**Table III.** Electrical Resistivity for $Eu_2RuH_6$

| $T$, °K | $\rho$, ohm cm | $T$, °K | $\rho$, ohm cm |
|---|---|---|---|
| 294 | $2.5 \times 10^5$ | 167 | $4.1 \times 10^6$ |
| 209 | $1.2 \times 10^6$ | 77 | $4.0 \times 10^9$ |

a $Eu^{II}Eu^{III}Ru^{I}H_6$ model and 3.24 BM for a $Eu^{III}{}_2Ru^0H_6$ model. These values are based on a consideration that one electron is occupying an $e_g$ ruthenium orbital in the mixed-valence model and two unpaired electrons are in the $e_g$ ruthenium orbitals for the trivalent model.

No field dependence within experimental limits was observed for $Eu_2RuH_6$ between 77 and 296°K from 3000 to 5700 Oe. A small but significant deviation from linearity in the curve of $\chi_A{}^{-1}$ vs. $T$ below 85°K was observed. It is possible that this deviation may be due to a small quantity of EuO impurity. EuO is ferromagnetic with a Curie temperature of 77°K.[16]

The results of the resistivity measurements are displayed in Table III.

Because of the possibility of fairly high contact and grain boundary resistances the indicated values of the resistivity are undoubtedly somewhat higher than the actual values. Nonetheless the order of magnitude and behavior with temperature strongly suggests that $Eu_2RuH_6$ is a semiconductor. The data could be fitted to the equation $\rho = \rho_0 e^{\Delta E/2kT}$ which describes semiconductors characterized by an activation energy $\Delta E$. The results in Figure 3 show the plot of log $\rho$ as a function of $1/T$. The value of $\Delta E$ was determined to be 0.15 eV.

**Acknowledgment.** We wish to acknowledge that this study was supported with a Cottrell College Science Grant administered by the Research Corp. We are also grateful to Professors B. Chamberlain, L. Katz, and J. Tanaka of the Department of Chemistry at the University of Connecticut for the use of some X-ray diffraction and DTA instrumentation. It is a pleasure to cite also the summer contribution of one of our undergraduates, Mr. Douglas Kuhn.

**Registry No.** $Eu_2RuH_6$, 55450-40-3; $EuH_2$, 13814-78-3; Ru, 7440-18-8.

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# Electrochemical Studies of Vanadium(III), -(IV), and -(V) Complexes of 8-Quinolinol in Acetonitrile. Formation of a Binuclear Mixed-Valence (IV,V) Complex

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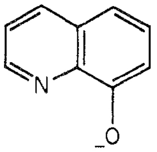
The electrochemistry of $VQ_3$, $VOQ_2$, $VO(OCH_3)Q_2$, and $VO(OH)Q_2$ (Q = 8-quinolinol anion) has been studied by cyclic voltammetry and controlled-potential coulometry in acetonitrile, dimethyl sulfoxide, and dimethylformamide at a platinum electrode. The complexes have been further characterized by infrared, uv–visible, and ESR spectroscopy and by magnetic susceptibility measurements. In acetonitrile $VQ_3$ is reversibly reduced by a one-electron process at −1.475 V vs. SCE and is irreversibly oxidized at +0.475 V. $VO(OCH_3)Q_2$ undergoes a half-electron reduction at −0.45 V to form a mixed oxidation state oxo-bridged dimer $[(V^VOQ_2){-}O{-}(V^{IV}OQ_2)]^-$. This dimer is reversibly oxidized at +0.025 V to give $[(V^VOQ_2){-}O{-}(V^VOQ_2)]$.

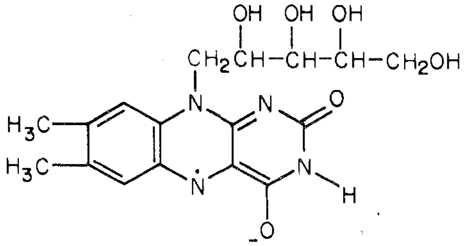
In recent years there has been increasing evidence for the biological importance of vanadium.[1] Several types of marine life contain vanadium, including the Ascidians[2] where it may function as an oxygen carrier.[3] Oxovanadium(IV) porphyrins commonly are found in petroleum, although their origins are unknown.[4] Recently vanadium also has been shown to be an essential nutrient in higher life forms.[1,5] It is involved in phospholipid oxidation, sulfur metabolism, and cholesterol biosynthesis[6] and probably plays a role in other biochemical processes.

The chemistry of vanadium also is of interest because of its similarity to molybdenum. The latter is an essential cofactor in a number of oxidation–reduction enzymes including xanthine oxidase, aldehyde oxidase, nitrate reductase, and nitrogenase.[7,8] The function of the molybdenum-containing enzyme, xanthine oxidase, is thought to be electron transport with the molybdenum associated with FAD–FADH· (flavine adenine dinucleotide–protonated radical of FAD).[7] Electrochemical studies of riboflavine (Rib)[9] have shown that the one-electron reduction product (Rib·⁻ or HRib·) complexes with metal ions, while the oxidized form does not. A similar electrochemical study of the molybdenum–riboflavine system also has been made.[10]

Because of the complexity of molybdenum–flavine systems, studies of model systems are an attractive simplification. 8-Quinolinol is structurally similar to the flavine radical, HRib·, when the isoalloxazine nucleus is in the enol form. Several complexes of molybdenum and 8-quinolinol are known[11] with the ligand bonded as an anion. This is similar to the enol form of the riboflavine radical anion. These model systems have been the basis for electrochemical studies of molybdenum(V) and -(VI)[12] and for NMR studies of molybdenum(V) and -(VI) and vanadium(V).[7] The present paper summarizes the results of an electrochemical and ESR investigation of va-



Q = 8-quinolinol anion (oxine)



riboflavine radical anion

nadium(III), -(IV), and -(V) complexes of 8-quinolinol as models for possible vanadium–flavine interactions.

Although vanadium complexes have been studied extensively by electrochemistry in aqueous solution, data for their oxidation–reduction properties in aprotic solvents are limited.[13–16] Furthermore, hydrogen bonding of water to the lipids and protein fragments of flavoenzymes may result in an aprotic environment[17] for the metalloflavine group in the enzyme. Hence, the present studies have been undertaken in acetonitrile, dimethyl sulfoxide (DMSO), and dimethylformamide (DMF).

## Experimental Section

Cyclic voltammetric measurements were made with a three-electrode potentiostat–amperostat constructed with solid-state operational amplifiers.[18] The voltammograms were recorded on a Hewlett-Packard Moseley Model 7030A X-Y recorder. A Wenking Model 61RH potentiostat was used for controlled-potential electrolysis with the current–time curves recorded by a Sargent Model SR strip-chart recorder. All electrochemical measurements were made inside a Vacuum Atmosphere Corp. Dri-Train HE-193-1 Dri-Lab glove box filled with purified nitrogen or argon and with provisions for external connections to the potentiostats.

The electrochemical cell consisted of a 100-ml electrolytic beaker and a Leeds and Northrup polyethylene electrochemical cell top. The cell top supported the electrodes and the auxiliary compartment (a Pyrex tube with a fine-porosity frit on the end). The top also had access holes for the addition and withdrawal of samples.

The working electrode for cyclic voltammetry was a Beckman platinum-inlay electrode. For controlled-potential electrolysis a cylindrical platinum-mesh electrode was used. The auxiliary electrode was a similar, smaller piece of platinum mesh. The reference electrode consisted of a silver wire coated with AgCl in a Pyrex tube having a small soft-glass cracked-bead tip. The electrode was filled with a solution of aqueous tetramethylammonium chloride (Matheson Coleman and Bell) with the concentration adjusted such that the electrode potential was 0.000 V vs. SCE. The reference electrode was placed inside a Luggin capillary in the cell assembly.

Infrared spectra of the solid complexes in KBr disks were recorded with a Perkin-Elmer Model 621 spectrophotometer. The uv–visible spectra for solutions of the complexes were recorded with a Cary Model 14 spectrophotometer. ESR spectra were obtained on a Varian Model V 4500 spectrometer by use of a standard flat-faced quartz solution cell. Magnetic susceptibility measurements were made by the Gouy method with diamagnetic corrections through use of Pascal's constants.[19]

**Reagents.** Spectroquality acetonitrile obtained from Matheson Coleman and Bell was found to contain no significant electrochemically active impurities. To minimize the amount of water present activated Linde molecular sieve was added to each bottle. Dimethyl sulfoxide (DMSO) (J. T. Baker Analyzed reagent) also was found to be electrochemically pure; the water content varied from 0.02 to 0.05% prior to the addition of molecular sieve. Spectroquality *N*,*N*-dimethylformamide (DMF) (Matheson Coleman and Bell) decomposed at a significant rate and was vacuum distilled over $P_2O_5$ before use.

Tetraethylammonium perchlorate (TEAP) and tetraethylammonium fluoroborate ($TEABF_4$) were used as supporting electrolytes. TEAP was prepared by the stoichiometric combination of reagent grade perchloric acid and reagent grade tetraethylammonium bromide. The crystallized product was collected, washed, and recrystallized from cold water. $TEABF_4$ (Southwestern Analytical Chemicals) was used as received. Tetraethylammonium hydroxide (TEAOH) was obtained from K & K Laboratories as a 40% aqueous solution. Tetrabutylammonium hydroxide (TBAOH) was obtained from Matheson Coleman and Bell as a 25% solution in methanol.

**Preparation of Complexes. 1. Tris(8-quinolinolato)vanadium(III).** Preparation of $VQ_3$ was first attempted by the method of Bielig and Bayer,[20] the only change being that the starting material used was $VCl_3$ (Alfa Inorganic Chemicals) rather than $HV(SO_4)_2{\cdot}6H_2O$. Attempts at refluxing under $N_2$ repeatedly led to partial oxidation to $VOQ_2$. $VQ_3$ was successfully synthesized by doing all the work in the drybox. To 2.90 g (20 mmol) of 8-quinolinol (Matheson Coleman and Bell) dissolved in 200 ml of reagent grade absolute methanol was added 1.05 g (6.6 mmol) of $VCl_3$; the solution immediately turned red-brown. The solution was stirred for a few hours, heated only by the magnetic stirrer motor. The solution volume was then taken down to about 50 ml by a rotary vacuum evaporator. The chilled solution was then filtered, washed three times with 20 ml of cold absolute methanol, and suction dried. Analysis indicated that the compound was isolated with one water molecule, $VQ_3{\cdot}H_2O$. Anal. Calcd for $VC_{27}H_{20}N_3O_4$: C, 64.68; H, 4.02. Found: C, 64.23; H, 4.45. For the magnetic susceptibility measurements a larger quantity of $VQ_3$ was prepared. Analysis indicated that the compound was isolated as $VQ_3{\cdot}1.5H_2O$.

**2. Oxobis(8-quinolinolato)vanadium(IV).** $VOQ_2$ was prepared by the method of Bielig and Bayer.[20] In addition to being washed with water to remove the sulfate, the product was washed with ethanol to remove any free 8-quinolinol. The product was not vacuum dried and analysis indicates that it was isolated as $VOQ_2{\cdot}0.5H_2O$. Anal. Calcd for $VC_{18}H_{13}N_2O_{3.5}$: C, 59.35; H, 3.60. Found: C, 59.74; H, 3.61.

**3. Oxohydroxobis(8-quinolinolato)vanadium(V).** $VO(OH)Q_2$ was prepared by the method of Amos and Sawyer,[7] as modified from earlier procedures.[20–22] The product was purified from hot benzene.

**4. Oxomethoxybis(8-quinolinolato)vanadium(V).** $VO(OCH_3)Q_2$ was prepared by the method of Blair et al.[21] and Nakamoto et al.[22] The procedure was modified only in that fresh absolute methanol was added for the second and third refluxes in order to shift the reaction completely to the methoxy product.

**5. (Tetra-*n*-butylammonium){μ-oxo-[oxobis(8-quinolinolato)vanadium(V)][oxobis(8-quinolinolato)vanadium(IV)]}.** $[(n\text{-Bu})_4N]^+[(VOQ_2){-}O{-}(VOQ_2)]^-$ was prepared by mixing equimolar amounts of the vanadium(V) complex, the vanadium(IV) complex, and base in absolute methanol (in the drybox). Specifically, 0.835 g of $VO(OH)Q_2$, 0.820 g of $VOQ_2$, and 3.1 ml of tetrabutylammonium hydroxide (25% in methanol) were mixed in 150 ml of methanol. After being stirred overnight, heated only by the magnetic stirrer, the solution was transferred to a clean flask, leaving a negligible residue. The volume was reduced by vacuum evaporation and the flask was chilled in an attempt to cause crystallization to begin. Crystallization did not occur and thus the solvent was taken off to dryness, leaving the product as a green crusty material in the bottom of the flask. Analysis indicates that the isolated compound has the formula $[(n\text{-Bu})_4N]^+[(VOQ_2){-}O{-}(VOQ_2)]^-$. Vanadium oxide vaporization may have interfered with the hydrogen determination. Anal. Calcd for $V_2C_{52}H_{60}N_5O_7$: C, 64.46; H, 6.24. Found: C, 64.69; H, 7.54.

## Results

**Electrochemistry.** The electrochemical behavior of the vanadium(III)–8-quinolinol complex, $VQ_3$, in acetonitrile is illustrated by Figure 1a, which indicates a cathodic couple at −1.475 V vs. SCE and an anodic couple at +0.45 V. In both cases the anodic and cathodic peak potential separations are near the theoretical value of 0.059 V for a reversible one-electron process. A more cathodic scan indicates another couple at about −1.97 V, but the peaks are less distinct than the others because the base line current increases sharply at −2.0 V due to solvent reduction.

Controlled-potential coulometry for the $VQ_3$ complex at −1.60 V establishes that the reduction is a one-electron-

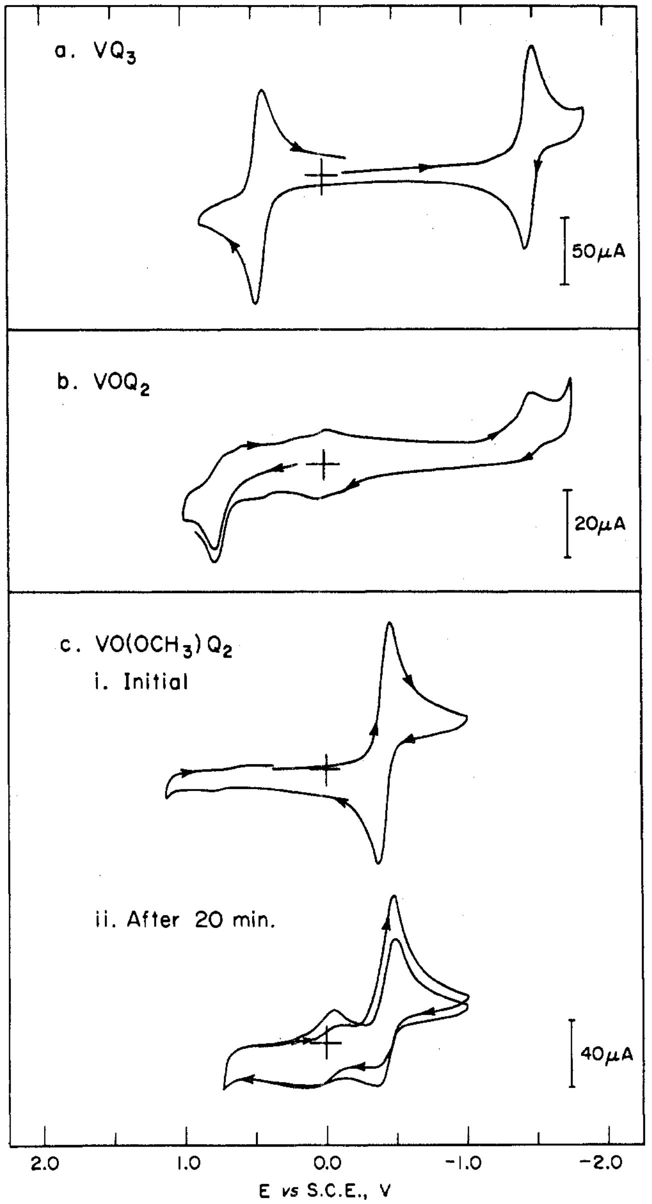


**Figure 1.** Cyclic voltammograms of 1 m*M* $VQ_3$, 0.1 m*M* $VOQ_2$, and 1 m*M* $VO(OCH_3)Q_2$ in acetonitrile containing 0.1 *F* TEAP; scan rate 0.2 V/sec.

per-vanadium process and yields the anodic peak of the couple on an initial scan. Subsequent coulometry of the product solution at −1.25 V also indicates a one-electron process; the cyclic voltammogram of the product solution is analogous to that for a $VQ_3$ solution.

Unlike the −1.475-V couple, the +0.45-V couple is not reversible on a long time scale. Controlled-potential coulometry at +0.60 V indicates that the oxidation of $VQ_3$ is a one-electron process but the product solution does not exhibit the cathodic peak of the original couple. Instead, the cathodic scan yields new reduction peaks at +0.55, +0.275, −0.425, −1.20, and −1.55 V, but no new oxidation peaks. Scanning for two cycles brings about the reappearance of the +0.425-V reduction peak in place of the peaks at +0.55 and +0.275 V.

The electrochemistry of $VOQ_2$ in acetonitrile is difficult to study because of its low solubility. Figure 1b indicates that only an oxidation peak at +0.775 V and a reduction peak at −1.475 V are observed. The oxidation appears to be a one-electron process, although the coulometric data are not conclusive. After controlled-potential coulometry at +0.80 V, a cathodic scan gives small reduction peaks at +0.275 and −0.025 V; the −1.475-V peak is unchanged from the original solution.

**Table I.** Summary of Controlled-Potential Electrolysis Data in Acetonitrile

| | | Potentials, V vs. SCE | | | |
|---|---|---|---|---|---|
| Compd | Couple | $E'$ | $E_{pc}$ | $E_{pa}$ | $e^-$ per vanadium |
| $VQ_3$ | V(III) ⇌ V(II) | −1.475 | | | 1 |
| | V(III) → V(IV) | (+0.45) | | +0.475 | 1 |
| $VOQ_2$ | V(IV) → V(V) | | | +0.775 | 1 (?) |
| $VO(OCH_3)Q_2$ (a) | V(V) → V(IV) | (−0.40) | −0.45 | | $^1/_2$ |
| (b) | V(IV) → V(V) | | | +0.10 | $^1/_2$ |
| (c) | V(V) → V(IV) | | −0.05 | | $^1/_2$ |

The solubility of the vanadium(V) complex $VO(OH)Q_2$ in acetonitrile is even less than that of $VOQ_2$. Cyclic voltammograms indicate a couple at +0.025 V, but no meaningful coulometric data have been obtained.

The methoxy form of the vanadium(V)-8-quinolinol complex $VO(OCH_3)Q_2$ is sufficiently soluble in acetonitrile to give well-defined cyclic voltammograms (see Figure 1c). The initial cyclic scan indicates a couple at −0.40 V with nearly equal peak heights, and a peak separation close to that expected for a reversible one-electron process. After the solution has aged for 20 min, a new couple is observed at +0.025 V (Figure 1c) and the height of the original oxidation peak is considerably smaller. Scanning continuously for two cycles indicates that the peak heights of the new couple increase and that those of the original couple decrease. Controlled-potential coulometric reduction at −0.50 V causes both reduction peaks to disappear; the product solution gives a cyclic voltammogram with only an oxidation peak at +0.10 V on an initial anodic scan. Controlled-potential electrolysis at +0.60 V for the product solution yields a solution that has a reduction peak at −0.05 V but not the reduction peak at −0.45 V. Finally, coulometric reduction of this solution at −0.20 V yields a product with the +0.10-V oxidation peak.

As indicated in Table I, each controlled-potential coulometric transformation in this series involves 0.5 electron per vanadium. When the initial reduction at −0.50 V is carried out in DMSO and DMF, a value of 0.5 electron per vanadium also is obtained. Figure 2 indicates the electron stoichiometry for the reduction at −0.50 V as a function of the extent of electrolysis. The number of coulombs passed up to a given time is determined from the integrated current–time curve; the extent of the reduction reaction is determined at each of these times by measuring the reduction peak height of a cyclic voltammogram.[23] The data of this figure indicate that the reduction initially is a one-electron process but that at the completion of the electrolysis 0.5 electron per vanadium is added to the complex. Such a change implies that the initial product species combines with the reactant to form a nonelectroactive adduct or dimer.

**Dimer.** An equimolar mixture of $VO(OCH_3)Q_2$ and $VOQ_2$ in acetonitrile gives the cyclic voltammogram illustrated in Figure 3a. Both the couple at −0.40 V and the one at +0.025 V are present, as is the $VOQ_2$ oxidation peak at +0.775 V. The identity of the reduction peak at +0.525 V is not certain. When small amounts of aqueous tetraethylammonium hydroxide (TEAOH) are added (a fraction of the total vanadium present), the rest potential shifts negatively and the peak heights change. The oxidation peaks at −0.35 and +0.775 V and the reduction peak at +0.525 V disappear, the reduction

**Table II.** Infrared V=O Stretching Frequencies and Magnetic Moments for the Solid Vanadium(III), -(IV), and -(V) Complexes of 8-Quinolinol

| | V=O ir band, $cm^{-1}$ | | Magnetic moments, BM | |
|---|---|---|---|---|
| Compd | This work | Previous data | This work (theor) | Previous data |
| $VQ_3$ | | | 2.80 (2.83) | 2.77,[24] 2.83[30] |
| $VOQ_2$ | 945 | 975,[25] 965,[28] 979[29] | 1.51 (1.73) | 1.73[25] |
| $VO(OCH_3)Q_2$ | 955 | 950[28] | | Diamag[30] |
| $VO(OH)Q_2$ | 950 | 950,[20] 952,[21] 955[27,28] | Diamag | |
| $[(n\text{-}Bu)_4N]^+[V_2O_3Q_4]^-$ | 880 | | 1.36 (1.73) | |
| $V_2O_3Q_4$ | | 955[27] | | |
| $M^+[VOQ_2O)]^-$ ($M^+ = Li^+, Na^+, K^+, NH_4^+$) | | 860-900[28] | | |

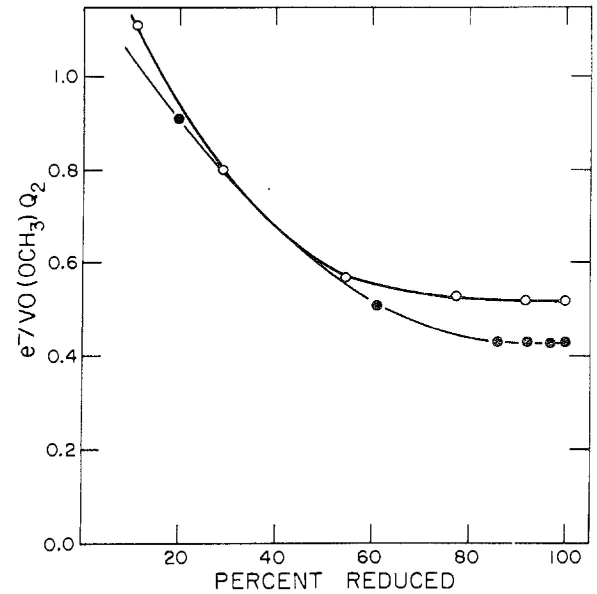


**Figure 2.** Electron stoichiometry as a function of percent electrolyzed for the controlled-potential electrolysis of 1 m*M* $VO(OCH_3)Q_2$ in 0.1 *F* TEAP-DMSO at −0.50 V. Results given are for two separate analyses.

peaks at −0.05 and −0.45 V decrease in height, and the +0.10-V oxidation peak height increases for an initial anodic scan.

When enough base is added such that the formal concentrations of $VO(OCH_3)Q_2$, $VOQ_2$, and TEAOH are all equal, only the couple at +0.025 V is present. A cyclic voltammogram for this combination with a slight excess of base is illustrated by Figure 3b; the oxidation peak at +0.45 V is due to the excess base. Controlled-potential coulometric oxidation at +0.60 V and subsequent reduction of the product at −0.20 V each yield electron stoichiometries of 0.5 electron per vanadium. Such results imply that the equimolar combination of $VO(OCH_3)Q_2$, $VOQ_2$, and TEAOH results in the formation of a mixed oxidation state binuclear vanadium complex. A compound with the same electrochemical properties has been prepared and isolated as a solid by mixing equimolar amounts of $VO(OH)Q_2$, $VOQ_2$, and TBAOH in methanol. When dissolved in acetonitrile it gives the cyclic voltammogram shown in Figure 3c.

**Spectroscopy.** This group of vanadium–8-quinolinol complexes has been further characterized by determining their uv–visible spectra, ir spectra, and magnetic moments.

The uv–visible spectra for the complexes are shown in Figure 4. The colors for solutions of the complexes in acetonitrile are as follows: $VQ_3$, red-yellow; $VOQ_2$, green-yellow; $VO(OCH_3)Q_2$, red-brown, $VO(OH)Q_2$, gray-brown; $[(n\text{-}Bu)_4N]^+[V_2O_3Q_4]^-$, yellow. The spectrum for $VQ_3$ is the same as it is in methanol[20] and is the same as the diffuse-reflectance spectrum.[24] The spectrum for $VOQ_2$ agrees with the diffuse-reflectance spectrum[25] but does not exhibit the absorption peak at 469 nm (in place of the 550-nm peak) that was reported by Selbin.[26] The spectra of $VO(OCH_3)Q_2$ and $VO(OH)Q_2$ are in agreement with previous studies.[20,21]

The infrared vanadium–terminal oxygen stretching frequencies of the complexes as well as their magnetic moments are summarized in Table II.

The ESR spectra of $VOQ_2$ and of the binuclear divanadium(IV,V) complex $[(n\text{-}Bu)_4N]^+[V_2O_3Q_4]^-$ in acetonitrile are shown in Figure 5. Both give eight-line spectra

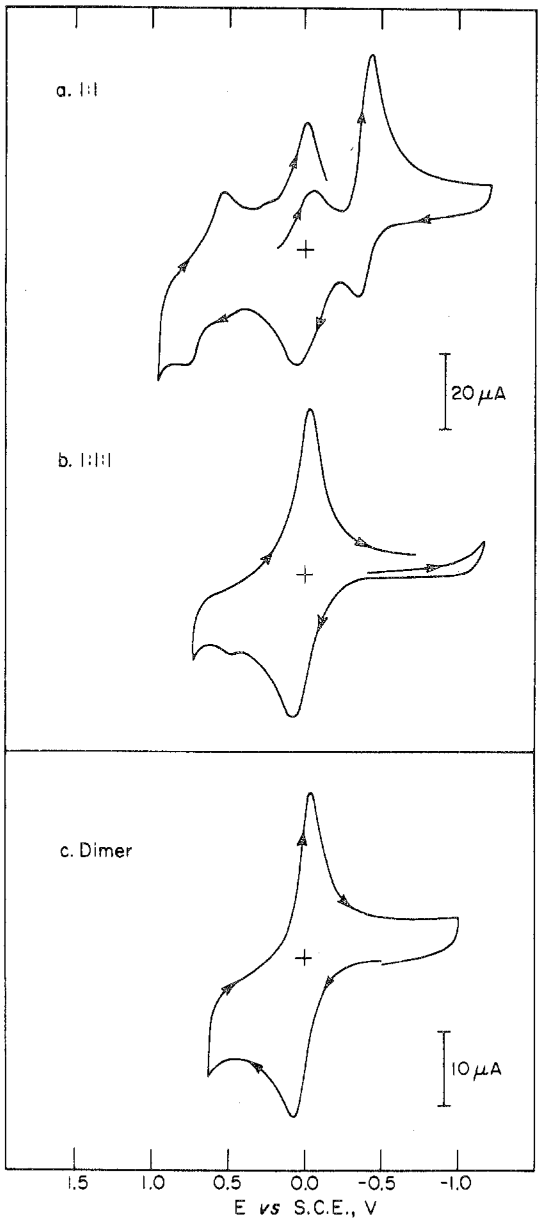


**Figure 3.** Cyclic voltammograms in 0.1 *F* TEAP-acetonitrile solutions of (a) 0.5 m*F* $VO(OCH_3)Q_2$ and 0.5 m*F* $VOQ_2$, (b) 0.5 m*F* $VO(OCH_3)Q_2$, 0.5 m*F* $VOQ_2$, and 0.5 m*F* TEAOH, and (c) 0.25 m*F* $[(n\text{-}Bu)_4N]^+[V_2O_3Q_4]^-$. Scan rate was 0.2 V/sec.

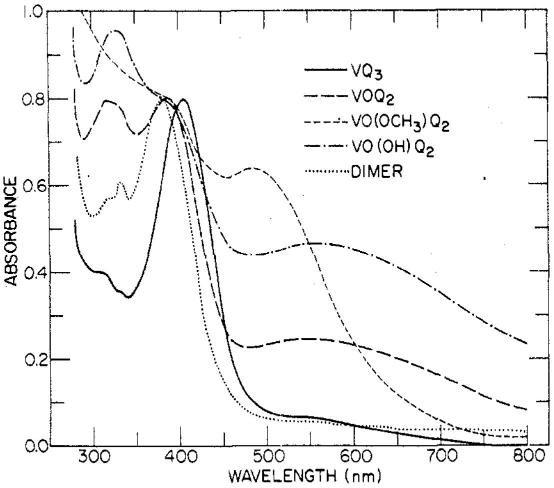


**Figure 4.** Absorption spectra for vanadium–8-quinolinol complexes in acetonitrile, including dimeric oxo-bridged $[(n\text{-}Bu)_4N]^+[V_2O_3Q_4]^-$.

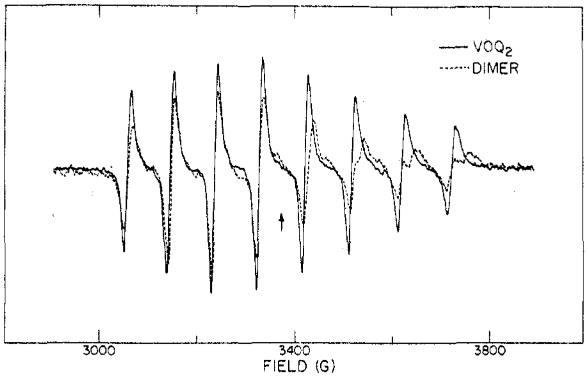


**Figure 5.** ESR spectra of 0.1 m*F* $VOQ_2$ and 0.1 m*F* $[(n\text{-}Bu)_4N]^+[V_2O_3Q_4]^-$ in acetonitrile. Position of DPPH resonance indicated by arrow.

that are characteristic of the IV oxidation state of the $^{51}V$ isotope (nuclear spin $^7/_2$) and have average *g* values of 1.98. Splittings are apparent on the right side of the spectrum for the binuclear complex which are indicative of complexation different from that in $VOQ_2$[31] and possibly of some exchange between the IV and V oxidation states.

**Other Solvents.** The electrochemical properties of the vanadium(III,IV,V)-8-quinolinol complexes in DMSO and DMF are nearly identical with one another but are significantly different from those in acetonitrile. The cyclic voltammograms of $VQ_3$ in DMSO and DMF are identical and differ from that in acetonitrile only in that the couple at +0.45 V is not reversible. This indicates that in DMSO and DMF the oxidation product undergoes a chemical reaction before it can be reduced on the reverse scan of the cyclic.

The initial oxidation peak for $VOQ_2$ is shifted to +0.50 V in DMSO or DMF and is reversible; a small reduction peak is observed at 0.00 V which increases in size after coulometric oxidation at +0.60 V.

In DMSO the cyclic voltammogram for $VO(OH)Q_2$ has a large reduction peak at 0.00 V for an initial cathodic scan and a couple at +0.50 V for the reverse scan. Following the coulometric reduction of the 0.00-V peak, the +0.50-V oxidation peak is present for an initial anodic scan. After coulometric oxidation at +0.60 V, the original reduction peak at 0.00 V is restored.

In both DMSO and DMF a similar series of controlled-potential electrolyses has been carried out on $VO(OCH_3)Q_2$. In this case, the initial reduction peak is at −0.45 V and is part of a reversible couple. The couple at +0.50 V also is present, but with much smaller peak heights. The series of electrolyses includes reduction at −0.50 V, oxidation at +0.60 V, and reduction at −0.20 V. After the initial reduction at −0.50 V, all of the cyclic voltammograms in this series correlate with those for the controlled-potential electrolyses of $VO(OH)Q_2$ and $VOQ_2$.

The controlled-potential electrolysis products of $VO(OCH_3)Q_2$ in DMSO also have been examined by ESR. The initial solution does not have a signal, but the product from reduction at −0.50 V gives an eight-line ESR spectrum that is characteristic of $d^1$ vanadium(IV). The spectrum, which is 900 G wide with a *g* value of 2.0, disappears after anodic electrolysis at +0.60 V and reappears after reduction at −0.20 V. The ESR results for $VO(OH)Q_2$ and $VOQ_2$ and their electrolysis products also are consistent with the electrochemical data.

The vanadium–8-quinolinol complexes and their electrolysis products in DMSO also have been studied by uv–visible spectrophotometry. The results correlate with the data from the cyclic voltammetric and ESR studies.

The cyclic voltammograms of the binuclear divanadium(IV,V) complex in DMSO and DMF are similar to each other but different from those in acetonitrile. The initial anodic scan in DMSO shows a small oxidation peak at about +0.50 V and a very large peak at +0.80 V. Small reduction peaks also are observed at +0.475 and 0.00 V. With the addition of acid, the +0.80-V peak becomes negligible, while the other peaks remain the same size. The initial anodic scan in DMF is identical except that the reduction peak at +0.475 V is not present. The addition of acid has the same effect as in DMSO.

## Discussion and Conclusions

The chemical and electrochemical reactions of the vanadium–8-quinolinol complexes in acetonitrile are summarized in Table III on the basis of the electrochemical and spectroscopic data. The $VQ_3$ complex is reversibly reduced to $VQ_3^-$ at −1.475 V and further reduced to a V(I) species at −1.975 V. The complex is oxidized by one electron to $VQ_3^+$ at +0.475 V with subsequent hydrolysis probably giving $VOQ_2$ (the cyclic voltammograms of the electrolysis products indicate that a mixture of species is formed). The $VOQ_2$ complex is oxidized to $VOQ_2^+$ at +0.775 V followed by hydrolysis to give $VO(OH)Q_2$.

The $VO(OCH_3)Q_2$ complex is reversibly reduced by one electron to $[VO(OCH_3)Q_2]^-$ at −0.40 V; the anion reacts with a molecule of $VO(OCH_3)Q_2$ and a molecule of water to form the mixed oxidation state dimer $[(V^VOQ_2)\text{–}O\text{–}(V^{IV}OQ_2)]^-$ (see Table III). $VO(OCH_3)Q_2$ also is hydrolyzed by residual water in the solvent to give $VO(OH)Q_2$ and methanol. The $VO(OH)Q_2$ complex is reduced to $[VO(OH)Q_2]^-$ at −0.05 V followed by a reaction analogous to that for $[VO(OCH_3)Q_2]^-$ to give the binuclear, mixed oxidation state complex.

An equimolar mixture of $VO(OCH_3)Q_2$, $VOQ_2$, and base in methanol also results in the formation of the binuclear complex (eq 1). Likewise, an equimolar mixture of $VO(OH)Q_2$, $VOQ_2$, and base in methanol yields the same product (eq 2).

$$VO(OCH_3)Q_2 + VOQ_2 + OH^- \rightarrow [(VOQ_2)\text{–}O\text{–}(VOQ_2)]^- + CH_3OH \qquad (1)$$

$$VO(OH)Q_2 + VOQ_2 + OH^- \rightarrow [(VOQ_2\text{–}O\text{–}(VOQ_2)]^- + H_2O \qquad (2)$$

This IV–V dimer has been synthesized and isolated as the tetra-*n*-butylammonium salt, $[(n\text{-}Bu)_4N]^+[(VOQ_2)\text{–}O\text{–}(VOQ_2)]^-$. The elemental analysis is consistent with this formula. Also, its electrochemical properties are identical with those of the electrochemically produced species (see Figure 3). The magnetic moment data indicate that the binuclear compound has one unpaired electron, which is consistent with a mixed oxidation state IV–V dimer.

**Table III.** Summary of Chemical and Electrochemical Reactions in Acetonitrile

| Vanadium | Reaction | Potentials, V vs. SCE | | |
|---|---|---|---|---|
| | | $E'$ | $E_{pc}$ | $E_{pa}$ |
| V(III) | $VQ_3 + e^- \rightleftharpoons VQ_3^-$ | −1.475 | | |
| | $VQ_3 \rightleftharpoons VQ_3^+ + e^-$ | +0.45 | | |
| | $VQ_3^+ + H_2O \rightarrow VOQ_2 + H_2Q^+$ | | | |
| V(IV) | $VOQ_2 \rightarrow VOQ_2^+ + e^-$ | | | +0.775 |
| | $VOQ_2^+ + H_2O \rightarrow VO(OH)Q_2 + H^+$ | | | |
| V(V) (a) | $VO(OCH_3)Q_2 + H_2O \rightleftharpoons VO(OH)Q_2 + CH_3OH$ | | | |
| | $VO(OCH_3)Q_2 + e^- \rightleftharpoons [VO(OCH_3)Q_2]^-$ | −0.40 | | |
| (b) | $VO(OH)Q_2 + e^- \rightarrow [VO(OH)Q_2]^-$ | | −0.05 | |
| (c) | $[VO(OCH_3)Q_2]^- + VO(OCH_3)Q_2 + H_2O \rightarrow [(VOQ_2)\text{-}O\text{-}(VOQ_2)]^- + 2CH_3OH$ | | | |
| | $[VO(OH)Q_2]^- + VO(OH)Q_2 \rightarrow [(VOQ_2\text{-}O\text{-}(VOQ_2)]^- + H_2O$ | | | |
| (d) | $[(VOQ_2)\text{-}O\text{-}(VOQ_2)]^- \rightleftharpoons [(VOQ_2)\text{-}O\text{-}(VOQ_2)] + e^-$ | +0.025 | | |
| | $[(VOQ_2)\text{-}O\text{-}(VOQ_2)] + H_2O \rightleftharpoons 2VO(OH)Q_2$ | | | |

The IV–V dimer is reversibly oxidized to a V–V dimer $[(VOQ_2)–O–(VOQ_2)]$ at +0.025 V. Because the cyclic voltammetric data indicate that $VO(OH)Q_2$ and the V–V dimer are both reduced at −0.05 V, this implies that an equilibrium may exist between the two species; the dimer probably predominates. Such a dimeric vanadium(V) complex has been discussed previously,[21,27,32] with the dimer being formed by dehydration of two molecules of $VO(OH)Q_2$ at 250°[32] (eq 3). The reaction proceeds more quantitatively by

$$2VO(OH)Q_2 \rightarrow (VOQ_2)\text{–}O\text{–}(VOQ_2) + H_2O \qquad (3)$$

use of the ester derivatives ($VO(OCH_3)Q_2$, $VO(OCH_2CH_3)Q_2$, etc.).[21] The uv–visible and infrared spectra for the dimer have been reported recently.[27]

Comparison of the V═O stretching frequencies in Table II provides additional evidence that the binuclear complex indicated by eq 1 and 2 is a mixed oxidation state dimeric anion. For some time there was the belief[20-22] that for this group of vanadium–8-quinolinol complexes the vanadium atom and two oxine groups were in a plane with the terminal oxygen and a sixth ligand trans to each other to give an octahedral configuration. On the basis of this structure the V═O stretching frequency should be dependent on the sixth ligand due to a trans effect.[28] However, more recent work (dipole moments,[33] crystal structures,[34] infrared spectra,[27] and NMR spectra[7]) provides convincing evidence that the sixth ligand is cis to the terminal oxygen. Nonetheless, the sixth ligand does affect the V═O infrared frequency. Table II summarizes the observed bands for the complexes and indicates that the $VOQ_2$ complex of the present study probably has a coordinated water molecule. This would account for the shift of the band to 945 $cm^{-1}$ from the 970 $cm^{-1}$ observed by others. The V═O band for the vanadium(V) dimer $V_2O_3Q_4$ is at 955 $cm^{-1}$ (which is almost identical with the monomeric vanadium(V) complexes[27]) with the bridging oxygen acting as the sixth ligand. The V═O band for several vanadium(V)–8-quinolinol salts,[28] $M^+[VOQ_2O]^-$, is observed at 860–900 $cm^{-1}$. The low stretching frequency is believed to be due to the negative charge of the anion. Comparison of the 880-$cm^{-1}$ V═O band for the binuclear divanadium(IV,V) complex of the present study to that for the vanadium(V)–8-quinolinol salts supports the conclusion that the complex is an anion.

Interpretation of the uv–visible spectra of the complexes (Figure 4) is difficult, but the spectrum for the binuclear complex clearly is shifted from those for the other complexes and exhibits some similarity to that of the V–V dimer ($V_2O_3Q_4$).[21,27]

The electrochemistry of the complexes in DMSO and DMF is basically the same as in acetonitrile, except for the effect of their water content. The reduction products of $VO(OCH_3)Q_2$ and $VO(OH)Q_2$ are oxidized at +0.50 V in DMSO and DMF, which is characteristic of $VOQ_2$, while in acetonitrile the oxidation occurs at +0.10 V due to the IV–V binuclear complex. Because the coulometric data indicate a half-electron-per-vanadium reduction in all three solvents, the IV–V binuclear complex may also be formed in DMSO and DMF, but it is not stable. This is supported by the cyclic voltammograms of the binuclear complex in DMSO and DMF, which indicate that it decomposes by a hydrolysis reaction. This reaction (eq 4) appears to go to completion because the

$$[(VOQ_2)\text{-}O\text{-}(VOQ_2)]^- + H_2O \rightarrow VO(OH)Q_2 + VOQ_2 + OH^- \qquad (4)$$

addition of acid causes the +0.80-V hydroxide ion oxidation peak to decrease to a negligible size while the size of the other peaks is not affected.

**Vanadium Complexes as Biological Models.** The oxidation–reduction reactions of the vanadium–8-quinolinol complexes are similar to those of the molybdenum(V)– and -(VI)–8-quinolinol complexes,[12] especially in their tendency to form oxo-bridged dimers and to undergo hydrolysis. The molybdenum-containing enzymes such as xanthine oxidase have two molybdenum atoms per molecule and these may be in the V oxidation state in the form of an oxo-bridged dimer. By analogy a binuclear oxo-bridged vanadium–flavine complex is a reasonable proposition for some forms of biological vanadium. To develop this idea further, the structure of the binuclear complex is being studied by X-ray methods and related binuclear complexes are being studied by electrochemical methods.

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**Registry No.** $VQ_3$, 18581-58-3; $VOQ_2$, 55162-22-6; $VO(OH)Q_2$, 19631-94-8; $VO(OCH_3)Q_2$, 19631-76-6; $[(n\text{-}Bu)_4N]^+[(VOQ_2)O(VOQ_2)]^-$, 55281-64-6.

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# Organometallic Nitrosyl Chemistry. I. Reactions of Nitrosyl Chloride with Some Anionic and Neutral Carbonyl Complexes

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The stoichiometric reaction of nitrosyl chloride with weakly nucleophilic metal carbonyl anions such as $(\eta^5\text{-}C_5H_5)M(CO)_3^-$ (M = Cr, Mo, or W), $W(CO)_5Cl^-$, $Mn(CO)_5^-$, and $Fe(CO)_4^{2-}$ is a new and convenient means of preparing the neutral nitrosyl compounds $(\eta^5\text{-}C_5H_5)M(CO)_2(NO)$ (M = Cr, Mo, or W), $W(CO)_4(NO)Cl$, $Mn(CO)_4(NO)$, and $Fe(CO)_2(NO)_2$. More nucleophilic anions are oxidized rapidly by ClNO. Treatment of the neutral compounds $(\eta^5\text{-}C_5H_5)M(CO)_2(NO)$ (M = Cr, Mo, or W) and $Fe(CO)_2(NO)_2$ with nitrosyl chloride provides a new and high-yield synthetic route to the chloronitrosyl compounds $(\eta^5\text{-}C_5H_5)M(NO)_2Cl$ (M = Cr, Mo, or W) and $Fe(NO)_3Cl$. Some reactions of compounds containing metal-metal bonds with ClNO are also described.

## Introduction

Nitrosyl chloride has previously been utilized to introduce the nitrosyl functionality into organometallic complexes. Typically, it may oxidatively add to coordinatively unsaturated substrates, or, when reaction occurs with coordinatively saturated compounds, each ClNO added may displace ligands capable of donating a total of four electrons to the metal.[1] However, previous attention has been focused almost exclusively on the interaction of nitrosyl chloride with neutral complexes. This paper describes the reactions of this versatile synthetic reagent with a variety of organometallic anions and outlines some new reactions between ClNO and neutral carbonyl-containing entities that readily lead to neutral chloronitrosyl compounds.

## Experimental Section

All chemicals used were of reagent grade or comparable purity. All reagents were either purchased from commercial suppliers or prepared according to reported procedures, and their purity was ascertained by elemental analyses and/or melting point determinations. Melting points were taken in capillaries and are uncorrected. All solvents were dried (if necessary), distilled, and deaerated just prior to use, and all manipulations were performed in an atmosphere of prepurified nitrogen.

Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer and were calibrated with the 1601-cm$^{-1}$ band of polystyrene film. Proton magnetic resonance spectra were recorded on a Varian Associates T60 spectrometer with tetramethylsilane being employed as an internal standard. The low-resolution mass spectra were taken at 70 eV on an Atlas CH4B spectrometer using the direct-insertion method, and the high-resolution mass spectrum was obtained on an MS902 spectrometer with the assistance of Mr. G. Eigendorf and Mr. G. Gunn. Elemental analyses were carried out by Mr. P. Borda of this department.

**Reaction of Nitrosyl Chloride with $Na[(\eta^5\text{-}C_5H_5)M(CO)_3]$ (M = Cr, Mo, W).** All three of these reactions were carried out in a similar manner. The experimental procedure, using the chromium complex as a typical example, was as follows. To a solution of $Na[(\eta^5\text{-}C_5H_5)Cr(CO)_3]$[2] (4.89 g, 21.8 mmol) in tetrahydrofuran (90 ml) at room temperature was added dropwise with rapid stirring a solution of ClNO[3] (1.4 g, 21 mmol) in tetrahydrofuran (20 ml). Gas evolution occurred throughout the course of the reaction and a dark solid precipitated. After addition of the ClNO was completed, a solution infrared spectrum revealed the final reaction mixture to contain $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ and $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$ as the principal carbonyl-bearing compounds. The reaction mixture was taken to dryness in vacuo and sublimation of the dried residue at 60° ($5 \times 10^{-3}$ mm) onto a water-cooled probe produced 1.01 g (5.0 mmol, 23% yield) of the bright orange-red $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$ which was identified by its infrared spectrum. The reactions involving the molybdenum and tungsten anions proceeded comparably, but it should be noted that if an excess of ClNO is employed in the above synthesis, significant amounts of the $(\eta^5\text{-}C_5H_5)M(NO)_2Cl$ compounds are also formed. The physical and chemical properties of the $(\eta^5\text{-}C_5H_5)M(CO)_2(NO)$ complexes have been extensively described.[4]

The treatment of other transition metal compounds with nitrosyl chloride was effected similarly and the experimental procedures are summarized in Table I.

**Reaction of Nitrosyl Chloride with $(\eta^5\text{-}C_5H_5)M(CO)_2(NO)$ [M = Cr, W].** Both of these reactions were performed in the same manner. The experimental procedure, using the chromium compound as a particular example, was as follows. To a solution of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$[17] (4.70 g, 23.2 mmol) in dichloromethane (30 ml) at −78° was added dropwise with rapid stirring a dichloromethane solution of ClNO (containing 2.0 g of ClNO in 30 ml of $CH_2Cl_2$). Gas evolution occurred and a small quantity of a dark solid precipitated. The reaction was monitored by infrared spectroscopy and the ClNO solution was added until the carbonyl absorptions due to the initial reactant had disappeared. The final reaction mixture was concentrated in vacuo to approximately 15 ml in total volume and it was then filtered through a short (30 × 40 mm) Florisil column. Addition of hexane to the filtrate induced the crystallization of golden needles of $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ (3.80 g, 17.9 mmol, 77% yield) which were collected by filtration. The analogous bright green tungsten compound was prepared similarly in 72% yield. The physical properties of both compounds are summarized in Table II.

**Reaction of Nitrosyl Chloride with $(\eta^5\text{-}C_5H_5)Mo(CO)_2(NO)$.** A stirred, orange solution of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(NO)$[17] (6.50 g, 26.3 mmol) in dichloromethane (100 ml) at room temperature was treated dropwise with a dichloromethane solution of ClNO. Gas was evolved, the reaction mixture developed a green coloration, and a small quantity of a red precipitate was formed. Again, the ClNO solution was added until the carbonyl absorptions due to the initial reactant had disappeared from the infrared spectrum of the reaction mixture's supernatant liquid. Hexane (50 ml) was then added and the volume of the reaction mixture was reduced in vacuo to approximately 60 ml at which point the red solid was removed by filtration. Further concentration of the filtrate in vacuo resulted in the formation of green