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Mechanism of Base Promoted Reduction of Nickel(III) Complexes of Macrocyclic Amines. A Coordinated Ligand Radical Intermediate

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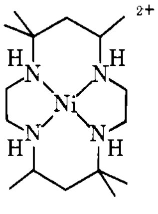
Abstract: The mechanisms of decomposition of two nickel(III) complexes which contain macrocyclic secondary amine ligands have been studied. When **2** is treated with basic solvents such as pyridine, triethylamine, or water a Ni(II) ligand radical species is formed according to: $\mathrm{N^{III}N{<}H + B \rightarrow Ni^{II}N{<}\cdot + BH^{+}}$. Chemical and spectroscopic evidence is presented in support of this species. A similar species is observed in the decomposition of **4** by pyridine but is not observed in water although product analyses suggest that a radical species is again formed. Depending upon the solvent 1–25% of the radicals formed decompose with rupture of the macrocyclic ring; the remainder are converted to Ni(II) tetramine complex by hydrogen abstraction from ligand fragments or from a second radical species. The latter process leads to monoimine complex formation. Under certain conditions monoimine may also be formed by oxidation of the Ni(II) ligand radical by Ni(III) complex. Such radical species have been proposed earlier as intermediates in macrocyclic amine complex reactions, but no direct evidence for their formation has previously been obtained.

Nickel(II) complexes of macrocyclic ligands of the 1,4,8,11-tetraazacyclotetradecane (cyclam) class have received a great deal of attention in the past several years.[1] More recently reports of nickel(III) complexes with these ligands have appeared.[2] The strong ligand field exerted by these macrocyclic ligands on the nickel(II) ion raises antibonding orbital energies sufficiently that removal of an electron is a low energy process. The charge placed on the metal ion by the four planar nitrogen donors stabilizes the resultant trivalent oxidation state. Similar arguments account for the formation and stabilities of Cu(III),[3] Ag(II),[4,5] and Ag(III)[5] complexes of these ligands.

Nickel(III) complexes of these tetramine ligands are easily formed by electrochemical and chemical oxidation and most of these are stable to reduction indefinitely as solids in a dry atmosphere and for extended periods in purified acetonitrile solution. However, all of the presently known complexes of this type decompose in a wet environment as solids and more rapidly in aqueous solution. The rate of decomposition depends upon the particular macrocyclic ligand and also the nature of the axial ligands present. Water is not unique in causing this decomposition as most solvents which are more basic than acetonitrile will induce rapid decomposition. It seemed to us that an understanding of the mechanism of this decomposition would be important for the study of these complexes as oxidizing agents and that it might permit the design of new trivalent complexes which were less suceptible to decomposition in basic solvents. Also we were aware that trivalent complexes are formed prior to oxidation of coordinated amines in iron(II),[6] nickel(II),[7] and ruthenium(II)[8] complexes and that ligand radical intermediates had been postulated as intermediates in these processes. A radical intermediate was proposed (but not observed) in the decomposition of a Cu(III)–tetramine complex which produced Cu(II) complexes containing imine donors.[3] A detailed study of the decomposition of analogous Ni(III) complexes where "long-lived" intermediates were observed might permit detection of such a species, if indeed it was formed.

For the mechanistic investigation we chose complexes **2** (meso isomer) and **4** as representative of this class of Ni(III) complexes. These are conveniently prepared from **1** and **3**, respectively by oxidation with $\mathrm{NOClO_4}$ in acetonitrile.

The results of this study will show that a novel mechanism of decomposition (reduction) exists for these complexes which involves, in the first step, base promoted intramolecular oxidation of a coordinated amine donor with for-



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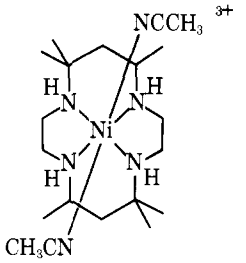

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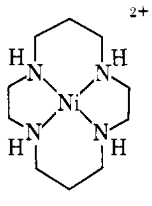

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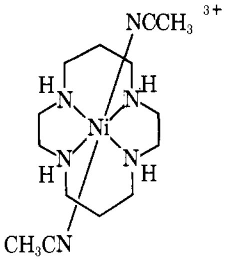

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mation of a ligand radical intermediate. This intermediate undergoes further reaction in a second step to yield products.

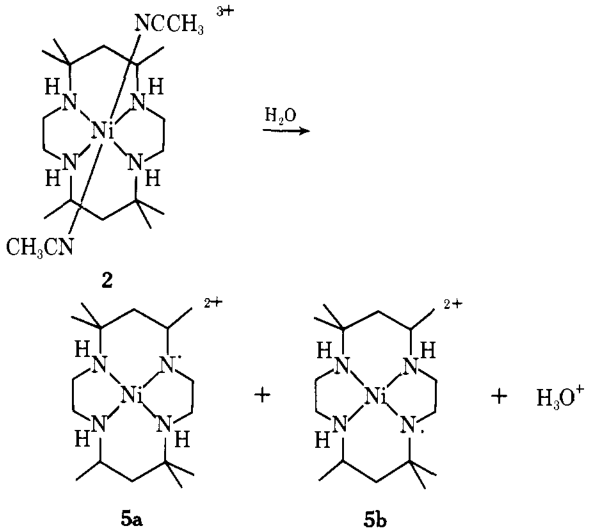
Results

Summary of Experimental Observations. The nickel(III) complexes **2** and **4** are, as previously stated, unstable in basic solvents; however, they differ considerably in their rates of decomposition and in the nature of the decomposition pathways leading to the final products. Addition of water to solid samples of **2** immediately gave an intense, transient ($t_{1/2}$ ca. 90 sec in pure water) red-violet color (λ_{max} 540 nm, log ϵ ~4). The decay of this colored species was first order and it was influenced by a variety of substrates. Decomposition in water gave only **1** as a macrocyclic complex at the completion of the reaction. Similarly, addition of pyridine to **2** also gave a red-violet color, but its decay was much more rapid ($t_{1/2} < 1$ sec) and the decay did not obey first-order kinetics. The final product solution contained more than one nickel(II) macrocyclic complex. The decomposition in triethylamine also gave the intensely colored intermediate, with only **1** as a macrocyclic complex in the product mixture. Acetonitrile solutions of **2** gradually changed over a period of days to a yellow-orange color typical of the nickel(II) macrocyclic complexes. No intermediate species was observed. More than one macrocyclic complex was present at the completion of the reaction.

In contrast to the behavior of **2**, addition of water to the cyclam complex **4** did not produce an intermediate color, but rather a gradual decay from the green color of **4** to yellow-orange over a period of hours. The rate of decay was not first order in complex. In pyridine-induced decompositions of **4** a transient red-violet color ($t_{1/2} < 1$ sec) was observed. In both solvents more than one macrocyclic complex was present at the completion of the reaction.

The Red Intermediate Species. Based on the chemical and physical studies described below, the intermediate red-violet color observed in the decomposition of **2** in water is ascribed to the products **5a** and **5b** formed by reaction 1. This reaction is best thought of as deprotonation of a coordinated amine followed by an intramolecular ligand to metal electron transfer process which produces the nickel(II) ligand radical species **5**.

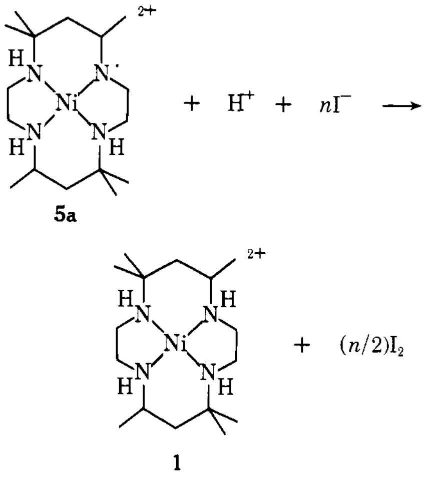
The above process predicts that one proton will be produced for each nickel(III) complex reacting. The experimental values of 0.97 and 1.01, determined by titration at the completion of the decomposition, are in good agreement with this value. Time dependent pH studies on the reaction indicated that the production of protons was complete within the response time of the pH meter (ca. 1 sec). There was no further change in the acidity of the reaction mixture during the course of the decomposition.



$+ \; H_3O^+$ (1)

Attempts to follow the decay of the green color of **2** and the appearance of the red-violet color ascribed to **5** were not completely successful. Both of these processes were too rapid to be followed in their initial stages by the stopped-flow apparatus that was available, which was limited to processes having a half-life of greater than ca. 10^{-3} sec. After a very rapid initial decay of most of the color due to **2** (the decay was monitored at 410 nm), there was a more gradual decay, suggesting (as does other experimental evidence, vide infra) that some **2** was still present in equilibrium with **5**. However, the rapid and apparently simultaneous appearance of protons and the red-violet color of **5** are consistent with reaction 1.

The species **5** are basically organic-like free radicals and as such should be reactive toward substrates used as free radical traps. These expectations were confirmed experimentally. The addition of alkali metal oxalates or iodides to the red-violet solution resulted in immediate quenching of the red color. In the case of iodide, iodine was produced and was partially precipitated as the triiodide salt of **1**. Such solutions showed a higher pH than solutions that were not quenched. Quantitative determination of both iodine and the acidity of such solutions gave the ratio of the sum of the moles of protons plus twice the moles of iodine produced per mole of **2** reacting as 0.98. This result is in good agreement with the proposed intermediate reacting according to (shown for **5a**) (eq 2) which predicts a value of 1.00 for this



$+ \; H^+ \; + \; nI^- \longrightarrow$

$+ \; (n/2)I_2 \; + \; (1 - n)H^+$ (2)

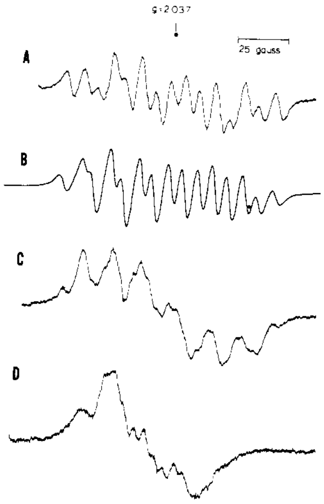


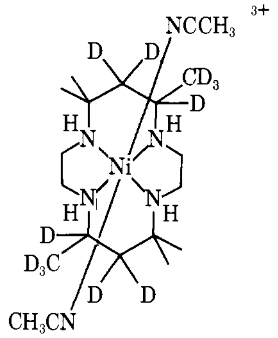
Figure 1. (A) ESR spectrum of the red intermediate produced by **2** in water. (B) Simulation of the spectrum shown in A assuming a 1.1:1 mixture of radical species **5a** and **5b** to be present (**5a,** $g = 2.037$, $a_N = 29.2$ G, $a_H = 14.6$ G; **5b,** $g = 2.036$, $a_N = 27.8$ G, $a_H = 13.9$ G). (C) ESR spectrum of the intermediate produced by **6** in water. (D) ESR spectrum of the intermediate produced by **7** in water.

ratio. It should be noted that while the above reaction accurately reflects the overall stoichiometry of the process, it does not necessarily have any mechanistic significance. While iodide ion may react directly with **5**, it could also undergo oxidation by one of the macrocyclic ligand fragments which are formed in the decomposition (vide infra). If this were the case, the reduced ligand fragment would then presumably add a proton to form a stable species and maintain the stoichiometry required by reaction 2. In summary, the decomposition of **5** in aqueous iodide solution occurs in two ways: either in the same fashion as in pure water, with one equivalent of protons produced, or else with oxidation of iodide to iodine and no net production of protons.

Also typical of an organic free radical, the lifetime of **5** in aqueous solution was strongly dependent upon added organic substrates and oxygen. Triphenylmethane derivatives and benzoate quenched the red color immediately. Significantly, quenching with benzoate produced no detectable salicylate, either colorimetrically with ferric ion or by mass spectroscopy. The implications of this fact will be considered later. The decay of the red-violet color ascribed to **5** was first order in both nitrogen and oxygen saturated water. However, the half-life of the decay in the latter case was about 15% of that in the former (ca. 0.5 vs. 3.5 min). The enhanced rate of decay of organic free radicals[9] and of metal complexes undergoing reactions involving free radical intermediates[10] in the presence of oxygen is a widely recognized phenomenon and is consistent with the proposed identity of the red-violet intermediate as **5.**

The above chemical evidence supports the identity of **5** as a free radical intermediate and its formation according to reaction 1, but it cannot be considered unambiguous. Further evidence for the identity of the radical species was provided by the ESR spectrum that was obtained on acetonitrile-water solutions containing the intermediate in a continuous flow system. The spectrum, shown in Figure 1A, consists of a 15-line pattern centered at ca. 2.037. This spectrum, although it has a *g* value somewhat greater than the free electron value, is quite unlike that expected for a Ni(III) complex. ESR spectra obtained on solutions of Ni(III) macrocyclic amine complexes typically have *g* values ranging from 2.1 to 2.2. Hyperfine interactions are observed only for axial ligands, as expected for a d_{z^2} ground state. Analysis of polycrystalline sample spectra suggests that mixing with $d_{x^2-y^2}$ is small.[11] The above arguments indicate that the hyperfine structure and low *g* value are inconsistent with a Ni(III) formulation if a d_{z^2} ground state is maintained. Also, no signal corresponding to a high spin nickel(II) complex should be observed under the experimental conditions, since the short electron spin relaxation time expected at room temperature would result in a very broad signal.[12]

Because of the unsymmetrical nature of the macrocyclic ligand there are two possible structures for a nitrogen based radical species, **5a** and **5b.** Attempts to simulate the observed ESR spectrum assuming either structure alone were unsuccessful. However, a simulation could be obtained by assuming that both species were present. Figure 1B shows a simulation based on a 1.1:1 ratio of **5a** to **5b.** The 15-line spectrum can be separated into an eight line signal due to **5a** and a seven line signal due to **5b.** These numbers of lines arise from the assumption that coupling constants for hydrogen atoms on carbons adjacent to the nitrogen are equal and are one-half the value of the nitrogen coupling constant, with all other couplings considered to be negligible. While the close similarity of the simulated spectrum to the experimental one cannot be considered as proof of the radical structure in view of the assumptions that went into the calculation, it does strongly suggest that the explanation given is a possible one. Further verification that the species giving rise to the observed ESR spectrum were **5a** and **5b** was provided by the observation in the flow system of the intermediates obtained from the deuterated complexes **6** and **7.** In these complexes one or more of the hydrogen atoms that was found to have a substantial hyperfine coupling constant according to the simulation in Figure 1B has been replaced with a deuterium atom. Replacement of hydrogen with deuterium in a free radical reduces the hyperfine coupling constant to about 15% of the hydrogen value, and the 1:1 doublet produced by coupling to a hydrogen atom is replaced with the 1:1:1 triplet characteristic of deuterium.[13] In the present case, with hydrogen hyperfine constants of ca. 14 G, the deuterium values would be expected to be ca. 2 G, which is smaller than the observed line widths. Thus the observed effect should be one of overall collapse of the spectrum, with the number of lines decreasing as the number of hydrogen atoms replaced with deuterium increases. The observed spectra shown in Figure 1C and D for radicals derived from **6** and **7**, respectively, are clearly in agreement with this proposal, and further support the identity of the red intermediate as a nickel(II) ligand radical species that has the unpaired electron localized primarily on nitrogen.



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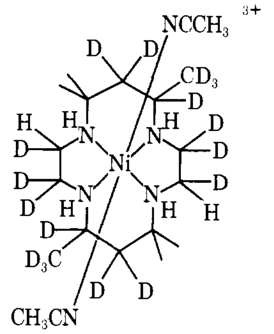

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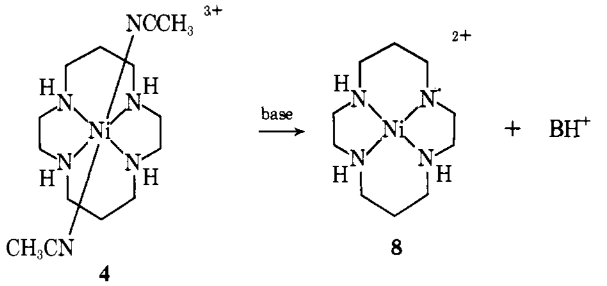
Two points concerning the structure of the radical species **5a** and **5b** deserve some comment. The values of the nitrogen and proton hyperfine coupling constants that were utilized for computing the spectrum shown in Figure 1B are not typical of those found for uncoordinated amino radicals.

Free amino radicals have nitrogen atom hyperfine coupling constants that are about half the magnitude of those of the hydrogen atoms on α-carbons.[14] The larger α-hydrogen atom hyperfine constants normally observed are a result of the planar nature of amino radicals, which places the unpaired spin density primarily in a 2p atomic orbital of nitrogen. This results in a small overlap with the nitrogen nuclear center. In the present case, the conformational requirements of the ligand ring system should prevent formation of fully planar amino radicals. The unpaired electron would then be in an orbital of substantial s character with considerable overlap with the nitrogen nucleus. The larger nitrogen atom hyperfine constants required for the simulation are consistent with this idea. The *g* value of 2.037 observed for **5** is somewhat greater than that observed for amino radicals which normally have *g* values very close to 2.003. It is unlikely that distortions from planarity could result in a *g* value of such magnitude; it is more likely that there is significant contribution of metal orbitals to the molecular orbital that contains the unpaired electron. The large extinction coefficient observed for the 540-nm absorption, which is ascribed to **5**, is indicative of a charge transfer transition. This probably corresponds to a transition from an orbital that is predominantly nitrogen based to one that is largely metal in character.

In an effort to obtain some idea of the *g* tensor anisotropy and perhaps an idea of the extent of metal orbital contribution to the orbital containing the unpaired electron, attempts were made to obtain ESR spectra on frozen solutions of the radical. However, solutions that were quenched in liquid nitrogen appeared green rather than red and these samples exhibited ESR spectra that were nearly identical with that of a polycrystalline sample of **2**. When the solution was thawed the red color of **5** was regenerated. This freeze-thaw process and the same color changes could be repeated a number of times until the red color decayed on the warm side of the cycle. This interconversion was truly a phase change phenomenon rather than simply a temperature dependent one, since partially frozen samples consisted of a green solid phase and a red liquid phase.

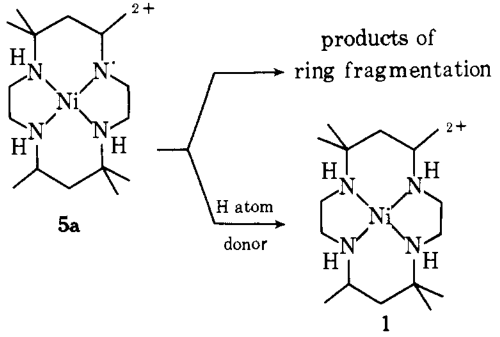
In addition to a signal attributable to the nickel(II) ligand radical species, the ESR spectrum of the flow mixture in all of the above experiments invariably also showed a broad signal at higher *g* values. This signal was identical in shape and position with that observed for an acetonitrile solution of **2**. This observation clearly indicates that there is a detectable amount of this complex that is probably in equilibrium with the corresponding nickel(II) ligand radical species. In fact, the red-violet color of **5** in aqueous solution could be quenched by the addition of a small amount of a variety of acids (e.g., nitric, acetic, perchloric, sulfuric). In contrast to other quenching experiments described earlier, the color of the solution was not the yellow-orange color of the nickel(II) complex but rather a green color typical of the nickel(III) complexes. Solutions of **2** in acidified water exhibited a greater stability than those in pure water. Small amounts of acids (e.g., solutions of pH ca. 4–5) resulted in a noticeably slower rate of decay of the intermediate **5** and larger amounts (e.g., solutions of pH ca. 1–2) prevented any detectable formation of the intermediate; instead the solutions, which were initially green, gradually decayed to orange. All of these observations suggest that reaction 1 is reversible.

Complex **4** was less extensively studied than **2** because the rates of formation and decay of an intermediate were either too fast or too slow. However, by analogy with **2**, the red-violet color observed in the decay of **4** in pyridine should be due to the radical **8** formed by a reaction similar to (1).



No direct evidence for the intermediate **8** could be determined spectroscopically. Attempts to do continuous flow ESR experiments using an acetonitrile solution of **4** mixing with pyridine–acetonitrile mixtures of varying concentration (from 1:1000 to 1:10, v/v) were not successful. Either the intermediate did not form rapidly enough or in high enough concentration at low pyridine concentrations or decayed too rapidly for detection as the pyridine concentration was raised. The similarity of the color of the intermediate and the further course of the decomposition with that determined for **2** in pyridine do, however, suggest the presence of the intermediate **8** (vide infra). No intermediate was observed in the decomposition of **4** in water. Again, however, the nature of the products of the decomposition suggest the presence of a radical intermediate (vide infra).

Decay of the Radical and Products. On the basis of information presented below the decays of the intermediates **5** and **8** are believed to occur by a combination of reactions (3–5) (shown for **5a**; analogous reactions can be written for



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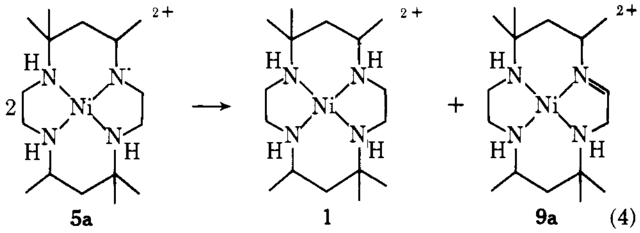

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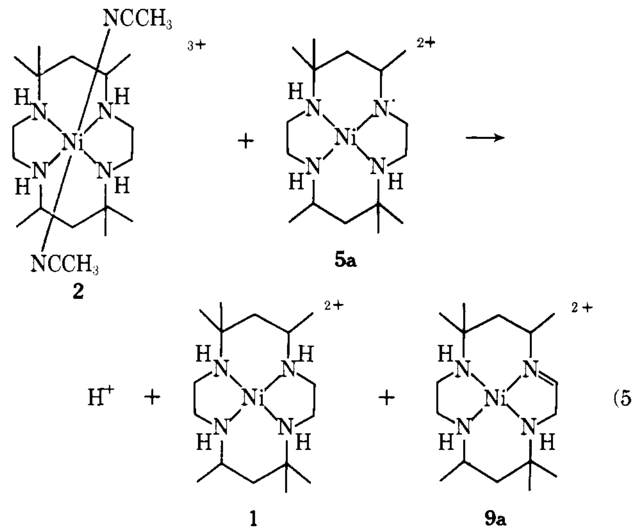

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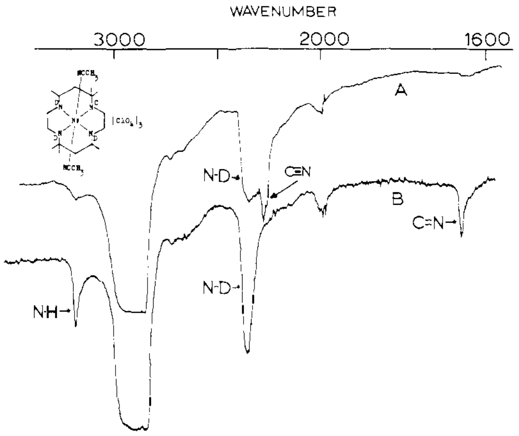


Figure 2. (A) Infrared spectrum of N-deuterated **2**. (B) Infrared spectrum of the macrocyclic ligand complexes isolated after decomposition of N-deuterated **2** in a pyridine-d_5/acetonitrile-d_3 mixture. Both spectra are of Nujol mulls.

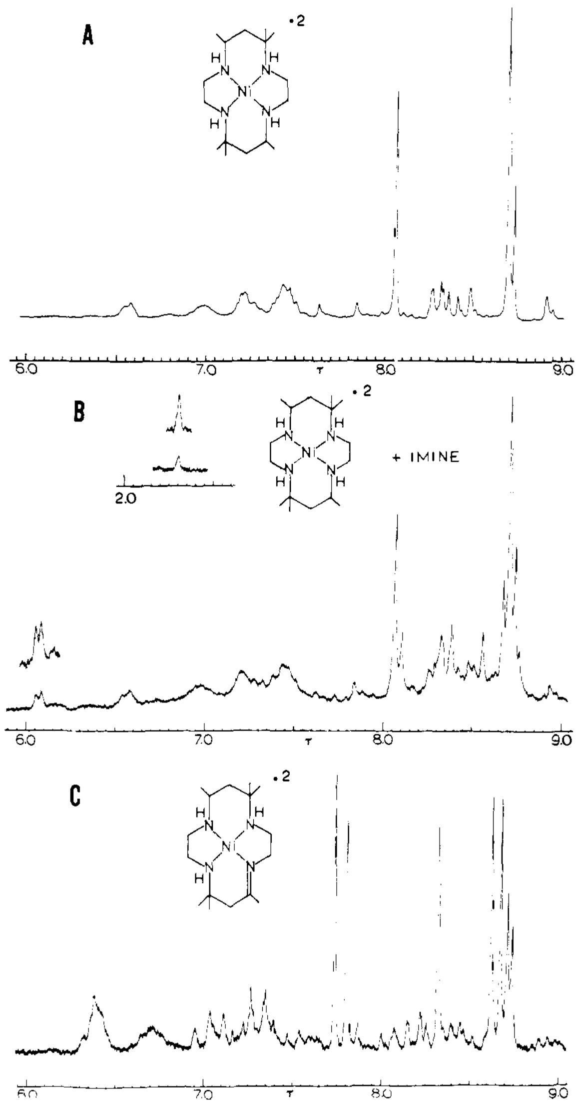


Figure 3. (A) NMR spectrum of **1**. (B) NMR spectrum of the macrocyclic ligand complexes isolated from the decomposition of **2** in pyridine. (C) NMR spectrum of monoimine complex **10**. All spectra were obtained at 220 MHz on trifluoroacetic acid solutions. TMS is the standard.

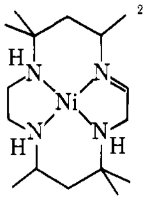
5b and **8**). The particular combination of pathways depends on both the complex and on the base utilized for the decomposition.

The decomposition of **5** in water was first order and **1** was the only macrocyclic complex formed as a product, thus suggesting net reduction of **5** either by electron transfer and protonation or by hydrogen atom capture. Several experiments that were designed to detect the involvement of water (HO· scavengers, tests for O_2, etc.) as the reducing agent gave negative results. However, tests for "free" nickel ion were positive and EDTA titrations revealed that a substantial amount of the total nickel was in titratable form. Since the macrocyclic complexes are exceedingly inert this observation indicates that ring rupture has occurred. Since added organic materials serve as quenching agents it is likely that the ligand fragments formed by decomposition could also. It was not possible to directly show for aqueous decompositions that ligand fragments supplied the reducing equivalents (hydrogen atoms) required by reaction 3. However, strong evidence for such a process was provided by a decomposition of N-deuterated **2** in a pyridine-d_5/acetonitrile-d_3 mixture. The infrared spectrum of the macrocyclic products (Figure 2) revealed that there was a significant incorporation of protons at amine positions. The only source of hydrogen in this particular system is the macrocyclic ligand. Thus, hydrogen atoms for reduction of **5** must come from ligand fragments (or other radical species, vide infra). We assume that a similar process is also operative in the aqueous decomposition.

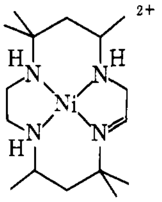
Although the ligand fragments could be separated from the macrocyclic ligand complex in the decomposition of **2** in water, their structure was not determined. The proton NMR spectrum of the mixture was very complex. Some of these fragments were complexed to nickel ion as evidenced by a 390-nm absorption in the spectrum of both the product mixture and of the products remaining after removal of **1**. In one series of experiments the red intermediate **5** was quenched with $C_2O_4^{2-}$ at intervals after its formation. The intensity of the 390-nm absorption and the amount of nickel that could be titrated increased with the time interval before quenching took place. This indicates that ring rupture in **5** competes with hydrogen atom capture. Several different fragments are undoubtedly formed judging by the complexity of their NMR spectrum and by the fact that the amount of nickel ion in the aqueous decomposition product mixture that could be titrated depended upon the pH at which the determinations were performed. This suggests that part of the nickel is more tightly bound and that some of the complexes of the ligand are susceptible to base hydrolysis.

As previously stated the decay of the radical species in pyridine solution did not show a first-order dependence on radical concentration but rather a more complex behavior that appeared to be a combination of first- and second-order processes. In addition to **1**, free nickel, and ligand fragments, an unsaturated macrocyclic ligand complex was present in the product mixture. The kinetic behavior and products formed are consistent with decay of **5** by a combination of pathways (3) and (4). The experiment described previously involving the decomposition of **2** in deuterated pyridine confirms decay by reaction 3 but is also consistent with decay by reaction 4. Reactions 3 and 4 should show first- and second-order kinetic dependence on **5**, respectively.

The evidence for the unsaturated complex and its structure requires some discussion. The infrared spectra of product mixtures contained sharp lines at 1660 cm^{-1}, typical of coordinated imine (Figure 2). The NMR spectrum (Figure 3B) was more complex than that of **1** alone (Figure 3A), with new lines in the methyl region as well as the appearance of lines at τ 6.1 and 2.3, downfield of the region where all of the resonances of **1** appear. These resonances are expected for a species containing an imine function in a five-membered ring, i.e., **9a** or **9b**.[15] Either species would be expected to show six magnetically nonequivalent methyl groups. Four or possibly five lines not attributable to **1** are observed. The resonance at τ 2.3 can be assigned to the imine proton. As only one peak is seen at this position, it appears that either **9a** or **9b** but not both was produced in the course of the reaction. The doublet (J = 6 Hz) at τ 6.1 is assigned to the adjacent methylene group in the imine containing ring. Irradiation at τ 2.3 resulted in collapse of the doublet at τ 6.1 thus showing that the doublet arises from coupling to the vicinal amine proton. The integrated spectrum intensities indicated the ratio **9**:**1** to be ca. 0.25.

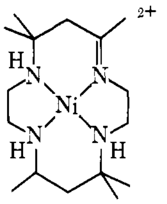


9a



9b

The monoimine complex **10** is a known compound and might be expected to be a product of a reaction such as (4). However, a comparison of the NMR spectrum of an authentic sample of **10** (Figure 3C) with a spectrum of the macrocyclic products of the pyridine decomposition (Figure 3B) showed that it could not be present in more than trace amounts. Unfortunately it was not possible to synthesize either **9a** or **9b** by an independent route.

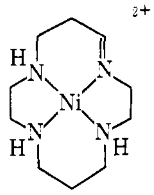


10

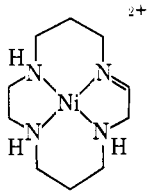
The decomposition of **2** in triethylamine, in contrast to pyridine, gave only **1** as a macrocyclic product. Lack of evidence for process (4) is consistent with the known ability of triethylamine to function as a radical scavenger by hydrogen atom donation.[16] Thus **1** is produced directly from **5** by hydrogen atom capture. Although the radical is formed in high concentration, reaction 4 cannot compete with hydrogen atom capture in the presence of such a high concentration of hydrogen atom donor. As in the case of $C_2O_4^{2-}$ quenching, little free nickel is observed in triethylamine decompositions.

The slow decomposition of **2** in acetonitrile must occur by a combination of processes (3) and (5). At the completion of the decomposition 1-2% of the total nickel ion could be titrated with EDTA. This suggests that the radical **5** was in fact formed during the decomposition, though in concentrations too low to be directly detected. This inference assumes that the formation of **5** is a necessary first step for macrocycle destruction and for formation of EDTA-titratable nickel ion. Isolation of the macrocyclic products from the decomposition and subsequent analysis by NMR and infrared spectroscopy show the presence of both **1** and **9** as in the pyridine decomposition. Integrated NMR intensities gave the ratio **9**:**1** to be ca. 0.3. Again, only one of the possible products **9a** and **9b** was indicated by the NMR spectrum. Process 4 is ruled out in this case, since the concentration of **5** is very low during the course of the reaction. Process 5 provides a reasonable alternative pathway. Since **2** is present at high concentration relative to **5** and is expected to be a good oxidizing agent, its interaction with **5** should produce the observed products. This is the same mechanism that has been proposed by Olson and Vasilevskis to explain the formation of macrocyclic imine in Cu(III) decompositions.[3]

The decompositions of the nickel(III) cyclam complex **4** also proved to be solvent dependent and appeared to occur by the same three pathways as previously described for **2.** The decomposition of **4** in aqueous solution proceeds by a combination of pathways (3) and (5). The reasoning is analogous to that used in the decomposition of **2** in acetonitrile. No intensely colored radical intermediate was observed, but the presence of ca. 5% of the total nickel ion in a form titratable with EDTA argues for its existence. Macrocyclic imine was produced, judging by the appearance of a sharp absorption at 1660 cm^{-1} in the infrared spectrum of the macrocyclic products of the reaction and the methine proton of the imine at τ 2.1 in the NMR spectrum. The ratio of macrocyclic imine to nickel(II) cyclam in the product mixture was ca. 0.3. In this case there were insufficient data to differentiate between the possible monoimine species **11a** and **11b.** There is, however, little detail in the spectrum, since the methyl groups of the (Me_6[14]aneN_4) macrocycle, which greatly aid the interpretation of the NMR spectra of its complexes, are absent here. The existence of such a species is of some interest, as no complexes containing the cyclam ligand with any degree of unsaturation involving the nitrogen donors have been characterized.



11a



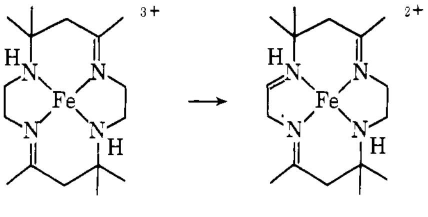
11b

The infrared and NMR spectra of the macrocyclic species from the decomposition of **4** in pyridine were very similar to the decomposition in water. The ratio of imine to nickel(II) cyclam was about 0.4. Also, ca. 2-3% of the total nickel ion present could be titrated with EDTA. The brief but clearly visible red-violet intermediate (presumably **8**) suggested that a relatively high concentration of the radical was present for a short time. The same arguments that were applied to the decomposition of **2** in pyridine suggest that both processes 4 and 5 occurred in the present case.

Discussion

A significant result of this work has been the observation and identification of nickel(II) ligand radical species which form as intermediates in the decompositions of nickel(III) complexes of the secondary amine macrocycles. As has been already noted, such species have previously been implicated but never before characterized as intermediates in the oxidation of amine ligands that are coordinated to transition metal ions.

For example, Goedken and Busch have reported[6b] that the iron(III) macrocyclic diene complex shown below decomposed with formation of the iron(II) triene complex when water was added to an acetonitrile solution of the



complex. No detailed product analyses were reported so it is not clear what other products were obtained, although oxygen was suggested as a possible oxidation product of water. In view of the results of this work it seems likely that the additional imine results from a base promoted intramolecular oxidation of a coordinated nitrogen followed by hydrogen atom transfer, analogous to reaction 4 of this work. An iron(II) radical–iron(III) complex reaction analogous to reaction 5 is also a possibility. Unexplained spectral bands, referred to by these researchers, in spectra of the solutions of the iron(III) diene complex undergoing reaction with water could be due to radical intermediates of the type observed in this work. Such radical species were in fact suggested by these researchers as possible intermediates and, as previously mentioned, by Olson and Vasilevskis for the Cu(III)–tetramine decompositions.[3] We reported earlier that silver(III) complexes analogous to **2** and **4** also decompose in the presence of base to give intensely colored, diamagnetic intermediates which decay to silver(II) complexes.[5] It was suggested that these were radical intermediates as well. All of these suggestions and others seem well founded based on the results reported here.

A surprising result of the base induced decomposition was the formation of unsaturated species **9**, which has the imine function in the five-membered rather than the six-membered chelate ring. This result is at variance with the often quoted work on chemical oxidations of **1** or its structural isomers.[7a] In those cases with nitric acid as the oxidant unsaturation is first produced in a six-membered chelate ring of the complex. Some effort was made during the course of this work to oxidize the nickel(II) ligand radical intermediates with external oxidizing agents. It seemed possible that when the oxidant was another radical species or the corresponding nickel(III) complex, as proposed in this work, some subtle factor such as the steric requirements of these oxidants might account for the unexpected preferential formation of imine in the five-membered ring of the macrocycle. However, all efforts to produce unsaturated species were unsuccessful. Nitric acid, which is known to be an effective oxidizing agent for **1**, is effective only at concentrations greater than ca. 2 *M*.[17] Under such acidic conditions, the nickel(II) ligand radical species simply reverted back to the corresponding nickel(III) species.

It is worthwhile at this point to consider the results of this study, in light of the considerable amount of work that has been done concerning the oxidation of ligands by metals in "high" oxidation states.[18,19] A good deal of effort has been made to establish that some of these oxidations proceed by an inner-sphere electron transfer process by spectroscopic searches for an intermediate formed before the electron transfer occurs. In fact, intermediates have been observed in some cases;[20] in other instances, the form of the rate law for the process has been used to argue for the presence of such intermediates.[21,22] However, as Taube has pointed out, the latter arguments provide no information on the nature of such an intermediate but only suggest its presence.[23] For a reaction of the type $M_{ox} + S_{red} \rightarrow M_{red} + S_{ox}$ there could exist two intermediates corresponding to M_{ox}–S_{red} and M_{red}–S_{ox} prior to formation of the products. Whether or not both forms actually exist for a single system is a very interesting and complicated question. To unequivocally answer such a question in the absence of experimental evidence for both species would require a detailed description of the potential energy surface for the system. Such a description is obviously unavailable for systems as complicated as those normally considered. In general the question has not been treated by experimentalists in the area.

Although chemical evidence for radicals has been obtained in reactions of organic substrates with oxidizing metal ions,[19] to our knowledge, no species corresponding to M_{red}–S_{ox} have been directly observed in inner-sphere oxidations of organic substrates although some intermediates previously ascribed to M_{ox}–S_{red} might by chance be of this form. In general the reduced metal-oxidized substrate forms are prone to rapid dissociation, and this fact combined with a slow reaction would result in too low a concentration to be detected. In the present study, the nickel(II) ligand radical species provides a definitive example of the existence of a M_{red}–S_{ox} intermediate for an inter-sphere process. The rapid dissociation of a potential reduced metal ion-oxidized substrate complex which would prevent its observation in other systems is not possible for these nickel(II) ligand radical species, where the complexation of the other amine donors in the macrocycle prevents metal–ligand bond cleavage at the radical site. It is important to note that we did not directly observe the species $Ni^{III}{-}N\!<\!:$, which probably really corresponds to M_{ox}–S_{red} in this system. The 540-nm charge transfer band observed for **5** might be taken as evidence that such a species is in fact an excited state of **5**. Identification of the radical intermediate was conveniently accomplished using ESR spectroscopy because of the coupling of the unpaired electron spin to the spins of the nitrogen and hydrogen nuclei. This identification was also a fortuitous result of the low spin nature of the nickel(II) ion in this complex. Such direct identification was not possible for an analogous silver(III) decomposition, where an intensely colored intermediate was diamagnetic, presumably because of spin coupling of the silver(II) to the ligand radical.[5]

Finally, a recognition of the possibility of intramolecular ligand to metal electron transfer as was found in this work may provide some insight into what may at first appear to be unrelated phenomena. For example, Siegel and Armor recently reported that photoreduction of $Ru(NH_3)_6{}^{3+}$ to $Ru(NH_3)_6{}^{2+}$ occurred to a very small extent in acidic solution but was enhanced upon addition of alcohols such as 2-propanol to the solutions undergoing irradiation.[24] The product of the photolytic reaction was not detected but a possible intermediate was suggested, $[Ru(NH_3)_6\dot{O}H]^{2+}$. On the basis of our own results we believe that the species $[Ru^{II}(NH_3)_5\dot{N}H_2]^{2+}$ that could be formed in the initial step according to

$$Ru(NH_3)_6{}^{3+} \longrightarrow Ru(NH_3)_5\dot{N}H_2{}^{2+} + H^+$$

is a more likely possibility. Such a species can readily be reconciled to the observed product distribution. The possibility that photoreduction could produce an M_{red}–S_{ox} species has been previously recognized. As this paper was nearing completion, Hoffman et al. reported the details of flash photolysis studies of $Co(C_2O_4)_3{}^{3-}$.[25] These results strongly support earlier suggestions that a species such as $[Co^{II}(C_2O_4)_2(C_2O_4{}^-)]^{3-}$ is the primary product of photolysis. Absorption spectroscopic and chemical evidence was consistent with the presence of such a species.

Experimental Section

General. Starting materials were of reagent or comparable grade. Chromatographic grade neutral alumina was dried at 200° prior to use. The synthesis and the handling of anhydrous solutions of the Ni(III) complexes were performed with oven-dried glassware in a drybox.

Solvents. The sensitivity of the Ni(III) complexes in solution to reducing agents requires high solvent purity. The following procedures were adopted. Acetonitrile was purified by a modification of the procedure of Sherman and Olson[26] which involved removal of oxidizable impurities with N_2O_4, reflux and distillation from CaH_2, and a second distillation from CaH_2. Diethyl ether was distilled in a nitrogen atmosphere after standing over calcium hydride for at least 1 week. Both acetonitrile and diethyl ether were then passed through an alumina column immediately before use. Pyridine and triethylamine were refluxed over barium oxide and distilled in a nitrogen atmosphere. Deionized water was distilled from an alkaline permanganate solution.

Syntheses. Complex **1** (meso isomer) was prepared by Raney nickel-base reduction of the parent 4,11-diene complex according to the procedure described by Curtis.[27] The rac and meso forms were then separated using sodium oxalate. The purity of the meso isomer **1** was confirmed by NMR spectroscopy.

Complex **3** and the tetraimine form of **1** were prepared by published procedures.[28,15] N-Deuterated **1** was prepared by multiple recrystallizations of this complex from basic D_2O solution. Nitrosium perchlorate hydrate was prepared by the method of Brauer,[29] then dehydrated by pumping in vacuo over phosphorus pentoxide for at least 24 hr immediately prior to use. Typical preparations of other complexes are given below.

C-7 and C-14 Deuterated 1. This labeled complex was prepared by reduction of the 4,11-diene by the same procedure used for the synthesis of **1**,[27] except that D_2O was substituted for H_2O as the solvent and a concentrated solution of NaOD was used in place of solid NaOH. The NMR spectrum and the D/H ratio (by analysis) obtained for the material from this reaction, after recrystallization from basic H_2O, indicated that there was extensive deuteration of the C-6 and C-13 carbon atoms and the C-7 and C-14 methyl groups, ca. 60%. This complex was subsequently oxidized to the trivalent form **6** as described in a later preparation.

5,5,12,12-Tetramethyl-7,14-bis(trideuteriomethyl)-2,2,3,6,6,7,9,9,10,13,13,14-dodecadeuterio-1,4,8,11-tetraazacyclotetradecanenickel(II) Perchlorate. An earlier report by Goedken and Busch indicated that all protons attached to carbon atoms that are α to an imine function in the tetraimine complex derived from the 4,11-diene undergo proton exchange in dilute basic (pH ca. 8) solution.[15] Although not stated by them it is necessary that this exchange be performed under oxygen-free conditions. The following procedure was used. About 5–6 g of the yellow tetraimine complex was suspended in 40 ml of nitrogen saturated D_2O under a nitrogen atmosphere; sufficient concentrated NaOD–D_2O solution was added to give a pD of 8–9. Addition of this base generated a green color in the solution. The reaction flask was placed in a 75° oil bath and stirred for 1 hr under positive nitrogen pressure. After being removed from the heating bath, the solution was acidified with 1–2 ml of concentrated perchloric acid. After the solution had cooled to room temperature the greenish yellow solid product was collected, washed with ethanol, and air dried. Recovery from this step was 50–75%. After repeating the exchange twice more, the material was recrystallized by dissolving in a minimum amount of concentrated nitric acid and, with ice bath cooling, adding cold acetone. The yellow product was collected, washed with acetone, and dried in vacuo. The NMR spectrum of this material contained resonances only for the vinylic and gem-methyl protons. Exchange was thus estimated to be at least 95% complete at all of the other sites. Then 2.55 g (4.70 mmol) of this material, 0.15 g (0.66 mmol) of PtO_2, and 70 ml of D_2O were placed in a moderate pressure reaction apparatus,[30] and the apparatus was charged with 50 psi (gauge) D_2. The mixture was stirred for 24 hr and then the apparatus was opened to the atmosphere. To the reaction solution was added 0.09 g (0.7 mmol) of sodium oxalate and the solution heated for 30 min in a 95° water bath, then gravity filtered. To the filtrate was added 0.08 g (0.5 mmol) of calcium chloride dihydrate, and the solution heated briefly to 90° and gravity filtered. To this filtrate was added 1 ml of concentrated perchloric acid and the solution reduced in volume to 10 ml with a stream of air. The solids collected by filtration were recrystallized from hot, dilute perchloric acid, yield 1.6 g (2.9 mmol, 62%). The identity of this complex was confirmed by its NMR spectrum. This complex was oxidized to the trivalent form as outlined below.

5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradec-4-enenickel(II) Perchlorate, 10. A solution of 10 g (18.5 mmol) of 4,11-diene dissolved in 200 ml of water was treated, at 70°, with a sodium borohydride–borax mixture (0.5 g/0.1 g) in small portions over a 30-min period. After the addition was complete the solution was heated to 80° for 1 hr, cooled to room temperature, and allowed to stand overnight. The yellow crystalline material which formed was collected, washed with ethanol, and air dried. A second crop of material was obtained by evaporation of the filtrate to 150 ml and a third by acidification of this filtrate with perchloric acid. Examination of these fractions by NMR indicated that the first fraction contained the largest amount of the desired product. A variety of solvent mixtures were examined as solvents for thin layer (cellulose) and paper chromatography. Of these a mixture of 1-butanol (three parts), ethanol (one part), water (two parts), and concentrated hydrochloric acid (one part) gave a satisfactory separation (R_f dien ca. 0.5, R_f monoimine ca. 0.7). Preparative scale separations were done using a 1.75 × 16 in. column of microcrystalline cellulose (J. T. Baker). A saturated solution of the first fraction in the eluting mixture was applied to the column until a 0.5 in. band was obtained. Eluting the column at 35 ml/hr caused this band to separate into two broad bands. The first band was eluted in a volume of ca. 90 ml and had an absorption maximum at 450 nm. The second band, which was eluted in ca. 150 ml, had an absorption maximum at 435 nm, as expected for the starting complex. The fraction containing the first band was evaporated to a paste, taken up in water, and acidified with perchloric acid. The NMR spectrum of the orange-yellow solid obtained confirmed this product to be the monoimine complex **10**.

Bis(acetonitrile)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecanenickel(III), 2. A solution of 2.50 g (4.61 mmol) of **2** in 100 ml of acetonitrile was stirred under anhydrous conditions for 1 hr with 0.70 g (5.4 mmol) of $NOClO_4$, then 100 ml of diethyl ether was added. The dark green solid product was collected by filtration and dried for several hours in vacuo, yield 2.6 g (3.6 mmol, 78%). Anal. Calcd for $Ni(C_{16}H_{36}N_4)(CH_3CN)_2(ClO_4)_3$: C, 33.2; H, 5.90; N, 11.6; Ni, 8.10; Cl, 14.7. Found: C, 33.1; H, 5.82; N, 11.8; Ni, 8.17; Cl, 14.4.

This complex could also be prepared by an "open air" method on the bench. The procedure was as follows. A mixture of 30 ml of reagent grade acetonitrile, 1.5 g (2.8 mmol) of **1**, 1 ml of concentrated perchloric acid, and 0.45 g (3.0 mmol) of $NOClO_4 \cdot H_2O$ was stirred for 45 min and filtered. The green solids were washed with diethyl ether and dried for several hours in vacuo, yield 1.8 g (2.5 mmol, 90%). The elemental analysis and infrared spectrum of this complex confirmed that it was identical with the material obtained by the first method.

Bis(acetonitrile)-1,4,8,11-tetraazacyclotetradecanenickel(III) Perchlorate, 4. This complex was prepared by the above procedures on a 1 g scale. Anal. Calcd for $Ni(C_{10}H_{24}N_4)(CH_3CN_2)(ClO_4)_3$: C, 26.3; H, 4.73; N, 13.1; Ni, 9.18; Cl, 16.6. Found: C, 26.7; H, 4.59; N, 13.3; Ni, 9.11; Cl, 16.4. Nickel(III) complexes **6** and **7** were prepared in similar fashion.

Physical and Chemical Methods. Proton NMR spectra were recorded on Varian A-60 or HA-220 MHz spectrometers. Trifluoroacetic acid was used as the solvent in all cases, with tetramethylsilane (TMS) as an internal standard. Visible–uv spectra and slow reaction kinetics were recorded on a Cary 14 recording spectrometer. Infrared spectra were recorded as mineral oil mulls on a Perkin-Elmer 457 spectrometer. Electron spin resonance spectra were recorded on Varian V-4502 or E-9 spectrometers. Flow experiments were performed using gravity feed bottles with a Y-shaped mixing device. Flow rates were such that there was a dead time of ca. 1 sec between mixing and observation of the solution in the ESR cavity. A flat quartz ESR solution cell was used to minimize the problem of high dielectric loss when working with aqueous or acetonitrile solutions. Simulation of ESR spectra was performed using a program developed by Mr. L. K. White of this department. Stopped flow kinetic experiments were performed using the apparatus of Dr. S. Smith of this department. The raw data as photographed oscilloscope traces were digitized using an OSCAR curve reader prior to kinetic analysis.

Quantitative determination of acid content was performed by titration with standardized NaOH solution. Iodine was determined by titration with standardized thiosulfate solution. Determination of the amount of nickel ion in solution titratable with ethylenediaminetetraacetic acid (EDTA) was done by adding an excess of standardized EDTA to the solution and back-titrating with standardized zinc nitrate solution. Work-up of solutions from the decomposition of N-deuterated **2** was performed using at least 0.1 *M* acid at all stages and vacuum drying of products over P_2O_5. Exposure to moist air was kept to a minimum. Experiments involving quenching of the red intermediate with various substrates, e.g., iodide and oxalate, were performed as follows. Water was rapidly added by syringe to the Ni^{III} complex to give a ca. 0.01 *M* solution. After stirring for a few seconds (or other times as noted) to allow the full development of the red color of the intermediate, the appropriate quenching agent was added as a solution (for anions, as its sodium salt) in a few milliliters of water. A five- to tenfold excess of quenching agent was generally used.

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Photochemistry of Metal–Metal Bonded Complexes. III. Photoreactivity of Hexacarbonylbis(η^5-cyclopentadienyl)dimolybdenum(I) and -ditungsten(I)

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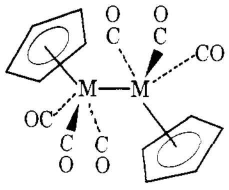
Abstract: The photolysis of $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ (M = Mo, W) in solution at 25° leads to efficient homolytic M–M bond cleavage. Photolysis in CCl_4 yields two molecules of the corresponding $(\eta^5\text{-}C_5H_5)M(CO)_3Cl$ per molecule of the M–M bonded species with quantum efficiency for dimer disappearance in the range 0.12–0.45 depending on M and the photolysis wavelength. Simultaneous photolysis of $M_2'(CO)_{10}$ (M′ = Mn, Re) and $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ yields $(OC)_5M'M(CO)_3(\eta^5\text{-}C_5H_5)$ complexes with good chemical yield. The photochemistry is discussed in terms of lowest excited states involving the population of an orbital which is σ-antibonding with respect to the M–M bond.

The photolysis of Mn and Re carbonyls containing direct metal–metal bonds was recently shown to result in homolytic cleavage of the metal–metal bond.[1-3] The photogenerated paramagnetic intermediates $M(CO)_5$ (M = Mn, Re) have some reactivity patterns in common with their isoelectronic analog $Co(CN)_5{}^{3-}$, and these d^7, 17-electron molecules react with halogens and alkyl halides apparently via a free radical mechanism.[1-4] Other metal carbonyls aside from Mn and Re have received some study[5] with respect to metal–metal bond cleavage and among these is $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$ (I), which was shown[6] to undergo efficient disproportionation upon photolysis in acetone solutions of Cl^-. Earlier work[7] also provides some evidence for a net heterolytic cleavage of the Mo–Mo bond upon prolonged photolysis in benzene solutions of PPh_3. Other workers claim that simple CO substitution products arise from the photolysis of I in the presence of nucleophiles such as $P(OPh)_3$[8] or PPh_3.[9] There seems to be no reported detailed studies of the photoreactivity of the third-row analog to I, $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$ (II). The structures of I and II are as shown below.[10]



I, M = Mo
II, M = W