contention that the excited state of **1** undergoes intramolecular electron transfer and conclusively demonstrates that the intramolecular radical ion pair must be a key intermediate to **4** and **8**. These results show that radical–radical coupling of the radical ion pair (path b) occurs, establishes that this process can occur in competition with back electron transfer and proton transfer, and requires that it be considered as a possible route in other systems. We are presently searching for other examples of this process.

One- and Two-Electron Photooxidation of a Molybdenum(III) Thiocyanate Complex

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There has been continuing interest in the properties of excited states of transition-metal complexes and in their use as catalysts for redox reactions. However, photoredox processes have generally been confined to one-electron transfers, while many desirable redox reactions require the transfer of two or more electrons in a single substrate molecule. One-electron photoredox reactions, such as those of polypyridine complexes of chromium(III)[1] and ruthenium(II),[2] and multielectron redox activity in ruthenium- and osmium-based systems,[3] have been investigated separately. Our goal has been to generate multielectron oxidants photochemically by beginning with d[3] complexes of the early transition metals: initial excited-state electron transfer is to be followed by a second thermal electron transfer, thus producing a net two-electron transformation. In addition to our recent work with vanadium(II),[4] we have been interested in the heavier d[3] ions, whose photoredox properties have not been studied before. We now report facile ground- and excited-state oxidation of the hexakis(thiocyanato-N)molybdate(3–) ion, $Mo(NCS)_6^{3-}$, and the disproportionation of the initial electron-transfer product $Mo(NCS)_6^{2-}$ to generate the molybdenum(V) dimer $(SCN)_3MoO(\mu\text{-}O)_2MoO(NCS)_3^{4-}$. These observations constitute the first photoredox reactions ever recorded in a molybdenum(III) complex. They indicate not only that a broad new class of transition-metal complexes can be used as redox sensitizers but that many such systems are likely to be useful in photoinitiated net two-electron-transfer processes.

Octahedral d[3] complexes have the $^4A_{2g}$ ground state and the low-lying d–d excited states $^4T_{2g}$, ^2E_g, $^2T_{1g}$, and $^2T_{2g}$.[1] The phosphorescent ^2E_g excited state is long-lived if it is lower in energy than $^4T_{2g}$; for chromium(III) this occurs only with strong-field ligands such as CN⁻ and 1,10-phenanthroline. In second- and third-row metal complexes, on the other hand, all three doublets lie below $^4T_{2g}$; this has been shown recently for $MoCl_6^{3-}$ in the elegant absorption and emission spectroscopic study of Flint and Paulusz.[5] A variety of molybdenum(III) complexes, then, should have excited states sufficiently long lived for photoredox reactions. We chose $Mo(NCS)_6^{3-}$ for our initial experiments because its
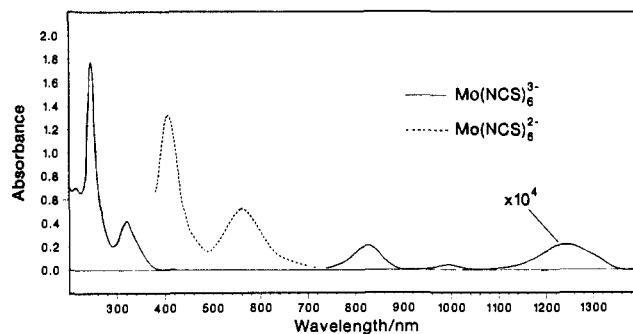

Figure 1. Room-temperature electronic absorption spectra: (—) K_3-$Mo(NCS)_6$ in water (2 × 10⁻⁵ M, 200–420 nm; 0.2 M, 740–1400 nm); (- - -) $Mo(NCS)_6^{2-}$ in CH_3CN (2 × 10⁻⁵ M).

Table I. Half-Wave Potentials from Cyclic Voltammetry

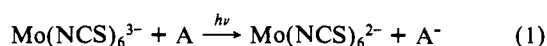| couple	$E_{1/2}/V^a$
$Mo(NCS)_6^{2-/3-}$	0.05
$TCNE^{0/-\,b}$	-0.16
$1,4\text{-}C_6H_4(NO_2)_2^{0/-}$	-1.08
$1,3\text{-}C_6H_4(NO_2)_2^{0/-}$	-1.27

a Reversible one-electron couples in CH_3CN (0.1 M $(C_4H_9)(O_3SCF_3)$), vs. Fc/Fc^+ (Fc = ferrocene). *b* TCNE = ethenetetracarbonitrile.

spectral and redox properties had been studied before.

The weak absorption bands between 740 and 1400 nm in $Mo(NCS)_6^{3-}$ (Figure 1) have been assigned to the three quartet → doublet transitions,[6] with $^4A_{2g} \rightarrow ^4T_{2g}$ probably obscured by the intense ligand-to-metal charge-transfer absorption that begins near 400 nm.[7] The ion has not been reported to luminesce.

Sykes and co-workers showed that $IrCl_6^{2-}$ oxidizes $Mo(NCS)_6^{3-}$ to the deep red-brown molybdenum(IV) complex $Mo(NCS)_6^{2-}$, which is stable in nonaqueous solvents but disproportionates in water to give $Mo(NCS)_6^{3-}$ and a molybdenum(V) species.[8] Thus, $Mo(NCS)_6^{3-}$ is subject to one-electron oxidation, and the initial molybdenum(IV) product can readily undergo a second electron transfer. We have now accomplished these one- and two-electron oxidations of $Mo(NCS)_6^{3-}$ photochemically.

Conventional flash irradiation (350–450 nm) of solutions of $K_3Mo(NCS)_6\cdot4H_2O^8$ and 1,4-dinitrobenzene in CH_3CN^9 leads to transient absorption signals characteristic of $Mo(NCS)_6^{2-}$ (410 and 560 nm; see Figure 1).[10] These absorptions decay with second-order kinetics, as expected for reaction 2 (A = 1,4-di-

$$Mo(NCS)_6^{3-} + A \xrightarrow{h\nu} Mo(NCS)_6^{2-} + A^- \quad (1)$$

$$Mo(NCS)_6^{2-} + A^- \xrightarrow{k_b} Mo(NCS)_6^{3-} + A \quad (2)$$

nitrobenzene). Based on kinetic data, and on absorption spectral data for $Mo(NCS)_6^{2-}$ (ϵ_{560} = 2.6 × 10⁴ M⁻¹ cm⁻¹[10]), k_b is approximately 8 × 10⁸ M⁻¹ s⁻¹, a reasonable value for a diffusion-controlled reaction between two anions. Comparable experiments in acetone solution give transient-absorption signals attributable to A⁻ (λ > 750 nm[11]) as well as those expected for $Mo(NCS)_6^{2-}$.

Electrochemical data for of $Mo(NCS)_6^{3-}$ and several electron acceptors are shown in Table I. Mixtures of $Mo(NCS)_6^{3-}$ and TCNE undergo slight spontaneous electron transfer; absorption spectra of the mixtures yield an equilibrium constant for the reaction $Mo(NCS)_6^{3-} + TCNE \rightleftharpoons Mo(NCS)_6^{2-} + TCNE^-$ of 0.0004 in CH_3CN at room temperature. This is in agreement with the half-wave potentials for the two redox couples. With

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(9) Solutions of $Mo(NCS)_6^{3-}$ and the electron acceptors are stable in the dark. We also observe no spectroscopic evidence for ground-state complex formation in these experiments.
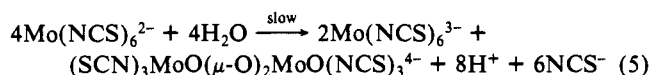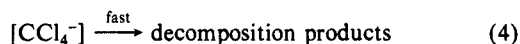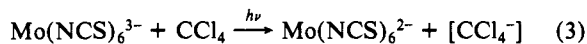(10) Mitchell, P. C. H.; Williams, R. J. P. *J. Chem. Soc.* **1962**, 4570–4578.
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the dinitrobenzenes, however, electron transfer can only be observed photochemically. Based on our observation of photochemical oxidation of $Mo(NCS)_6{}^{3-}$ by 1,3-dinitrobenzene, the redox-active $Mo(NCS)_6{}^{3-}$ excited state may have an energy as high as 1.3 eV. Since the $Mo(NCS)_6{}^{3-}$ absorption spectrum indicates that the lowest energy excited state lies no higher than 1.0 eV, our photochemical experiments suggest that upper excited states of $Mo(NCS)_6{}^{3-}$ may be participating in these electron-transfer reactions.

The properties of photogenerated $Mo(NCS)_6{}^{2-}$ can be explored further by using CCl_4 as an irreversible electron acceptor. One-electron reduction of CCl_4 is followed by rapid fragmentation;[12] thus, back electron-transfer reactions such as (2) should be inhibited. Flash irradiation of $Mo(NCS)_6{}^{3-}$ in CH_3CN–CCl_4 (90:10 w/w) results in immediate permanent formation of red-brown $Mo(NCS)_6{}^{2-}$, which is stable under these conditions.

Photooxidation of $Mo(NCS)_6{}^{3-}$ (ca. 8×10^{-3} M; 0.2 M KNCS) is also observed in CCl_4–H_2O–CH_3CN (7:31:62 w/w; chosen to keep H_2O and CCl_4 stable in the same phase), but the $Mo(NCS)_6{}^{2-}$ that is produced slowly disappears. After several flashes, each of which leads to formation and slow disappearance of $Mo(NCS)_6{}^{2-}$, a new, permanent absorbance at 456 nm is observed. We attribute this new feature to the molybdenum(V) product formed by disproportionation of $Mo(NCS)_6{}^{2-}$. Of the three possible Mo(V) products suggested by Sykes and co-workers,[8] both $MoO(NCS)_5{}^{2-}$[13] and $Mo_2O_4(NCS)_6{}^{4-}$[10] exhibit intense absorption near 456 nm. However, the mononuclear complex is stable only in strongly acidic solutions.[13b,14] Thus, $Mo_2O_4(NCS)_6{}^{4-}$ is the most likely product under our conditions, and the overall sequence of reactions is as follows:

$$Mo(NCS)_6{}^{3-} + CCl_4 \xrightarrow{h\nu} Mo(NCS)_6{}^{2-} + [CCl_4{}^{-}] \quad (3)$$

$$[CCl_4{}^{-}] \xrightarrow{fast} \text{decomposition products} \quad (4)$$

$$4Mo(NCS)_6{}^{2-} + 4H_2O \xrightarrow{slow} 2Mo(NCS)_6{}^{3-} +$$
$$(SCN)_3MoO(\mu\text{-}O)_2MoO(NCS)_3{}^{4-} + 8H^+ + 6NCS^- \quad (5)$$

We observe first-order kinetics (k_{obsd} ca. 7 s^{-1}) for disappearance of $Mo(NCS)_6{}^{2-}$; this is consistent with a mechanism for reaction 5 that involves initial rate-limiting aquation of $Mo(NCS)_6{}^{2-}$.

We have therefore shown for the first time that molybdenum(III) complexes can undergo facile photoredox reactions and that photoinitiated two-electron oxidations can be accomplished by disproportionation of the initial electron-transfer products.[15] Experiments now in progress include nanosecond flash photolysis[16] and selective irradiation of $Mo(NCS)_6{}^{3-}$ in its weak low-energy absorption bands, in order to examine the redox-active excited states more directly. These results are of particular interest because of the possibility that electron transfer may be occurring from upper excited states. Also under study are the extension of these reactions to other second- and third-row d^3 complexes and the reactivity of the photogenerated oxo complexes toward organic and inorganic substrate molecules.

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(16) Preliminary experiments (Nd:YAG, 355-nm excitation) suggest an excited-state lifetime of at least 1 μs for $Mo(NCS)_6{}^{3-}$ in CH_3CN at room temperature.

Stereochemistry of Methylation in Thienamycin Biosynthesis: Example of a Methyl Transfer from Methionine with Retention of Configuration

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The carbapenem antibiotic thienamycin[1] (I) is derived biosynthetically from glutamic acid, which provides the pyrroline ring,[2] acetate and cysteine, providing C-6 and C-7 of the β-lactam ring and the cysteamine side chain, respectively,[3] and the methyl group of methionine, which gives rise to both carbon atoms of the hydroxyethyl side chain.[3] In a double-labeling experiment, Williamson et al.[3] demonstrated that [methyl-^{14}C,^{3}H]methionine is incorporated with 58% tritium retention, relative to ^{14}C, corresponding to 87% of the maximum value for retention of four of the six hydrogens of the two methyl groups.

In order to obtain more information on this intriguing double-methylation sequence, we examined the steric course of the transfer of the methionine methyl group. We first confirmed the incorporation of an intact methyl group into C-9 by using L-[methyl-^{13}C,^{2}H$_3$]methionine. This material, synthesized[4] from ^{13}C^{2}H$_3$I (Merck, 99% ^{13}C, 98% ^{2}H), was fed at a concentration of 0.74 mM to 1.2 L (3 × 40 mL) of a resting cell suspension of *Streptomyces cattleya*.[3] The fermentation was terminated 19 h later and I (3.2 mg) was isolated as described earlier.[3,5] The ^{13}C NMR spectrum of the sample was recorded at 4 °C at 75.5 MHz (Bruker WM 300) with proton broad-band decoupling and with and without deuterium broad-band decoupling. The results (Figure 1) clearly show that ^{13}C is incorporated into C-9 with retention of all three deuterium atoms and into C-8 with retention of one atom of deuterium. There seems to be little or no washout of deuterium from either position.

With this information at hand, we fed (*methyl-R*)- and (*methyl-S*)-[methyl-^{2}H$_1$,^{3}H]-L-methionine[6] (R, 2.79 mCi/mmol, max 80% ee *methyl-R*; S, 1.10 mCi/mmol, max 75% ee *methyl-S*[7]) to 80-mL cultures of *S. cattleya* (15 μCi per experiment). When tritium incorporation into I had reached a maximum, as determined by HPLC and liquid scintillation counting, 2 mg of unlabeled I was added and the labeled I was isolated and purified[3,5] (1–4% tritium incorporation). Kuhn–Roth oxidation of the products gave acetic acid samples which were analyzed for their chirality by the method of Cornforth[8] and Arigoni[9] using our previously described procedure.[10] The acetic acid obtained by

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