Electrophilic Behavior of Coordinated Nitric Oxide

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Transition-metal complexes containing nitric oxide[1] (metal nitrosyl complexes) have been known for over a century.[2] However, in comparison to the related metal carbonyl complexes, they have been very little investigated. One of the main reasons for this inattention was almost certainly their apparent lack of reactivity. On the one hand, the M–NO bond is very strong, and the ligand replacement reactions which are so important in the chemistry of metal carbonyl complexes (consider catalytic processes such as the OXO process) were not found. On the other hand, reactions of the coordinated NO ligand were not found either. Something approaching a myth of the unreactivity of metal nitrosyl complexes arose, and such myths are a powerful deterrent to prospective investigators.

The one exception which proved the rule of the unreactivity of metal nitrosyl complexes was $[Fe(CN)_5NO]^{2-}$.[3,4] Since the middle of the 19th century it had been known that in this complex the NO ligand could be attacked by nucleophiles such as OH^- (eq 1).

$$[Fe(CN)_5NO]^{2-} + 2OH^- \rightleftarrows [Fe(CN)_5NO_2]^{4-} + H_2O \tag{1}$$

This reaction has an equilibrium constant of 1.5×10^6 $L^2\ mol^{-2}$,[3] which may be compared to the value of 2.3×10^{31} for the "parent" reaction, eq 2. Clearly, co-

$$NO^+ + 2OH^- \rightleftarrows NO_2^- + H_2O \tag{2}$$

ordinated NO^+ in $[Fe(CN)_5NO]^{2-}$ is a much weaker electrophile than "free" NO^+. Here we are making the assumption that we can compare NO^+ (which is known in salts such as $NOPF_6$) and the coordinated NO in $[Fe(CN)_5NO]^{2-}$, i.e., that in the complex NO acts as a three-electron donor and we have, formally, coordinated NO^+. Such a simple formalism is not intended to be a general description of the bonding in metal nitrosyl complexes, but it is an extremely useful concept for describing the complexes to be discussed in this Account (see below).

Our own activity in this area arose from a desire to prepare complexes containing dinitrogen oxide (nitrous oxide, N_2O) as a ligand. The dinitrogen oxide molecule is a very poor ligand; either it is reduced by the metal or it forms complexes which lose N_2O very readily in solution.[5-7] One answer, at least to the second problem, appeared to be to use the reaction of a coordinated ligand to produce coordinated N_2O in situ; if the product could be precipitated rapidly from solution the problems of N_2O dissociation might be avoided. In considering suitable syntheses we noted that NO^+ reacted with NH_2OH to produce N_2O and with N_2H_4 to produce N_3^- (N_3^- also reacted with NO^+ to give N_2O and N_2),[8,9] and we felt that similar reactions might take place with coordinated NO^+. Accordingly, we performed the reaction between NH_2OH and $[Ru(NH_3)_5NO]^{3+}$ (eq 3) and did indeed obtain an essentially

$$[Ru(NH_3)_5NO]^{3+} + NH_2OH \rightarrow [Ru(NH_3)_5N_2O]^{2+} + H_3O^+ \tag{3}$$

quantitative yield of $[Ru(NH_3)_5N_2O]^{2+}$.[10]

With N_2H_4, at room temperature, only the well-known $[Ru(NH_3)_5N_2]^{2+}$ was produced. However, at −23 °C, a mixture of $[Ru(NH_3)_5N_2O]^{2+}$ and $[Ru(NH_3)_5N_3]^+$ was obtained. Redox reactions of the azido and dinitrogen oxide complexes probably account for the formation of the dinitrogen complex, which is very stable with respect to redox reactions and substitution. The mechanisms of the reaction of both NH_2OH and N_2H_4 with $[Ru(NH_3)_5NO]^{3+}$ involve initial nucleophilic attack at coordinated NO^+;[11] it appears that the postulated intermediate, $[Ru(NH_3)_5N(O)NNH_2]^+$, in the N_2H_4 reaction can be observed spectroscopically when the reaction is carried out with the $[Ru(NH_3)_5NO]^{3+}$ adsorbed on Y-type zeolite.[12] However, there is still controversy over the nature of $[Ru(NH_3)_5N_2O]^{2+}$ (see ref 13 and 14).

Our initial attempts at nucleophilic attack at coordinated nitrosyl had been successful, and we felt we should explore this type of chemistry with $[Ru(NH_3)_5NO]^{3+}$ further. The most obvious reaction to investigate was that with OH^-, with the expectation (based on the chemistry of $[Fe(CN)_5NO]^{2-}$) that $[Ru(NH_3)_5NO_2]^+$ would be formed. This in fact occurred, but it was complicated by the surprisingly facile formation of the amido complex $[RuNH_2(NH_3)_4NO]^{2+}$. In aqueous solution equilibria 4 and 5 were simultaneously set up. Each member of the equilibria could be isolated under the appropriate conditions, but we were unable to obtain the equilibrium constants for technical rea-

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[1] According to the latest IUPAC rules nitric oxide, NO, should be described as nitrogen monooxide.

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$$[Ru(NH_3)_5NO]^{3+} + OH^- \rightleftarrows [RuNH_2(NH_3)_4NO]^{2+} + H_2O \quad (4)$$

$$[Ru(NH_3)_5NO]^{3+} + 2OH^- \rightleftarrows [Ru(NH_3)_5NO_2]^+ + H_2O \quad (5)$$

sons.[15] This was disappointing; the equilibrium constant for the reaction with OH^- was the obvious way to compare the electrophilicity of coordinated nitric oxide in various complexes. The equilibria between $[Ru(NH_3)_5NO]^{3+}$, $[Ru(NH_3)_5NO_2]^+$, and $[RuNH_2(NH_3)_4NO]^{2+}$ also have consequences for the substitution reactions of $[Ru(NH_3)_5NO]^{3+}$. In basic solution $[Ru(NH_3)_5NO]^{3+}$ reacts to produce a variety of *trans*-$[RuX(NH_3)_4NO]^{2+}$ complexes (X = unidentate negative ligand). Since $[Ru(NH_3)_5NO]^{3+}$ is inert to substitution in acid solution (as expected, since NO^+ shortens and presumably strengthens the metal ligand bond trans to it[16–18]), it is probable that the reactions in basic solution occur via the intermediacy of $[Ru(NH_3)_5NO_2]^+$ or *cis*-$[RuNH_2(NH_3)_4NO]^{2+}$ (NO_2^- lengthens the trans Ru–NH_3 bond,[19] and NH_2^- may be expected to increase the rate of substitution of an NH_3 ligand trans to it[20]). The remarkable acidity of the NH_3 ligand of $[Ru(NH_3)_5NO]^{3+}$ (which is paralleled by its osmium analogue, for which the equilibrium constant for the reaction (eq 6) is 1.2×10^{-11}[21]) must be due to

$$[Os(NH_3)_5NO]^{3+} + OH^- \rightleftarrows [OsNH_2(NH_3)_4NO]^{2+} + H_2O \quad (6)$$

the strong electron-withdrawing properties of NO^+.

A surprise occurred during our attempts to obtain the equilibrium constants of the reactions of $[Ru(NH_3)_5NO]^{3+}$ with OH^-. Alkaline solutions of $[Ru(NH_3)_5NO]^{3+}$ were unstable over a time period; investigation showed that $[Ru(NH_3)_5N_2]^{2+}$ was produced.[15] Having eliminated air as the source of N_2, we first thought that NH_3, released from $[Ru(NH_3)_5NO]^{3+}$, $[RuNH_2(NH_3)_4NO]^{2+}$, or $[Ru(NH_3)_5NO_2]^+$, on substitution by H_2O or OH^-, could nucleophilically attack residual $[Ru(NH_3)_5NO]^{3+}$. By analogy with the reactions of N_2H_4 or NH_2OH, $[Ru(NH_3)_5N_2]^{2+}$ would be produced. That this was not true was first indicated by the observation that adding NH_3 did not increase the yield of $[Ru(NH_3)_5N_2]^{2+}$, whereas increasing the OH^- concentration did. Identification of all the constituents of the reaction mixture, together with isotopic labeling experiments, proved that $[Ru(NH_3)_5N_2]^{2+}$ was produced by a remarkable reaction in which one coordinated ligand (NH_2^-) intermolecularly attacked another coordinated ligand (NO).[22,23] The proposed intermediate, $[ON(NH_3)_4RuNH_2(O)NRu(NH_3)_5]^{5+}$, has not been isolated. The formation of the *cis*-$[RuOH(NH_3)_4NO]^{2+}$ implies the attacking $[RuNH_2(NH_3)_4NO]^{2+}$ is the cis isomer. This probably occurs because the cis isomer is a stronger base than the trans isomer (which may also be present), as judged from NMR experiments on the rate of exchange of the NH_3 protons of $[Ru(NH_3)_5NO]^{3+}$.[24]

$$\begin{aligned}
&[Ru(NH_3)_5NO]^{3+} + OH^- \rightleftarrows [RuNH_2(NH_3)_4NO]^{2+} + H_2O \\
&[Ru(NH_3)_5NO]^{3+} + [RuNH_2(NH_3)_4NO]^{2+} \rightarrow \\
&\quad ([ON(NH_3)_4RuNH_2(O)NRu(NH_3)_5]^{5+}) \rightarrow \\
&\quad cis\text{-}[RuOH(NH_3)_4NO]^{2+} + [Ru(NH_3)_5N_2]^{2+} + H^+ \quad (7)
\end{aligned}$$

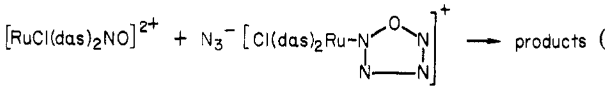
During our work on the electrophilic behavior of coordinated NO in $[Ru(NH_3)_5NO]^{3+}$ we had been thinking of how the observed reactions might be extended to other complexes and other nucleophiles. The unreactivity of metal nitrosyl complexes was clearly a myth, and there had to be other examples of the electrophilic behavior of coordinated NO. Our understanding of the situation was greatly helped by concurrent work on reactions of $[RuCl(bpy)_2NO]^{2+}$ (bpy = 2,2′-bipyridine) in the laboratories of T. J. Meyer and on $[RuCl(das)_2NO]^{2+}$ (das = *o*-phenylenebis(dimethylarsine)) by R. D. Feltham and co-workers. Both complexes underwent a variety of electrophilic reactions. With OH^-, the corresponding nitro complexes were formed[25–28] (eq 8). The equilibrium constant for

$$[RuCl(A\text{-}A)_2NO]^{2+} + 2OH^- \rightleftarrows [RuCl(A\text{-}A)_2NO_2] + H_2O \quad (8)$$

reaction 8, in the case when A-A = bpy, was 1.6×10^9 $L^2\ mol^{-2}$.[27] Reaction with N_3^- proceeded according to eq 9, where S indicates a solvent molecule. Use of a

$$[RuCl(A\text{-}A)_2NO]^{2+} + N_3^- \rightarrow [RuCl(A\text{-}A)_2S]^+ + N_2 + N_2O \quad (9)$$

large excess of N_3^- gave, by substitution, $[RuCl(das)_2N_3]$,[29] whereas with a lesser amount of N_3^- $[RuCl(bpy)_2S]^+$ (S = H_2O, MeCN, MeOH, or Me_2CO) was isolated.[30,31] The formation of the labile $[RuCl(bpy)_2S]^+$ has been synthetically exploited for preparation of $[RuCl(bpy)_2X]^{n+}$ complexes, where X is a monodentate ligand.[32,33] In the case of the reaction between $[RuCl(das)_2NO]^{2+}$ and N_3^-, isotopic labeling gave evidence for attack of N_3^- at coordinated NO with formation of a cyclic N_4O intermediate[29] (eq 10).



(10)

$[RuCl(das)_2NO]^{2+}$ and N_2H_4 gave $[RuCl(das)_2N_3]$; again ^{15}N labeling indicated the first step was nucleophilic attack of N_2H_4 at coordinated NO; with $PhNHNH_2$, the intermediate addition product could be isolated[25] (eq 11 and 12). With hydroxylamine

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$$[RuCl(das)_2NO]^{2+} + N_2H_4 \rightarrow ([RuCl(das)_2N(O)NNH_2] + 2H^+) \rightarrow [RuCl(das)_2N_3] + H_2O \quad (11)$$

$$[RuCl(das)_2NO]^{2+} + NH_2NHPh \rightarrow [RuCl(das)_2N(O)NNHPh] + 2H^+ \quad (12)$$

$[RuCl(das)_2NO]^{2+}$ gave mainly $[RuCl_2(das)_2]$ (eq 13);

$$[RuCl(das)_2NO]^{2+} + NH_3OHCl + OH^- \rightarrow [RuCl_2(das)_2] + N_2O + H^+ + 2H_2O \quad (13)$$

some infrared evidence for formation of $[RuCl(das)_2N_2O]^+$ was obtained, but the evidence was not conclusive.[29]

There are two very interesting and potentially useful reactions between aromatic amines and $[RuCl(bpy)_2NO]^{2+}$. Primary aromatic amines are diazotized[34] (eq 14). This reaction provides a very convenient route

$$[RuCl(bpy)_2NO]^{2+} + ArNH_2 \rightarrow [RuCl(bpy)_2N_2Ar]^{2+} + H_2O$$
$$(Ar = p\text{-}CH_3OC_6H_4\text{-} \text{ or } p\text{-}CH_3C_6H_4\text{-}) \quad (14)$$

to diazonium complexes, which are of interest because of their relationship to nitric oxide in their mode of bonding to transition metals. On the other hand, the para carbon of secondary or tertiary aromatic amines attacks the NO of $[RuCl(bpy)_2NO]^{2+}$, giving $[RuCl(bpy)_2(N(O)C_6H_4NRCH_3)]^+$ (R = CH_3, H), which formally contains an N-bonded nitrosoarene ligand[35] (eq 15). This is the first well-characterized example of C–N

$$[RuCl(bpy)_2NO]^{2+} + C_6H_5NRCH_3 \rightarrow [RuCl(bpy)_2N(O)C_6H_4NRCH_3]^+ + H^+ \quad (15)$$

bond formation (good evidence for such bond formation in solution was found for the reactions between $[Fe(CN)_5NO]^{2-}$ and ketones[3]), and the reaction has potential for the in situ synthesis of organic ligands.

In addition to the extensive investigations of $[Fe(CN)_5NO]^{2-}$, $[Ru(NH_3)_5NO]^{3+}$, $[RuCl(bipy)_2NO]^{2+}$, and $[RuCl(das)_2NO]^{2+}$, more restricted investigations showed that a few other nitrosyls underwent similar reactions. The ruthenium and osmium analogues of $[Fe(CN)_5NO]^{2-}$ reacted in an analogues manner with OH^- [36,37] (eq 16). It is probable that these complexes

$$[M(CN)_5NO]^{2-} + 2OH^- \rightleftarrows [M(CN)_5NO_2]^{4-} + H_2O \quad (16)$$
$$M = Ru, Os$$

would have as extensive a chemistry as $[Fe(CN)_5NO]^{2-}$ if only their incredible insolubility in all solvents could be overcome; our own attempts at reactions between $[Ru(CN)_5NO]^{2-}$ and N_2H_4 and NH_2OH have foundered on this problem.[38] The nucleophiles ROH (R = C_2H_5 or CH_3) reacted with $[IrCl_3(PPh_3)_2NO]^+$ [39] (eq 17). The

$$[IrCl_3(PPh_3)_2NO]^+ + ROH \rightleftarrows [IrCl_3(PPh_3)_2(N(O)OR)] + H^+ \quad (17)$$

alkyl nitrite complex, $[IrCl_3(PPh_3)_2(N(O)OR)]$, is the alkyl analogue of the nitrous acid complex, $[Fe(CN)_5(N(O)OH)]^{3-}$, which has been shown by kinetic evidence to be the intermediate in the reaction of OH^- with $[Fe(CN)_5NO]^{2-}$,[3] and by implication to be the intermediate in all metal nitrosyl–hydroxide ion reactions of this type. Surprisingly, $[IrCl_3(PPh_3)_2NO]^+$ did not react with water to give a nitrous acid or nitrite complex.[39] Finally, scattered reports of unsuccessful attempts at attacking coordinated NO with nucleophiles were beginning to be found in the literature,[40] and our investigations had shown that complexes such as *trans*-$[RuOH(NH_3)_4NO]^{2+}$ and $[Os(NH_3)_5NO]^{3+}$ were also unreactive.[15,21]

The question at this stage was: given that the electrophilic behavior of coordinated nitrosyl was a fairly general reaction, could one find an indication of which metal nitrosyl complexes might be reactive? By investigating such reactive complexes one might then find just how general the reactivity was and where and how it would occur. Our aim was therefore to find and investigate nitrosyls which were electrophiles. To be an electrophile, coordinated NO must have as low an electron density as possible. Applying the well-known Dewar–Chatt–Duncanson model of the bonding between a metal and a π-acceptor ligand such as NO,[41] σ donation of electrons from NO to the metal will decrease the electron density on NO, whereas π-electron back-donation from the metal to NO will increase this electron density. As is also well-known, π-electron donation from the metal involves NO orbitals which are antibonding with respect to NO. One manifestation of this is that ν_{NO}, the infrared active NO stretching frequency, decreases markedly from the value in uncoordinated NO^+ (again, we are assuming NO acts as a three-electron donor (see below)). Hence one can conclude that nitrosyl complexes with very high ν_{NO} frequencies will have the lowest electron density and may behave as electrophiles. This argument is similar to that used by Angelici in his work on carbonyls.[42,43] Of the nitrosyls that are discussed above, those which behave as electrophiles have ν_{NO} in the range 1886 ($[RuCl(das)_2NO]^{2+}$) to 1945 cm^{-1} ($[IrCl_3(PPh_3)_2NO]^+$). Other obvious complexes to investigate were therefore $[IrX_5NO]^-$, where X = Cl (ν_{NO} 2006 cm^{-1}) and Br (ν_{NO} 1953 cm^{-1}), these having the highest ν_{NO} frequencies known to date.

We found that both these complexes reacted essentially instantaneously with nucleophiles according to eq 18–21.[44,45] A more complicated reaction which

$$[IrX_5NO]^- + 2OH^- \rightleftarrows [IrCl_5NO_2]^{3-} + H_2O \quad (18)$$

$$[IrX_5NO]^- + NH_2OH + H_2O \rightarrow [IrX_5(H_2O)]^{2-} + N_2O + H_3O^+ \quad (19)$$

$$[IrX_5NO]^- + N_3^- + H_2O \rightarrow [IrX_5(H_2O)]^{2-} + N_2O + N_2 \quad (20)$$

$$[IrX_5NO]^- + 2NH_3 \rightarrow [IrX_5(NH_3)]^{2-} + N_2 + H_3O^+ \quad (21)$$

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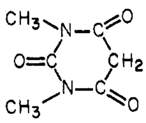
occurs with N_2H_4 may not necessarily proceed via nucleophilic attack at $[IrX_5NO]^-$. The equilibrium constants for reaction 18 are $K > 6 \times 10^{29}$ for $[IrCl_5NO]^-$ and $K = 6.8 \times 10^{27}$ L^2 mol^{-2} for $[IrBr_5NO]^-$. The K value for $[IrCl_5NO]^-$ implies that the electron density on the coordinated NO in this complex is similar to that in uncoordinated NO^+ (cf. $K = 2.3 \times 10^{31}$ L^2 mol^{-2} for reaction 2). This was a surprising result; it was difficult to accept that the synergic σ–π interaction between Ir and NO could be small enough to produce such an electron density on NO and still leave a complex with an Ir–NO bond strong enough to survive substitution. However $[IrCl_5NO]^-$ survives refluxing in concentrated hydrochloric acid. It is intriguing to speculate on the existence of nitrosyls with still higher stretching frequencies. In principle a nitrosyl in which σ donation from NO was greater than π back-donation of electrons from the metal could exist and would have an electron density less than that of NO^+. Such a species would be an extremely potent nitrosating agent. The fact that the $[IrX_5]^{2-}$ moiety is not a good π donor is shown by its inability to retain N_2 or N_2O as a ligand; we found no evidence for these complexes, though they must exist as intermediates.

We also investigated reactions of $[RuOH(NO_2)_4NO]^{2-}$ (ν_{NO} 1902 cm^{-1}). With OH^-, $[RuOH(NO_2)_5]^{4-}$ was formed and isolated (eq 22). However, in alkaline

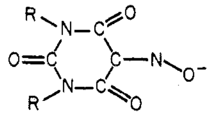
$$[\mathrm{RuOH(NO_2)_4NO}]^{2-} + 2\mathrm{OH}^- \rightleftarrows [\mathrm{RuOH(NO_2)_5}]^{4-} + \mathrm{H_2O} \tag{22}$$

solution $[RuOH(NO_2)_5]^{4-}$ was unstable with respect to slow replacement of one or more NO_2^- ligands, with reversion of one of the remaining NO_2^- ligands to NO. Among the decomposition products $[Ru(OH)_3(NO_2)_2NO]^{2-}$ was identified. There were rapid reactions between N_2H_4 or NH_2OH and $[RuOH(NO_2)_4NO]^{2-}$, but determination of the gas evolved indicated complicated reactions, probably involving the NO_2^- ligands.[44,46] Later, the reaction of $[RuOH(NO_2)_4NO]^{2-}$ with 3,5-dimethylbarbituric acid (DMBH, I) was used to prepare



I

the dimethylviolurato ligand II[47] (eq 23).



II

R = CH_3, abbreviated DMV:[47]

$$[\mathrm{RuOH(NO_2)_4NO}]^{2-} + 3\mathrm{DMBH} \rightarrow [\mathrm{Ru(DMV)_3OH}]^- \tag{23}$$

Infrared spectroscopy shows that the DMV ligand is coordinated to the metal through the nitrogen atom of the (C═N—O) group, and hence it is very probable that the reaction takes place by in situ C═N bond formation resulting from nucleophilic attack at coordinated NO.

The closely related violurato (abbreviated V; R = H above) complex $[RuCl(V)_2NO]^{4-}$ (ν_{NO} 1885 cm^{-1}) gave $[RuCl(V)_2NO_2]^{6-}$ with OH^- (eq 24), the K value for this reaction being 5.0×10^{-2}.[48]

$$[\mathrm{RuCl(V)_2NO}]^{4-} + 2\mathrm{OH}^- \rightleftarrows [\mathrm{RuCl(V)_2NO_2}]^{6-} + \mathrm{H_2O} \tag{24}$$

Both *cis*-$[RuCl(NH_3)_4NO]^{2+}$ and *cis*-$[RuCl(en)_2NO]^{2+}$ (en = ethylenediamine) have ν_{NO} frequencies (1920 and 1904 cm^{-1}, respectively) which indicate a low electron density on the nitrosyl ligand. However, both complexes undergo very rapid substitution of OH^- for Cl^- (perhaps promoted by formation of an amido ligand trans to Cl^-), and we have not been able to demonstrate electrophilic behavior of the NO in these complexes. The analogous hydroxo complexes have much lower ν_{NO} and are unreactive.[15,46]

We then synthesized the previously unknown $[OsX(das)_2NO]^{2+}$ (X = Cl, Br, I) complexes to investigate whether they would react in a manner analogous to $[RuCl(das)_2NO]^{2+}$. We were prompted to attempt this not only to extend our knowledge of nitrosyl reactivity but also to add some of the missing members to the very interesting series of complexes $[MX(das)_2AB]^{n+}$, where M = Fe, Ru, or Os; X = Cl, Br, I, OH, or other unidentate ligand; and AB = NO^+, CO, or N_2. One can also envisage other AB ligands such as CN^-, NS^+, or CS. Such a series would be invaluable for studying the relative reactivities, nature of the bonding, etc., of the isoelectronic ligands mentioned. The $[OsX(das)_2NO]^{2+}$ complexes could be synthesized, and the chloro complex did indeed react with the nucleophiles OH^-, N_2H_4, and NH_2NHPh, but not with N_3^- (eq 25–27). $[OsCl(das)_2N_2]^+$ was obtained by treatment of

$$[\mathrm{OsCl(das)_2NO}]^{2+} + 2\mathrm{OH}^- \rightleftarrows [\mathrm{OsCl(das)_2NO_2}] + \mathrm{H_2O} \tag{25}$$

$$[\mathrm{OsCl(das)_2NO}]^{2+} + \mathrm{N_2H_4} \rightleftarrows [\mathrm{OsCl(das)_2N_3}] + \mathrm{H_2O} + 2\mathrm{H}^+ \tag{26}$$

$$[\mathrm{OsCl(das)_2NO}]^{2+} + \mathrm{NH_2NHPh} \rightarrow [\mathrm{OsCl(das)_2(N(O)NNHPh)}] + 2\mathrm{H}^+ \tag{27}$$

$[OsCl(das)_2N_3]$ or $[OsCl(das)_2(N(O)NNHPh)]$ with acid or by free-radical reactions of these complexes.[49]

The iron complex, $[FeCl(das)_2NO]^{2+}$, has been synthesized by us and, independently, by Feltham and co-workers.[50] It also reacted with OH^- and N_2H_4, but the electrophilic reactions are complicated by concurrent redox reactions. Work on these complexes, and on the carbonyl and cyano analogues, is being continued (with Dr. Ivan Lin).

Recently very detailed analyses have been made of the mechanisms of the reaction of $[Fe(CN)_5NO]^{2-}$ with N_3^- [51] (eq 28) and between $[Fe(CN)_5NO]^{2-}$ and

$$[\mathrm{Fe(CN)_5NO}]^{2-} + \mathrm{N_3}^- + \mathrm{H_2O} \rightarrow [\mathrm{Fe(CN)_5H_2O}]^{3-} + \mathrm{N_2O} + \mathrm{N_2} \tag{28}$$

NH_2OH[51,52] (eq 29). Both reactions proceed via initial

$$[\mathrm{Fe(CN)_5NO}]^{2-} + \mathrm{NH_2OH} + \mathrm{OH}^- \rightarrow [\mathrm{Fe(CN)_5H_2O}]^{3-} + \mathrm{N_2O} + \mathrm{H_2O} \tag{29}$$

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Table I

Complex	ν_{NO}[a], cm^{-1}	Nucleophile
$[IrCl_5NO]^-$	2006[b]	OH^-, NH_3, N_3^-, NH_2OH
$[IrBr_5NO]^-$	1953	OH^-, NH_3, N_3^-, NH_2OH
$[IrCl_3(PPh_3)_2NO]^+$	1945[b]	MeOH, EtOH
$[Fe(CN)_5NO]^{2-}$	1938	OH^-, SH^-, NH_2OH, N_3^-, ketones
$[Ru(NH_3)_5NO]^{3+}$	1925	OH^-, N_2H_4, NH_2OH, $[RuNH_2(NH_3)_4NO]^{2+}$
$[RuCl(bpy)_2NO]^{2+}$	1927	OH^-, N_3^-, $ArNH_2$, $ArNR_2$
$[Ru(CN)_5NO]^{2-}$	1927[b]	OH^-
$[Os(CN)_5NO]^{2-}$	1905[b]	OH^-
$[RuOH(NO_2)_4NO]^{2-}$	1902	OH^-, $DMBH_2$[c]
$[RuCl(das)_2NO]^{2+}$	1886	OH^-, N_3^-, N_2H_4, $PhNHNH_2$
$[RuCl(V)_2NO]^{4-}$[c]	1885	OH^-
$[OsCl(das)_2NO]^{2+}$	1861	OH^-, N_2H_4, NH_2OH, $PhNHNH_2$

[a] In solution. [b] Nujol mull. [c] For abbreviation see text.

nucleophilic attack of NH_2OH or N_3^- at the coordinated NO. The thorough kinetic and isotopic labeling experiments indicate that the cyclic intermediate proposed for the reaction between $[RuCl(das)_2NO]^{2+}$ and N_3^- [29] (see reaction 10) does not occur for $[Fe(CN)_5NO]^{2-}$. Instead, addition to form $[Fe(CN)_5N(O)N_3]^{3-}$ and direct decomposition of this intermediate are the favored mechanism.

Nucleophilic attack of acetylacetonate (acac) at coordinated NO is almost certainly responsible for the production of $[Ru(acac)_2(hia)]$, where hia is the bidentate (N,O) ligand N(O)C(COMe)C(Me)O, from $RuCl_3NO$ and acetylacetone.[53] However, the identity of the actual RuNO complex attacked is uncertain. It has also been suggested that the reaction of $[(\eta^5\text{-}C_5H_5)NiNO]$ with organolithium reagents, giving ultimately $[(\eta^5\text{-}C_5H_5)_3Ni_3NR]$ (R = Ph, Bu-*t*), proceeds via initial attack of R^- at coordinated NO. However, concrete evidence is lacking.[54]

Summarizing the results to date, Table I lists all the complexes for which electrophilic behavior is definitely established, their ν_{NO} stretching frequencies, and the nucleophiles which react with them. One should note that $[Fe(CN)_5NO]^{2-}$, $[Ru(NH_3)_5NO]^{3+}$, and $[RuCl(bpy)_2NO]^{2+}$ undergo reversible one-electron reduction, and the reduction site is the nitrosyl ligand.[3,55-59] Reduction and nucleophilic attack at the nitrosyl ligand (and also photochemical reactions of the NO ligand, e.g., in $[Fe(CN)_5NO]^{2-}$ [60]) are obviously related, and one might even hope for some simple relationship between reduction potential and electrophilic reactivity.

At this stage the reader might well ask a number of questions. The first is, probably, how can we know which metal nitrosyl complexes will be reactive? Some generalizations to this point may be made. So far, all complexes with $\nu_{NO} \gtrsim 1890$ cm^{-1} react with at least one nucleophile, unless competing reactions which produce a complex with lower ν_{NO} intervene. However, all complexes do not react with all nucleophiles, and this is often difficult to understand; for instance, $[IrCl_3(PPh_3)_2NO]^+$ reacts with ROH but not with H_2O, and $[Ru(NH_3)_5NO]^{3+}$ does not react with N_3^-. For complexes with $1890 \lesssim \nu_{NO} \gtrsim 1860$ cm^{-1} the situation is even less clear; complexes with ν_{NO} as low as 1861 cm^{-1} ($[OsCl(das)_2NO]^{2+}$) are reactive, others with ν_{NO} as high as 1886 cm^{-1} ($[RuCl_5NO]^{2-}$) are not. For the electrophilic reactions of metal carbonyls a similar situation exists, but because it has been possible to produce small variations in the CO electron density by subtle changes in the other ligands of the complex, a more rational relationship between electron density, electrophilicity, and the infrared spectrum exists, at least within a closely related group of complexes reacting with one nucleophile.[42,43] To date such subtle changes have not proved possible for nitrosyls, as is shown by the huge spread of the values of the known equilibrium constants for the reaction of nitrosyls with OH^- (from 5×10^{-2} to $>10^{29}$).

The second question which might be asked is, how can we be sure we are dealing with a linear MNO moiety, i.e., formally with NO acting as a three-electron donor? Aside from the reactions themselves, all of which clearly involve electrophilic behavior of coordinated NO, two other lines of evidence are available: (1) by the most recent criteria, the ν_{NO} frequencies of the complexes shown in Table I indicate the presence of a linear MNO;[61] (2) crystal structures of the complexes $[IrCl_5NO]^-$,[18] $[IrBr_5NO]^-$,[18] $[Fe(CN)_5NO]^{2-}$,[62] $[Ru(NH_3)_5NO]^{3+}$,[17] and $[RuOH(NO_2)_4NO]^{2-}$ [63] are available and show MNO angles between 170.3 (2.6)° and 180°, i.e., effectively linear.

The third question might be, to what use can we put these reactions? The answer to this is in several parts: (1) there is the possibility of performing organic nitrosation under mildly acidic or even neutral conditions; normal production of NO^+ requires highly acidic media; (2) it may be possible to obtain a complex containing a "super electrophilic" NO^+, with an effective electron density less than NO^+ itself; (3) the in situ synthesis of N-bonded ligands (such as N_2O or more complicated multidentate ligands) by reaction at coordinated NO is likely to be further exploited, along with the preparation of labile solvent-coordinated complexes by reaction of NO and subsequent facile loss of the product ligand; (4) the attack of coordinated NO^- or uncoordinated CO at coordinated NO^+ is a conceptually simple way of considering the use of transition-metal nitrosyl complexes in the environmentally important conversion of NO and CO into N_2O (or N_2) and CO_2, a reaction of considerable current interest.[64] Progress in all of these areas, as well as in extending the metal nitrosyl complexes which behave as electrophiles and the nucleophiles used to attack them, can be expected.

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Syntheses, Crystalline Structure, and Ion-Exchange Properties of Insoluble Acid Salts of Tetravalent Metals and Their Salt Forms

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Amorphous insoluble acid salts of tetravalent metals have been known for a long time, but starting from 1956 there has been increased interest in these compounds.[1] This revived interest is chiefly due to their good ion-exchange properties and their high resistance toward temperature and radiation, so that practical applications in nuclear technology or in ion-exchange processes occurring at high temperature were hoped for. Systematic studies were therefore performed in several laboratories. Almost all the possible combinations of tetravalent metals and polybasic acids were examined and the ion-exchange properties of the obtained precipitates investigated. Some of these materials exhibited the expected high stability toward radiation and temperature.[2,3] They are, however, not very stable toward hydrolysis of their acid groups, and therefore their composition is often not well defined.[4-6]

Starting from 1964 several insoluble acid salts of tetravalent metals were obtained as crystalline compounds,[6-8] and these materials were found to be considerably more stable than the amorphous ones.[5,6,8] Apart from their possible applications, the study of the insoluble acid salts of tetravalent metals is of interest in itself for the information that can be derived in several fields, such as the synthesis of new materials, the formation of crystalline precipitates, the sorption of ions by precipitates, electrical transport and self- or interdiffusion of counterions in crystals, structural chemistry, and phase transitions obtained by changing the counterions or the hydration water in the crystals, and so on.

Many interesting properties of the insoluble acid salts of tetravalent metals depend on the crystalline structure of the material obtained rather than on the metal ion or polyvalent acid involved. It is therefore convenient to discuss these materials according to their crystalline structure.

Amorphous Acid Salts of Tetravalent Metals

These are usually obtained by direct mixing of a salt solution of a given tetravalent metal with an excess of a polybasic acid. The protons of the acid groups of the insoluble acid salt can be replaced by other cations; therefore several acid salts possess an appreciable ion-exchange capacity. Furthermore, it was found that they have high selectivity for certain cations[9-12] and that this selectivity can be increased by thermal treatment.[13-15]

The systematic researches, essentially performed in view of their practical applications as inorganic ion exchangers, led also to a better understanding of their formation and composition. For example, it was found that the precipitate obtained by mixing a Zr(IV) salt solution and phosphoric acid, commonly reported in the literature as zirconyl phosphate, is a polyhydrated zirconium (bis monohydrogen orthophosphate), $Zr(HPO_4)_2 \cdot nH_2O$.[4,7] The interested reader is referred to ref 1, 2, 5, 6, and 16 for particulars on the synthesis and properties of amorphous materials.

Crystalline Acid Salts of Tetravalent Metals

Acid Salts with Layered Structure. Some important insoluble acid salts of tetravalent metals with a layered structure are shown in Table I (see ref 6, 8, 17–26). Among them, the most investigated acid salt

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