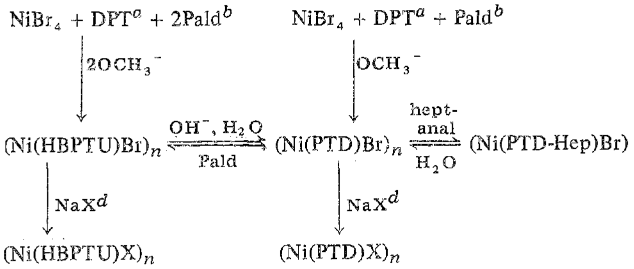
Scheme I[c]



[a] DPT = dipropylenetriamine. [b] Pald = pyrrole-2-carboxaldehyde. [c] All other symbols are defined in the text of this paper. [d] X = $B(C_6H_5)_4$, PF_6, SeCN, SCN.

from ligand reaction while allowing other functional groups to become more susceptible to a ligand reaction.

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Registry No. Ni(PTD)Br, 53293-21-3; $Ni(PTD)(C_6H_5)_4B$, 53293-23-5; $Ni(PTD)PF_6$, 53293-24-6; Ni(PTD)SCN, 53293-25-7; Ni(PTD)SeCN, 53293-26-8; Ni(PTD-Hep)Br, 53293-27-9; pyrrole-2-carboxaldehyde, 1003-29-8; dipropylenetriamine, 56-18-8; $((C_2H_5)_4N)_2NiBr_4$, 1185-60-0; heptanal, 111-71-7.

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Reactivity of Coordinated Nitrosyls. IV. One-Electron Reduction of Ruthenium Nitrosylpentaammine(3+) Ion in Aqueous Solution[1,2]

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The reduction of $Ru(NH_3)_5NO^{3+}$ by metal ion reducing agents, such as Cr^{2+}, proceeds *via* multiple-electron-transfer pathways[3] and implies the existence of $Ru(NH_3)_5NO^{2+}$ as an important reactive intermediate.[4] Because of further reaction of this one-electron-reduced species with the reductant to produce ultimately $Ru(NH_3)_6^{2+}$, characterization has not been possible.[3] This species is of particular interest because of the ability of the coordinated NO to show properties ranging from those of NO^- to those of NO^+.[5-8] We have used cyclic voltammetric and pulse radiolytic techniques to effect the one-electron reduction and to permit the characterization of the reduced species.

Experimental Section

$Ru(NH_3)_5NO^{3+}$ was prepared either by the direct addition of NO(aq) to $[Ru(NH_3)_6]Cl_3$ in acidic medium[9] or by the addition of $(NH_4)_2S_2O_8$ to $[Ru(NH_3)_5Cl]Cl_2$.[10] The nitrosyl complex was then recrystallized twice as the Cl^-, Br^-, ClO_4^-, or $TFMS^-$ (trifluoromethylsulfonate) salts.[3] Trifluoromethylsulfonic acid (3M Corp.) was distilled under vacuum at 10 Torr and 62°. The pure acid was diluted immediately to a concentration of 3 *M* and stored in a polyethylene bottle.

Cyclic voltammetry and dme polarography equipment at Stanford University and the California Institute of Technology was used for these experiments. Similar electrochemical devices have been described in the literature.[11] Cyclic voltammograms of the substitution-inert $Ru(NH_3)_5NO^{3+}$ were recorded on an X-Y recorder at a sweep rate of 0.1 V/sec. In order to obtain more symmetrical anodic and cathodic waves, higher sweep rates (0.4–40 V/sec) were employed with the use of a storage oscilloscope. A hanging mercury drop (area 0.032 cm^2) was used as the working electrode. In the experiments involving dme polarography, h = 90 cm, drop time = 5.3 sec, m = 1.35 mg/sec. Potentials were measured with respect to a calomel electrode saturated with NaCl; such an electrode has a potential 5 mV more negative than sce. The values given in this paper correspond to the formal potentials converted to the nhe scale.

Controlled-potential coulometry[12] was performed on $Ru(NH_3)_5NO^{3+}$ in 0.1 *M* NaCl at pH ~3 or in 0.1 *M* $NaClO_4$ at pH ~7.

Solutions of $Ru(NH_3)_5NO^{3+}$ (as the Cl^- or $TFMS^-$ salt) were subjected to 30-nsec pulses of 2.3-MeV electrons using the Febetron 705 pulse radiolysis system at the U. S. Army Natick Laboratories. Transient spectra and the decay behavior of intermediates were examined by kinetic spectrophotometry using a 2-cm optical path length as has been described in the past.[13] All rates were measured at 23°.

Results and Discussion

Cyclic voltammograms of deoxygenated solutions of $Ru(NH_3)_5NO^{3+}$ in 0.1 *M* NaCl (pH 3–7) or NaTFMS yielded a reversible, one-electron wave (Figure 1). At fast scan rates, the anodic and cathodic peak heights at the maxima were similar to those observed for the same number of moles of $Ru(NH_3)_6^{3+}$ [11] in the same medium, thereby establishing the one-electron change, a fact that was further confirmed by conventional dme polarography and controlled-potential coulometry. At a scan rate of 1.0–10 V/sec (between 0.0 and −0.45 V *vs.* sce), the potentials of the anodic and cathodic peaks were separated by approximately 70 ± 10 mV indicative of a reversible, one-electron process (theoretical separation 57 mV). This fact argues strongly that the coordination shell of the one-electron-reduced species maintains its integrity and does not undergo rapid aquation. However, at a slower scan rate (0.1 V/sec between 0.0 and −0.45 V *vs.* sce), the intensity of the anodic wave was diminished and broadened showing that the stability of the one-electron reduction product, designated as $Ru(NH_3)_5NO^{2+}$, perhaps toward aquation, is limited.

From the average of the anodic and cathodic peak potentials at the fast scan rates, an estimate of the standard reduction potential of $Ru(NH_3)_5NO^{3+}$ can be made: $E° = -0.12$ V at 23°. In comparison, $E°$ for $Ru(NH_3)_6^{3+}$ is +0.05 V.[11] It is interesting to note that despite the fact that $Ru(NH_3)_5NO^{3+}$ contains a reducible ligand, this complex is harder to reduce than is $Ru(NH_3)_6^{3+}$.

The electrochemical results indicate that $Ru(NH_3)_5NO^{3+}$ can be reduced in a one-electron step and that the product is moderately stable. By using the pulse radiolysis technique, specific reducing radicals can be generated in the submicrosecond time range from aqueous solutions containing se-

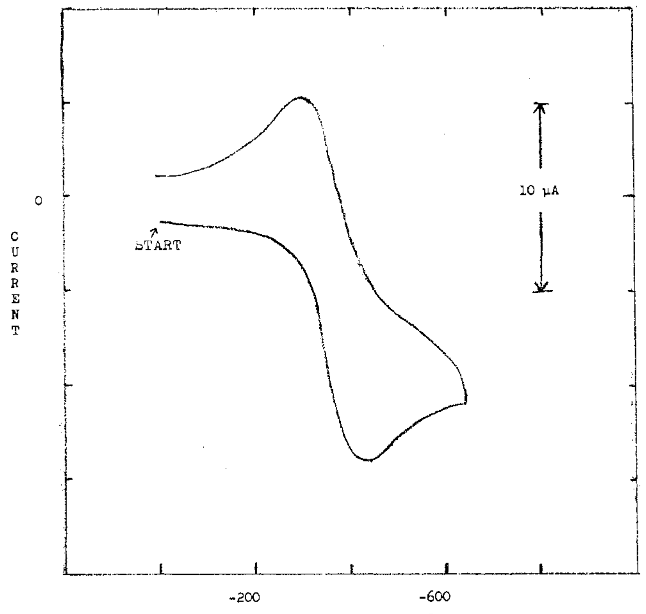

Figure 1. Cyclic voltammogram of 1.0×10^{-3} *M* [$Ru(NH_3)_5NO$]-($TFMS)_3$ in 0.1 *M* Na(TFMS). Scan rate is 1 V/sec, pH 6.0, hanging mercury electrode area 0.032 cm², and $T = 23°$. Lower curve represents the cathodic scan.

lective scavengers, and spectrophotometric detection of transient intermediates enables the spectra and decay kinetics to be determined. The radiolytic decomposition of water produces e_{aq}^- (2.8), OH (2.8), and H (0.6).[14] In acidic solution, $e_{aq}^- + H^+ \rightarrow H$ ($k = 2.2 \times 10^{10}$ M^{-1} sec^{-1})[15] while OH radicals can be scavenged by *tert*-butyl alcohol ($k = 5.2 \times 10^8$ M^{-1} sec^{-1})[16] producing $\cdot CH_2C(CH_3)_2OH$, 2-propanol ($k = 2.0 \times 10^9$ M^{-1} sec^{-1})[16] producing $(CH_3)_2\dot{C}OH$, or formate ($k = 2.8 \times 10^9$ M^{-1} sec^{-1})[16] producing CO_2^-. In the presence of N_2O (1 atm partial pressure $\equiv 2.5 \times 10^{-2}$ *M*), e_{aq}^- is converted to OH ($k = 8.7 \times 10^9$ M^{-1} sec^{-1}).[15] Hydrogen atoms are also scavenged efficiently by 2-propanol and formate to produce $(CH_3)_2\dot{C}OH$ and CO_2^-, respectively.[17]

The reaction of e_{aq}^-, H, $(CH_3)_2\dot{C}OH$, or CO_2^- radicals with $Ru(NH_3)_5NO^{3+}$ produces the same optical transient absorption spectrum, shown in Figure 2, which is attributed to $Ru(NH_3)_5NO^{2+}$. The rate constants for these one-electron reductions, determined from the decay kinetics of e_{aq}^- monitored at 700 nm or the formation kinetics of $Ru(NH_3)_5NO^{2+}$ monitored at 280 nm, are given in Table I. The reaction with e_{aq}^- is diffusion controlled, a feature common to most transition metal coordination complexes;[15] the rate constants for the reaction of e_{aq}^- with $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_5Cl^{2+}$ are 6.8×10^{10} and 6.2×10^{10} M^{-1} sec^{-1}, respectively.[18] The rates with $(CH_3)_2\dot{C}OH$ and CO_2^- are comparable to those reported for $Ru(NH_3)_6^{3+}$ ($k = 9.2 \times 10^8$ and 2.0×10^9 M^{-1} sec^{-1}, respectively).[19] Most interesting is the rather high rate of reaction of H atoms with $Ru(NH_3)_5NO^{3+}$ as compared to the reactions of H atoms with $Ru(NH_3)_6^{3+}$ ($k = 1.8 \times 10^6$ M^{-1} sec^{-1}).[20] Clearly, the value of the rate constant is not dictated solely by the free energy change and the reaction cannot be assumed to be occuring *via* an outer-sphere electron-transfer mechanism. Direct attack of H on the nitrosyl ligand in the same manner as the H + NO → HNO reactions in aqueous solution would provide a pathway for facile electron transfer.[21-23]

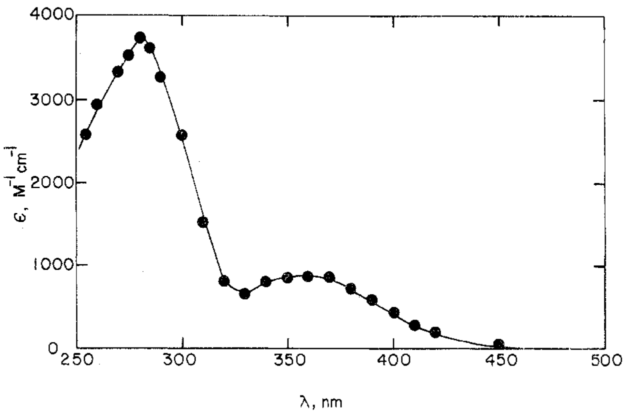

Figure 2. Spectrum of $Ru(NH_3)_5NO^{2+}$ obtained from the reaction of CO_2^- radicals with 2×10^{-4} *M* $Ru(NH_3)_5NO^{3+}$. The solution contained 0.5 *M* HCO_2^- at pH 6.6 and was saturated with N_2O. The identical spectrum was obtained from the pulse radiolysis of the following solutions: (1) 5×10^{-4} *M* complex, 1 *M* *tert*-butyl alcohol, Ar purged, pH 7.5; (2) 5×10^{-4} *M* complex, 1 *M* *tert*-butyl alcohol, Ar purged, pH <1; (3) 5×10^{-4} *M* complex, 0.2 *M* 2-propanol, Ar purged, pH 5.0; (4) 5×10^{-4} *M* complex, 0.2 *M* 2-propanol, N_2O saturated, pH 5.0; (5) 1×10^{-3} *M* complex, 1 *M* *tert*-butyl alcohol, O_2 saturated, pH 5.9.

Table I. Reactivity of $Ru(NH_3)_5NO^{3+}$ with One-Electron Reducing Radicals

Reducing radical	Solutes	pH	k, M^{-1} sec^{-1}
e_{aq}^-	[Complex] = 2×10^{-5} *M*; 0.5 *M* *tert*-butyl alcohol; Ar purged	8.6	5.3×10^{10}
H	[Complex] = 5×10^{-4} *M*; 0.5 *M* *tert*-butyl alcohol; Ar purged	<1	4.0×10^8
CO_2^-	[Complex] = 2×10^{-4} *M*; 0.5 *M* HCO_2^-; N_2O saturated	6.6	3.1×10^9
$(CH_3)_2\dot{C}OH$	[Complex] = 5×10^{-4} *M*; 0.5 *M* 2-propanol; N_2O saturated	5.0	5.5×10^8

$Ru(NH_3)_5NO^{2+}$ is a very reactive species and it can be viewed as a free radical coordinated to Ru(II) or as an NO^- complex of Ru(III). By monitoring the disappearance of its spectrum, we have established that $Ru(NH_3)_5NO^{2+}$ reacts with O_2 in air-saturated solution at a rate ($k = 7.6 \times 10^6$ M^{-1} sec^{-1}) that is considerably faster than that of other simple ruthenium(II) ammines.[24] It reacts rapidly with $\cdot CH_2C(CH_3)_2OH$ radicals ($k = 3.4 \times 10^9$ M^{-1} sec^{-1}) to provide an alkyl–nitroso complex by radical addition to the N atom of the ligand; details of the preparation and characterization of this species will be published separately.[25] In the absence of radicals with which to react, $Ru(NH_3)_5NO^{2+}$ is only moderately stable, undergoing slow secondary reactions, presumably substitution, with the solvent or other solutes in a matter of seconds. Because of this reactivity, isolation of a solid salt does not appear to be possible.

In summary, $Ru(NH_3)_5NO^{2+}$, generated by pulse radiolytic and electrochemical techniques, is shown to be a viable intermediate resulting from the one-electron reduction of $Ru(NH_3)_5NO^{3+}$. Its free-radical characteristics and high reactivity offer synthetic possibilities that are currently being explored.

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Registry No. $Ru(NH_3)_5NO^{3+}$, 37874-79-6; $Ru(NH_3)_5NO^{2+}$, 53011-05-5.

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Molecular Orbital Approach to Photochemical Assignments of Excited States. Photoreactions of Coordinated Azide

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Recent molecular orbital calculations have shown that photosolvation reactions of first-row transition metal complexes can be understood in terms of the metal–ligand antibonding character acquired in the vertical ligand field photoexcited state.[1] One of the important implications of the excellent correlation between the calculated changes in antibonding character in the ligand field excited state and the observed photoinduced ligand losses is that the initial internuclear motions on the excited-state surface induced by the bond weakenings play an important role in the course of the photoreaction even if the surface is nondissociative. In order to determine the generality of the above method, a calculation of the photoreactions of a coordinated ligand initiated by transitions other than ligand field absorptions was carried out. The ligand chosen for study was the azide ion coordinated to cobalt(III), rhodium(III), and iridium(III) which has been systematically studied by Basolo and coworkers[2-4] and others.[5] In this note we show that the trends in the calculated bonding changes within the azide ion correlate with the trends in the observed photoreactions as the metal is varied from cobalt to iridium. A new interpretation for the formation of the aquated metal is proposed which is consistent with all of the experimental data. Finally, it is shown how the calculations combined with the experimental data provide an approach to the chemical assignment of excited states.

Methods of Calculations

The details of both the molecular orbital calculations of the complete acidiopentaammine complexes and the model problem are discussed elsewhere.[1] For $Co(NH_3)_5N_3^{2+}$, the bond distances used were $M\text{–}N(NH_3) = 1.968$ Å, $M\text{–}N_1(\text{azide}) = 1.943$ Å, $N_1\text{–}N_2 = 1.208$ Å, and $N_2\text{–}N_3 = 1.145$ Å.[6] The $M\text{–}N_1N_2$ bond angle was 125°.[6] The numbering system is $M\text{–}N_1\text{–}N_2\text{–}N_3$.

In the model problem calculation of the M–N–N–N unit, the overlap integrals and VOIP's from the full EHMO-SCC calculation were used. The effect of varying the metal through the series Co^{3+}, Rh^{3+}, Ir^{3+} was simulated by increasing the $M\text{–}N_1$ overlap integral and decreasing the metal VOIP. The important states (*vide infra*) were more sensitive to the overlap integral than to the VOIP.

Only the calculated trends in bonding properties were used in this paper. Trends in the Mulliken overlap population[7] were used to interpret changes in the bonding.

The relative orderings of the levels in coordinated azide ion agree with those calculated for the free ion.[8] However, the metal has a profound effect on the energies of the orbitals and the N–N bonding characteristics. The importance of the perturbing effect of a coordinated group is illustrated by the unequal N–N bond lengths in coordinated azide (*vide supra*) and the large changes in N–N force constants (*e.g.*, in HN_3, $k_{N_1\text{–}N_2} = 1.01 \times 10^{-6}$ dyn/cm^{-1} and $k_{N_2\text{–}N_3} = 1.73 \times 10^{-6}$ dyn/cm^{-1},[9] while in free azide $k_{N_1\text{–}N_2} = k_{N_2\text{–}N_3} = 1.25 \times 10^{-6}$ dyn/cm^{-1}).[10] The changes in the N–N overlap populations upon coordination to a metal are discussed below.

Results and Discussion

The four one-electron orbitals which will be considered here are in order of increasing energy π_{non}, d_π, d_σ^*, and π^* where π_{non} and π^* are ligand-centered nonbonding and antibonding π orbitals and d_π and d_σ^* are primarily metal-localized d orbitals. The π_{non} orbital is weakly π bonding with the metal when coordinated. The first two sets are filled. Thus, the four lowest energy transitions are $d_\pi \rightarrow d_\sigma^*$ (ligand field, LF), $d_\pi \rightarrow \pi^*$ (MTLCT), $\pi_{\text{non}} \rightarrow d_\sigma^*$ (ligand to metal charge transfer, LTMCT), and $\pi_{\text{non}} \rightarrow \pi^*$ (ligand localized, LL). The bonding changes caused by excitation into the LF bands have been extensively treated[11-16] and will not be discussed further here. Based on the known optical electronegativity[17] of the azide and cobalt(III) ions, the energies of the remaining three states in the cobalt complex probably follow the order LTMCT < MTLCT ~ LL. We will return to the question of the ordering. In the series of Co, Rh, and Ir complexes, the energy of the LTMCT state increases, and in the series Rh to Ir, the energy of the MTLCT state increases relative to the ground state.

The changes in bonding caused by populating the excited states are summarized in Table I. The calculated changes in the overlap populations from which the table is taken are graphically shown in Figure 1. Pertinent comparisons of the reactions expected on the basis of the calculated bond weakenings with those experimentally observed are enumerated below. (1) The predominant photoproducts observed from uv irradiation of azide–ammine complexes of cobalt(III) are Co(II) and azide radicals.[18,19] The calculation shows that no N–N bond breaking of azide is expected in the LTMCT state. Thus, the N_3 fragment is lost as a unit. (2) The observed photoproducts from 3500-Å irradiation of $Rh(NH_3)_5N_3^{2+}$ are