi acid ligand. Typical of them is the following: While the equilibrium quotient governing the reaction of isonitrile with trans-[Ru(NH\textsubscript{3})\textsubscript{4}(SO\textsubscript{3})H\textsubscript{2}O] is 3.8 \times 10\textsuperscript{3} (Ref. 16), for the reaction with aquomethylamine complex it is in excess of 10\textsuperscript{8} (Ref. 33). The point that neither SO\textsubscript{2}\textsuperscript{2-} nor P(OEt)\textsubscript{3} are representative of simple \pi acid ligands needs to be made, and will be further elaborated presently, and quantitative experiments with ligands such as pyridine are needed.

Lacking a detailed understanding of the activation process for substitution, it would be impossible to predict from the equilibrium effects how \pi 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 reagents 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 pentaaminenitrosylruthenium(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 NH₃ trans to NO⁺ and Bottomley suggests that the rather facile replacement of NH₃ trans to NO⁺ by OH⁻ is a result of conversion of NO⁺ to NO₂⁻ and labilization by NO₂⁻. 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)amine 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 H₂O in cis or trans Ru(NH₃)(L)H₂O by isonicotinamide as a function of Eₚ for the Ru³⁺/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 Eₚ depend on the back bonding capacity of the ligands.

Much more difficult to understand are groups which are strongly trans labilizing. These include SO₃²⁻ (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 SO₃²⁻ it has been shown that when it replaces NH₃, a water molecule cis to it is in fact delabilized (Ref. 16). The trans labilizing effect of SO₃²⁻ 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 H₂O₂ as an oxidant. This converts SO₃²⁻ to SO₄²⁻, 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)₃P(OEt)₃]²⁺ by direct substitution, the product obtained is always trans-[Ru(NH₃)₄P(OEt)₃]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(NH₃)₄P(OEt)₃(H₂O)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 = 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 nd 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). This case the change is even more facile than it is for glycine. Thus, back bonding 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 significant 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

\[ \text{Ru(NH}_3)_5^3+ + \text{NO} + \text{OH}^- = \text{(NH}_3)_5\text{RuN}_2^2+ + 2\text{H}_2\text{O} \]

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 acid 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):

\[ \text{Os(NH}_3)_5\text{Cl}_2^+ + \text{HNO}_2 + \text{H}^+ = \text{(NH}_3)_5\text{OsN}_2^2+ + \text{NO} + \text{H}_2\text{O} \]

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=N 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 observations. The values of E_p for the 3+/2+ couples for Os(NH_3)_5Cl_2, Os(NH_3)_5(ONO)_2, and Os(NH_3)_5(N_2)_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 aquton decreases markedly in the series when NH_3 is
Ruthenium (II) and osmium (II) amines replaced by $I^- : k = 2 \times 10^{-2}\text{sec}^{-1}$ for $[\text{Os(NH}_3)_5\text{N}_2]^3^+ \text{(Ref. 59)}$ and $1.75 \times 10^{-3}\text{sec}^{-1}$ for $[\text{Os(NH}_3)_5\text{N}_2]^2^+ \text{(Ref. 55)}$.

In Table 8 are summarized results on the $\text{N=N}$ stretching frequencies for a series of dinitrogen species which afford some instructive comparisons:

<table>
<thead>
<tr>
<th>Species</th>
<th>$\nu_\text{N=N}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{N}_2$</td>
<td>2331</td>
</tr>
<tr>
<td>$[\text{Ru(NH}_3)_5\text{N}_2]^2^+ \text{Cl}_2$</td>
<td>2114</td>
</tr>
<tr>
<td>$[\text{Os(NH}_3)_5\text{N}_2]^2^+ \text{Cl}_2$</td>
<td>2037</td>
</tr>
<tr>
<td>$[\text{Os(NH}_3)_5\text{N}_2]^2^+ \text{Cl}_3$</td>
<td>2212</td>
</tr>
<tr>
<td>$[\text{Os(NH}_3)_4\text{(N}_2)^2\text{I}_2]^2^+ \text{Br}_2$</td>
<td>2200</td>
</tr>
<tr>
<td>$\text{trans}-[\text{Os(NH}_3)_3\text{(N}_2)^2\text{I}_2] \text{Br}$</td>
<td>2174</td>
</tr>
<tr>
<td>$\text{trans}-[\text{Os(NH}_3)_3\text{(N}_2)^2\text{Cl}_2] \text{Br}$</td>
<td>2105</td>
</tr>
</tbody>
</table>

A back-bonding interaction between $\text{N}_2$ 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 $p\text{K}_a$ for a coordinated NH$_3$ on $[\text{Os(NH}_3)_5\text{N}_2]^3^+$ is $\approx 6-7 \text{(Ref. 58)}$, 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 $[\text{Os(NH}_3)_5\text{N}_2]^2^+ \text{to [Os(NH}_3)_6\text{(N}_2)^2]^{2+}$. 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.

Acknowledgment—In concluding, I want to thank the numerous collaborators who have contributed to that part of the research I have described which I have had a share in, and the National Institutes of Health, the National Science Foundation and the Petroleum Research Fund for generous support.

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