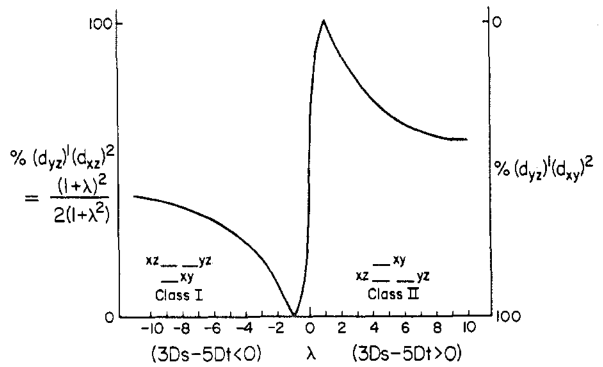

Figure 2. Plot of the per cent composition of the $^2E(^2T_{1g})$ state as a function of the mixing parameter λ. The 50% composition occurs at the crossover point between class I and class II when λ = 0.

$(d_{xz})^2(d_{yz})^1$ and $(d_{yz})^2(d_{xz})^1$ and the lowest doublet will be mainly $(d_{xy})^2(d_{xz})^1$ and $(d_{xy})^2(d_{yz})^1$ in character. The results of an explicit calculation of the per cent $(d_{xy})^2(d_{xz})^1$ or $(d_{xy})^2(d_{yz})^1$ character in the lowest ^2E state are shown in Figure 2. In the figure, the square of the coefficient of the above-named configurations in the ^2E wave function of eq 22 and 23 (representing the per cent contribution of them to the wave function) is plotted *vs.* the mixing coefficient λ. The 50% composition occurs exactly at the crossover between class I and class II, *i.e.*, where $3Ds - 5Dt = 0$.

The variation in quantum yield of ligand aquation which occurs as the axial ligand is continuously changed from a π donor (class I) to a π acceptor (class II) may be explained in terms of the continuous change of composition of the lowest ^2E state. The previous assumption that the changing relative populations of several doublet states caused the variation in quantum yield is not necessary.

Consider next the quartet states which are primarily responsible for the photoactivity of six-coordinate chromium(III) complexes.[7] The per cent composition of the lowest quartet state of all three classes, $^4E(^4T_2)$, is 75% d_{z^2} not including configuration interaction. As λ increases from −1.73 to +0.59, the per cent d_{z^2} character increases from 0 to 100%. Using eq 15, 26, 28, and 29 and previously calculated tetragonal crystal field parameters,[8,9] we calculate that for *trans*-$Cr(en)_2X_2^+$, when $X^- = F^-$, % d_{z^2} = 66%; when $X^- = Cl^-$, % d_{z^2} = 87%; and when $X^- = Br^-$, % d_{z^2} = 88%. It is thus expected that populating the $^4E(^4T_2)$ state will result in increasing amounts of *x*- and *y*-axis labilization relative to *z*-axis labilization in the series $Br^- \cong Cl^- < F^-$. The *trans*-difluoro complex is unique in the series of *trans*-dihalo complexes because it is the only one with the majority of its labilizing character in the *xy* plane when the antibonding character of a pure d_{z^2} orbital in the *xy* plane is taken into account. This result, in addition to π stabilization discussed in a previous publication,[1] explains the aquation of ethylenediamine in *trans*-difluorobis(ethylenediamine)chromium(III) ion.

The above calculations of configuration interaction between the excited doublet states and between the excited quartet states of tetragonal chromium(III) complexes reveal that the concept of per cent composition of a configuration in a state is important when applying our ligand field model to predict photoreactions and relative quantum yields. The results are particularly satisfying for the doublet-state considerations because they remove the necessity of assuming that varying *populations* of the doublet states result in varying quantum yields.[1] The populations probably do vary in the manner suggested in the previous work when the energy differences between the doublets are small. When the energy differences become large because of a rapid decrease in ^2E energy, the quantum yields are governed by the per cent composition of the lowest state.

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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Contribution from the Department of Chemistry,
Boston University, Boston, Massachusetts 02215

Controlled Mechanisms of Electron-Transfer Reduction of Coordinated Nitrosyls[1]

J. Armor

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Although the reduction of metal-ligand systems has been the subject of recent attention,[2-4] generally,[5] the ligands have not been among those recognized as being reducible in multiple steps. We wish to report the results of some recent investigations into the area of the reduction of coordinated nitrosyls which demonstrate the importance of considering both the type of metal nitrosyl undergoing reduction and the dramatic variations in reactivity which can occur.

Nitrosyl,[6] as a ligand, can be reduced successively through several stable intermediate oxidation states (NO^0, NO^-, N_2, NH_3OH^+, N_2H_4, NH_3). Although the physical properties[7,8] of metal nitrosyls are under intensive investigation, their chemical properties have received little attention. Several years ago, Griffith[9] described some initial experiments on the reduction of ruthenium nitrosyls with Sn(II) in Cl^- media. These studies indicated that ruthenium ammines *may* be produced; however, Griffith concluded that none of his "formulations were convincing, and, clearly, this is a field which should be more fully investigated."[9]

At the outset, the extent of the reduction of the nitrosyl might be expected to be controlled by the metal centers and/or the ligand environment. Three nitrosyls, $Ru(NH_3)_5NO^{3+}$, $Co(NH_3)_5NO^{2+}$, and $CrNO^{2+}$, will be discussed. We have chosen as our common reductant Cr^{2+}. This ion has several

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[1] Presented in part at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972, and at the American Chemical Society Symposium on the "Activation of Small Molecules by Transition Metals," Buffalo, N. Y., June 1972.

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distinct advantages[10] which make it an ideal candidate to probe the reducibility of metal nitrosyls. In addition, it has been suggested[11] that when Cr^{2+} serves as a simultaneous 2e reductant, Cr(III) dimer is produced, whereas when it acts by successive 1e reduction, monomeric Cr(III) species are produced.

The ruthenium-nitrosyl complex $[Ru(NH_3)_5NO]^{3+}$ is extremely stable in acidic media, and its electronic distribution is best described as $Ru^{II}NO^+$. Treatment of $>3 \times 10^{-3}$ *M* solutions of the complex with greater than 6 equiv of Cr^{2+} (pH <2, $T = 25.0°$, $\mu = 0.2 \rightarrow 0.6$ with NaCl)[12] results in a rapid reaction which is complete within 5 min. The product of the reaction (isolated as the Cl^- salt) displayed ir, uv, and vis spectra identical with those reported for $[Ru(NH_3)_6]Cl_2$.[13] Ion exchange of the air-sensitive product solution under argon indicated >90% yield of $Ru(NH_3)_6{}^{2+}$. Saturation of the product solution with O_2 results in the production of $Ru(NH_3)_6{}^{3+}$, which was isolated in >82% yield as the Br^- salt.[14] Upon rotary evaporation of the product solution to dryness, the ir spectrum of the solid residue revealed the absence of any nitrosyl compound. Potentiometric titration of a 5.95×10^{-3} *M* solution of $Ru(NH_3)_5NO^{3+}$ with Cr^{2+} (in 0.5 *M* HCl) results in a characteristic S-shape curve with an inflection point at 5.9 ± 0.1 mol of Cr^{2+} per mole of $Ru(NH_3)_5NO^{3+}$. The Cr(III) product of the reaction consisted of a mixture of 90% ($Cr^{3+} + CrCl^{2+}$) and 10% of the Cr(III) dimer.[15] The net reaction can then be written

$$Ru(NH_3)_5NO^{3+} + 6Cr^{2+} \xrightarrow[H^+]{Cl^-} Ru(NH_3)_6{}^{2+} + 6Cr(III)$$

Preliminary stop-flow kinetic studies in which the ratio of Cr^{2+} to Ru was varied from 1:1 to 10:1 revealed the existence of several short-lived intermediates.

The results for the reduction of the ruthenium nitrosyl (in Cl^- media) indicate that the reaction is complete with the production of a 6e reduction product: $Ru(NH_3)_6{}^{2+}$. The major chromium product is the monomeric Cr(III) species, consistent with the view that the reduction proceeds by six successive one-electron steps. In addition, the production of the coordinated ammine from the coordinated nitrosyl suggests that this type of a reaction is useful for the preparation of ammine complexes which cannot be prepared by the direct reaction of NH_3 with the metal complex. This idea has been applied to the synthesis of a monoamine-bis(ethylenediamine) complex of ruthenium.[16] (Numerous synthetic routes[13,17] exist for the preparation of metal nitrosyls.)

Reactions involving the black cobalt nitrosyl $[Co(NH_3)_5NO]^{2+}$ have been largely ignored, possibly because of the report that the black chloride cannot be dissolved in water without decomposition to basic cobalt(II) chlorides.[18] The rapid reduction of the ruthenium nitrosyl by Cr^{2+} led us to question whether we might find the redox reaction competing favorably with decomposition. Addition of an equivalent of Cr(III) in 0.1 *M* HCl to argon-purged vessels containing the black $[Co(NH_3)_5NO]Cl_2$ results in the immediate release of NO with the production of 1 mol of Co^{2+} per mole of Co complex.[19] However, the addition of 150 μmol (in 10 ml) of Cr^{2+} to an equivalent amount of the black cobalt nitrosyl does not result in the immediate evolution of any gas. Instead, the result is the immediate, quantitative production of $CrNO^{2+}$ (100 ± 2%) and Co^{2+}. The presence of the chromium nitrosyl was confirmed by uv-vis spectroscopy and its ion-exchange behavior.[20,21] Unlike the ruthenium system the nitrosyl is *not* reduced immediately to ammonia. Since Cr^{3+} does not react rapidly with NO(g),[1] the $CrNO^{2+}$ could not have been formed from NO(g) after the oxidation of Cr^{2+} to Cr^{3+}. However, Cr^{2+} does react rapidly[21] and quantitatively with NO(g) ($t_{1/2} < 4$ sec at 25° and millimolar levels of the reactants). Therefore, it becomes difficult to distinguish between the two possibilities: (1) NO elimination through decomposition of the Co complex in acid, the freed NO [solubility of NO (25.0°): 1.95×10^{-3} *M*] then reacting with Cr^{2+}, or (2) Cr^{2+} attack on the coordinated nitrosyl, with transfer of the nitrosyl function and the production of Co^{2+}. Since we do not observe any gas evolution, the first possibility is less likely. The action of Cr^{2+} on this complex is not unique. We have also observed that $FeNO^{2+}$ is produced when $[Co(NH_3)_5NO]Cl_2$ is treated with Fe^{2+}. (Fe^{2+} also reacts rapidly with NO; Fe^{3+} does not.[22]) While the mechanism for attack by the reductant is not clear, the cobalt complex does serve as an effective nitrosylating agent. Complete reduction of the nitrosyl is *not* observed, and the treatment of the cobalt nitrosyl with a reductant is suggestive of a rapid, convenient, and quantitative method for the preparation of metal nitrosyls. The stable, black cobalt complex can be weighed out and thus the amount of NO available for production of $CrNO^{2+}$ can be accurately controlled.

Recently, we have completed studies on the reduction of the chromium nitrosyl $Cr(H_2O)_5NO^{2+}$ by Cr^{2+}.[21,23] The reaction was observed to consume 2 mol of Cr^{2+} per mole of $CrNO^{2+}$, and the products were observed to be free NH_3OH^+ and only the Cr(III) dimer. The reaction is also rapid ($k = 0.49\ M^{-1}\ sec^{-1}$ at 25°; $[H^+] = 1.0\ M$, first order in both Cr^{2+} and $CrNO^{2+}$) while the reduction of free NH_3OH^+ by Cr^{2+} is ~40 times slower. Therefore, the reduction of $CrNO^{2+}$ by Cr^{2+} is illustrative of a *partial* (2e) reduction of the nitrosyl to NH_3OH^+ and not to NH_3.

In summary, it has been demonstrated that treatment of a series of metal nitrosyls by a common reductant can result in at least three alternatives: (1) the complete six-electron reduction of the metal nitrosyl to the metal ammine, (2) the partial (2e) reduction of the metal nitrosyl, and (3) the transfer of the nitrosyl function to the reductant. It has also been demonstrated that the metal center is capable of controlling the extent of the reduction of the nitrosyl, and the results may be applicable toward the preparation of intermediate metal-nitrogen derivatives. In addition, the possibility emerges for preparing several metal-nitrogen derivatives from the same reactant by controlling the amount of

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(11) M. Ardon and R. A. Plane, *J. Amer. Chem. Soc.*, 81, 3197 (1959).

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(20) M. Ardon and J. Herman, *J. Chem. Soc.*, 507 (1962).

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Cr^{2+} added. We are presently in the process of investigating a wider range of metal nitrosyls with the intention of pursuing the last possibility offered above.

Experimental Section

[Ru(NH$_3$)$_5$NO]Cl$_3$ was prepared by saturating a concentrated solution of Ru(NH$_3$)$_6$$^{3+}$ (pH <2 with HCl) with NO(g) for 1–2 hr.[13] Addition of NaCl precipitated the nitrosyl complex as the chloride salt. The solid was then washed with acetone and anhydrous ether. [Co(NH$_3$)$_5$NO]Cl$_2$ was prepared[24] by the addition of a degassed solution of CoCl$_2$ to a cold, degassed solution of aqueous ammonia (12%). The solution was saturated with NO for 3 hr resulting in the formation of a black precipitate. The crystalline, black solid was washed with absolute alcohol and anhydrous ether and stored in a vacuum desiccator. CrNO^{2+} was prepared by two different methods. (1) Stock solutions of CrNO^{2+} were prepared by the dropwise[21] addition of 0.5 *M* Cr^{2+} (10 ml/20 min) to a stirred solution of 200 ml of 0.1 *M* HClO$_4$. The latter solution was saturated with NO by means of a gas dispersion tube. After removing the NO from solution, the red solution was stored at 5°. Aliquots of the stock solution were purified by adsorption of the complex onto Dowex 50W-X8, 200–400 mesh (in the H$^+$ form). The red band was eluted with 0.5 *M* HClO$_4$. (2) The black [Co(NH$_3$)$_5$NO]Cl$_2$ was ground into a fine powder and placed inside a vial. The vial was stoppered with a rubber septum cap and purged with dry argon. A solution containing an equal number of moles of Cr^{2+} was injected directly into the vial.

Nitric oxide (chemically pure, Matheson Gas Products) was purified by vigorous scrubbing through towers of molecular sieve (−78°), solid KOH, and 5 *M* NaOH, respectively. All gases were passed through a final, common scrubbing tower of 0.1 *M* NaCl. Before and after the NO gas flow, argon was admitted to our all-glass system by rotation of a three-way stopcock (placed between the 5 *M* NaOH and 0.1 *M* NaCl towers). Chromium(II) perchlorate solutions were prepared (under argon) by the reduction of Cr(H$_2$O)$_6$$^{3+}$ with amalgamated zinc. Stock solutions of Cr(III) perchlorate were prepared by reduction of primary standard K$_2$Cr$_2$O$_7$ with acidic H$_2$O$_2$ and boiling the solution for several hours.[21] The solution was cooled overnight, and the KClO$_4$ was removed by filtration. Stock solutions of Fe^{2+} were prepared by treatment of iron wire (Baker and Adamson, reagent grade) with HClO$_4$.[25]

The solubility of NO was determined by injecting an aliquot of an NO-saturated solution (at 25.0° and 1 atm) into an excess of O$_2$-saturated water. The resulting NO$_2$$^-$ was determined quantitatively.[26,27]

All reactants and products were characterized by their uv–vis spectra, their behavior on a cation-exchange column, and their ir spectra (KBr disks).

Registry No. Ru(NH$_3$)$_5$NO^{3+}, 37874-79-6; Co(NH$_3$)$_5$NO^{2+}, 38402-80-1; CrNO^{2+}, 40187-02-8; chromium, 7440-47-3.

Acknowledgment is made for partial support from the donors of The Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation (Grant No. GP-38513X), and the Graduate School of Boston University.

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Correspondence

A Linear Relationship between the Enthalpy of Formation and the Frequency of the Maximum in the Electronic Absorption Spectra of the Copper(II)–Tetramine Complexes

Sir:

Recently a considerable amount of experimental material relating to the reactions between 3d metal ions and linear aliphatic tetramines has been reported.[1] In particular for copper(II) it has been found that complexes containing a system of three fused chelate rings in which five- and six-membered rings alternate, *e.g.*, [Cu(2,3,2-tet)]$^{2+}$[2] and [Cu(3,2,3-tet)]$^{2+}$,[3] are more stable than complexes in which the chelate rings are either all five-membered (2,2,2-tet[4a]) or six-membered (3,3,3-tet[4b]).[5] Furthermore calorimetric titrations have shown that the greater stability is due to a more favorable enthalpic contribution.[1] The more negative ΔH° reflects the capacity of the ligand to place the donor atoms in positions better suited to the steric requirements of the copper(II) ion (probably at the corners of a square plane) thus giving a configuration with less strain as is also shown by the construction of molecular models. The formation of both [Cu(2,3,2-tet)]$^{2+}$[6] and [Cu(3,2,3-tet)]$^{2+}$[7] is more exothermic even than that of [Cu(en)$_2$]$^{2+}$[8] with two separated five-membered rings, so that any cumulative steric strain must be considered absent in these compounds.

In the solid state, salts of [Cu(2,3,2-tet)]$^{2+}$, which has the highest heat of formation in the series under consideration, are bright red, while complexes of the other ligands have the usual blue-purple color. In other words both in the solid state and in solution the frequency of the electronic absorption maximum of the complex [Cu(2,3,2-tet)]$^{2+}$ is higher than those of the corresponding complexes of homologous ligands.

This led us to think that there must be a relation between the thermodynamic and the spectral properties of these complexes.

Figure 1 shows the ΔH of formation of these complexes plotted against the frequency of the maximum in their electronic absorption spectra in aqueous solution. The least-squares equation describing the relation is $-\Delta H^\circ = 3.75\bar{\nu}_{\mathrm{max}} - 43.36$ (ΔH° being expressed in kcal mol^{-1} and $\bar{\nu}_{\mathrm{max}}$ in kK). The linear relationship between these two quantities is not a completely unexpected result. In fact it has been found that the values of ΔH° become more negative as the coordinate bonds formed by the equatorially coordinated ligand become stronger.[6]

On the other hand, it was shown that the frequency of the maximum of the d–d band could be considered as an approximate measure of the in-plane bond strength (*i.e.*, the

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