Figure 4. Unit cell of $M_3(\mu_3\text{-S})(\mu\text{-S})_3Br_4(PEt_3)_3(OPEt_2H)(H_2O)\cdot2THF$ (M = Mo, **2**; M = W, **3**). The hydrogen atom was found for compound **2** only. Axes orientation: *b*, down; *a*, across; *c*, toward viewer. Atoms are represented by their ellipsoids at the 20% probability level.

attached by a hydrogen bond to a coordinated H_2O molecule. In compounds **2** and **3**, however, a far more interesting product is to be found, namely, a Et_2HPO ligand attached to one metal atom. We suggest the following explanation for the formation of this unusual molecule. First, Et_3P is oxidized to Et_3PO, which then coordinates to a metal atom through the oxygen atom. This is then followed by reactions 2 and 3, where (3) may take place in two stages with a hydrido intermediate.

The structures of the three products are not unusual, apart from the Et_2HPO ligand in **2** and **3**. All three structures are of the
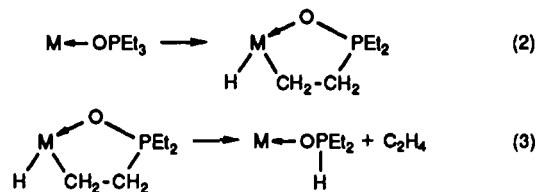
B_1 type of M_3X_{13} structure.[22] Compound **1** is much like one reported by Saito[16] except that in that case there were two coordinated methanol molecules instead of two H_2O molecules. There is, however, also a difference in the position of the PEt_3 ligand on Mo(2), cis rather than trans to the capping sulfur atom. The isomorphous compounds **2** and **3** have all phosphine ligands trans to μ_3-S. They are the first such isomorphous pair of Mo_3S_4 and W_3S_4 compounds, and it is interesting that the mean W–W distance appears to be slightly shorter than the mean Mo–Mo distance, although statistically the difference is not real, 0.006 (10) Å.

Supplementary Material Available: Full listings of crystallographic data, bond distances and angles, and anisotropic displacement parameters for **1–3** (17 pages); listings of observed and calculated structure factors for **1–3** (62 pages). Ordering information is given on any current masthead page.

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Photophysics and Photochemistry of Hexachlororhenate(IV) and Hexabromorhenate(IV)

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A study of the solution photophysical and photoredox properties of $ReCl_6^{2-}$ and $ReBr_6^{2-}$ is reported. The solutions are phosphorescent at room temperature, with emission maxima (lifetimes) of 1340 nm (80 ns) and 1380 nm (40 ns) for $(Bu_4N)_2[ReCl_6]$ and $(Bu_4N)_2[ReBr_6]$, respectively, in CH_3CN. The phosphorescences are assigned to the $\Gamma_8(^2T_{1g}) \rightarrow \Gamma_8(^4A_{2g})$ transition. Although the ions also phosphoresce from upper excited states when they are doped into host crystals, no such phosphorescence is observed for the pure solids or for solutions, either at room temperature or at 77 K. Both ions undergo one-electron oxidation on irradiation in the presence of 2,3,5,6-tetrachloro- (chloranil) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ); with $ReCl_6^{2-}$, this process is reversible, and back-electron-transfer reactions are essentially diffusion-controlled. Photochemical reactions with some acceptors, such as tetracyanoethylene, are complicated by the formation of charge-transfer complexes. Irradiation of $ReCl_6^{2-}$ with $C(NO_2)_4$ in CH_3CN or CH_2Cl_2 yields ReO_4^-, along with NOCl (produced by reaction of NO_2 with $ReCl_6^{2-}$ or Cl^-) and $C(NO_2)_3^-$.

Introduction

We have begun an exploration of the photophysical and photochemical properties of d^3 complexes of the early transition metals. These experiments have been designed to combine the attractive photophysical properties of the d^3 configuration with the multiple stable oxidation states of elements such as V, Mo, W, and Re. We have described the photoinitiated two-electron oxidation of $V(phen)_3^{2+}$ (phen = 1,10-phenanthroline) to VO^{2+}[1] and $Mo(NCS)_6^{3-}$ to $Mo_2O_4(NCS)_6^{4-}$.[2] More recently, we have reported that, like the extensively studied complexes of chromium(III), room-temperature solutions of species such as $MoCl_6^{3-}$ and $ReCl_6^{2-}$ phosphoresce in the near-infrared region (1100–1400 nm).[3] We have now studied the properties of $ReCl_6^{2-}$ and $ReBr_6^{2-}$ in more detail. $ReCl_6^{2-}$ is photooxidized to perrhenate by $C(NO_2)_4$; this is an unusual example of a photoinitiated three-electron oxidation.[4]

Experimental Section

Materials. Chloranil (MCB) and DDQ (Aldrich) were purified by recrystallization from 1,2-dichloroethane and chloroform, respectively. For experiments to be conducted in the absence of H_2O, CH_3CN and CH_2Cl_2 were distilled from CaH_2 under N_2 and stored in an inert-atmosphere drybox. $H_2{}^{18}O$ (10 atom %, Aldrich) was handled in a glovebag. Other materials and solvents were of the highest grade commercially available and were used as received. Samples for photochemical measurements were prepared by degassing on a Schlenk or high-vacuum line; Ar was added in some cases (especially for CH_2Cl_2 solutions) to inhibit boiling during flash-photolysis experiments.

The method of Rulfs and Meyer[5] was used to prepare K_2ReCl_6, substituting an equimolar mixture of $HReO_4$ (Aesar) and KCl for $KReO_4$.

† Louisiana State University.
‡ Washington University.

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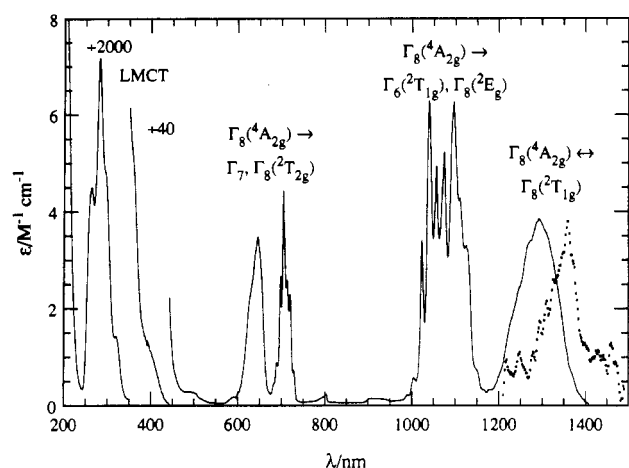
Figure 1. Electronic absorption (—) and corrected emission (···) spectra for $(Bu_4N)_2[ReCl_6]$ in CH_3CN at room temperature. The emission spectrum was recorded on a 2×10^{-3} M solution, with 360-nm excitation and 15-nm emission band-pass.

Figure 2. Electronic absorption (—) and corrected emission (···) spectra for $(Bu_4N)_2[ReBr_6]$ in CH_3CN at room temperature. The emission spectrum was recorded on a 1×10^{-3} M solution, with 414-nm excitation and 15-nm emission band-pass.
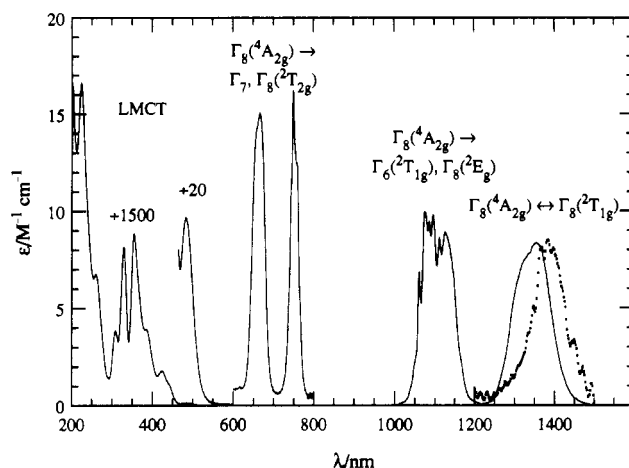
$(Bu_4N)_2[ReCl_6]$ was prepared from K_2ReCl_6 by metathesis using a stoichiometric amount of Bu_4NHSO_4 (Aldrich) in a near-boiling solution containing HCl (6 M) and H_3PO_2 (1 M). The precipitated salt was purified by washing with small amounts of warm (≈ 60 °C) 6 M HCl, dissolving in CH_2Cl_2, drying over $MgSO_4$, filtering, and evaporating to dryness. The resulting product was purified by dissolving in the minimum amount of acetone, filtering, and precipitating with hexane, giving a light green powder. Anal. Calcd for $C_{32}H_{72}N_2ReCl_6$: C, 43.49; H, 8.21; N, 3.17. Found: C, 43.51; H, 8.43; N, 3.33. An analogous procedure employed concentrated HBr as the reducing agent to prepare deep red-brown K_2ReBr_6. Metathesis in hot 3 M HBr(aq) afforded bright yellow $(Bu_4N)_2[ReBr_6]$, which was purified in a manner similar to that employed for the chloro complex. Anal. Calcd for $C_{32}H_{72}N_2ReBr_6$: C, 33.41; H, 6.31; N, 2.43. Found: C, 33.55; H, 6.44; N, 2.34. K_2SnCl_6:Re^{4+} (ca. 1% Re) was prepared by the method of Black and Flint.[6]

Instruments and Procedures. Cyclic voltammograms were recorded by using either a PAR Model 174A polarographic analyzer or a Wenking TS70/1 potentiostat with a home-built microcomputer interface. The cell contained Pt working and counter electrodes and an aqueous Ag/AgCl (3 M NaCl) reference electrode. The half-wave potential for the Fc/Fc⁺ (Fc = ferrocene) reference redox couple under these conditions was 0.47 V (in CH_3CN) or 0.52 V (in CH_2Cl_2).

Electronic absorption spectra were recorded on Aviv 118DS, Cary 14, and Cary 219 spectrophotometers, and infrared spectra, on a Perkin-Elmer Fourier-transform instrument. Luminescence spectra were recorded by using a Spex Industries Fluorolog 2 Model F112X spectrometer and were corrected for variations in detector sensitivity with wavelength. Correction curves were prepared by the method of Demas and Crosby[7] using a tungsten–quartz–halogen lamp and $BaSO_4$ reflecting plaque calibrated between 250 and 2500 nm (Optronic Laboratories Inc., Orlando, FL, Models 245-C and 25RS). The solutions used for recording the emission spectra in Figures 1 and 2 were sufficiently dilute that reabsorption of the emitted light by the complexes was insignificant. However, CH_3CN also shows substantial vibrational-overtone absorption in the near-infrared region; the spectra were therefore corrected for this type of reabsorption.

A Hamamatsu R928 photomultiplier tube was the detector for the higher energy emissions (600–800 nm). Near-infrared emissions were measured by using an aspheric condensing lens to image the exit slit of the emission monochromator on a Judson Infrared Model J16D liquid-nitrogen-cooled Ge photodiode (2-mm diameter). For operation with the Ge detector, a Rofin Model RSC 7021/7022 chopper (ca. 315 Hz) was mounted in the excitation monochromator, and the signal from the photodiode was processed by using a PAR Model 181 preamplifier and Model 5101 lock-in amplifier (with internal tuned amplifier matched to the chopping frequency).

For measurements of extremely weak near-IR emissions (e.g. those produced by irradiation of spin-forbidden bands in dilute solutions), the Ge detector was placed at the focus of an aluminum paraboloidal reflector (90° off axis, effective focal length 38 mm; Aero Research As-

sociates, Port Washington, NY) that was mounted between the first grating and its collection mirror in the emission monochromator.

Continuous photolyses employed a Kratos-Schoeffel 150-W Xe arc lamp and Corning or Schott colored-glass filters. In a typical photo-oxidation, a solution of $(Bu_4N)_2[ReCl_6]$ (0.03 M) and $C(NO_2)_4$ (0.06 M) in CH_2Cl_2 was irradiated. A noticeable brown color attributable to NOCl appeared within ca. $^1/_2$ h; after a total of ca. 2 h of irradiation, the brown color of NOCl had faded, and the deep yellow color of $C(NO_2)_3^-$ dominated. Similar results were obtained when the apparatus was assembled in a glovebox and dry solvent and reagents were used; in these experiments, $C(NO_2)_4$ was dried in vacuo over $Mg(ClO_4)_2$ before being brought into the glovebox. When water was deliberately added (ca. 0.5% w/v) to the solutions before irradiation, the final products were similar, but NOCl was not observed as an intermediate.

Microsecond flash-photolysis experiments were carried out by using a xenon flash lamp (maximum flash energy 300 J; fwhm ca. 20 μs) mounted along one focus of a home-built polished aluminum elliptical cylinder 15 cm in length. The sample cell was mounted at the other focus. Corning colored-glass filters inserted between the flash lamp and the sample served to isolate specific spectral regions for irradiation. (A very similar apparatus has been described by Milder and co-workers.[8]) The monitoring light was passed through a Jarrell-Ash Mark X monochromator to a Hamamatsu R928 photomultiplier. Kinetic data were recorded and analyzed by using a LeCroy Model WD8256 waveform digitizer interfaced to a microcomputer.

Experiments on the nanosecond time scale utilized either a Quantel Nd:YAG (355 nm; 620 nm, using the 532-nm second harmonic to pump an R640 dye laser) or a Lambda-Physik excimer laser (XeCl, 308 nm). Kinetic data from these experiments were recorded and analyzed by using Tektronix (with the Nd:YAG laser) or Hewlett-Packard digitizer/microcomputer systems (with the excimer laser). Solutions of $(Bu_4N)_2$-$[ReBr_6]$ in CH_3CN decompose slowly over a period of ca. 1 h under ultraviolet illumination; the data reported for $ReBr_6^{2-}$ were recorded for freshly prepared solutions.

Near-infrared luminescence lifetimes were measured with these apparatus, but using the Ge detector described above operated at room temperature (response time ca. 100 ns). The experimental detector response function was used to estimate actual emission lifetimes by deconvolution;[9] the uncertainties in the resulting lifetimes are ca. ±20 ns.

Results

Absorption and Emission Spectra. Both $ReCl_6^{2-}$ and $ReBr_6^{2-}$ exhibit weak d–d absorptions in the visible and near-IR regions and LMCT bands at higher energy. The spectra of $(Bu_4N)_2$-$[ReCl_6]$ and $(Bu_4N)_2[ReBr_6]$ in CH_3CN are shown in Figures 1 and 2, respectively. (The absorption spectra in the near-infrared region required high concentrations of the rhenium complexes; for these measurements, solutions of $(Bu_4N)Cl$ or $(Bu_4N)Br$ in CH_3CN were used as the reference so as to eliminate absorptions due to vibrational overtones in the cation.)

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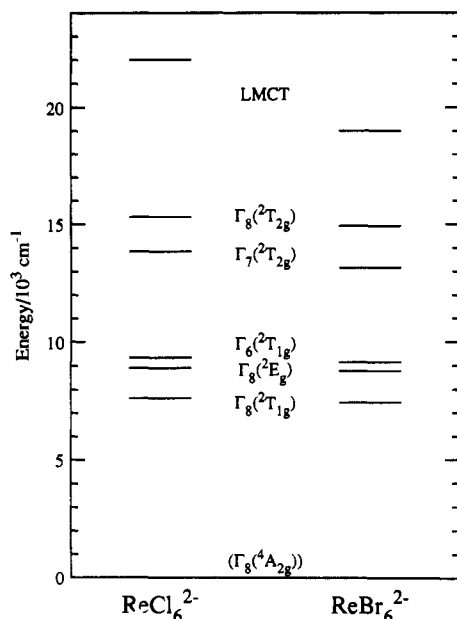
Figure 3. Energy diagram for $ReCl_6^{2-}$ and $ReBr_6^{2-}$, based on data in ref 12. Levels labeled LMCT represent the onset of LMCT absorptions in Figures 1 and 2.

Several features of the complexes are responsible for the significant differences between these spectra and those of first-row d^3 ions. First, the ligand-field strengths (represented by $10Dq$) for these complexes are much larger, causing the spin-allowed d–d transitions to be buried under the intense LMCT absorption bands in the UV region. Second, interelectronic repulsion (represented by the Racah parameter B) is considerably weaker than in first-row species. Since the lowest lying doublet terms, ^2E_g, $^2T_{1g}$, and $^2T_{2g}$, all arise from the same strong-field electronic configuration (t_{2g}^3) as the ground term, their energies depend primarily on B. Thus, they are considerably lower in energy than those of ligher d^3 metals. And, finally, the relatively strong spin–orbit coupling in these systems results in substantial splitting of the $^2T_{1g}$ and $^2T_{2g}$ terms.

Eisenstein presented the first detailed discussion of the absorption spectrum of $ReCl_6^{2-}$.[10] On the basis of ligand-field calculations, he proposed the energy-level scheme for $ReCl_6^{2-}$ shown in Figure 3. The assignments for $ReBr_6^{2-}$ are identical, except that the LMCT absorptions begin at lower energy.

Phosphorescence data for $ReCl_6^{2-}$ and $ReBr_6^{2-}$ are summarized in Table I. Both the lowest energy $\Gamma_8(^2T_{1g})$ state[11–13] and the upper $\Gamma_7(^2T_{2g})$ state[6,11,14–16] phosphoresce in single-crystal hosts. The lifetime of the $\Gamma_7(^2T_{2g})$ emission, which is one of the few independent phosphorescences known from upper excited states under any conditions,[17] is at least 20 μs in several host crystals even at room temperature.[6,11] Also, in $ReBr_6^{2-}$, phosphorescence occurs from both the Γ_7 and Γ_8 states of $^2T_{2g}$.[12,15] This phenomenon is distinctive as well: the states are electronically similar and differ in energy by less than 2000 cm^{-1}, and yet the $\Gamma_8(^2T_{2g}) \rightarrow \Gamma_7(^2T_{2g})$

Table I. Phosphorescence of Hexahalorhenates(IV)

ion	matrix	exc st	λ/nm^a	$\bar{\nu}/cm^{-1\,a}$	$\tau/\mu s$	ref
$ReCl_6^{2-}$	K_2PtCl_6	$\Gamma_7(^2T_{2g})$	722.5	13841	20[b]	6, 12
		$\Gamma_8(^2T_{1g})$	1310	7634	350[b]	12, c
	CH_3CN	$\Gamma_8(^2T_{1g})$	1330	7500	0.08	c
$ReBr_6^{2-}$	Cs_2ZrBr_6	$\Gamma_8(^2T_{2g})$	670.2	14922	<20	18
		$\Gamma_7(^2T_{2g})$	760.5	13150		18
		$\Gamma_8(^2T_{1g})$	1343	7446		12
	CH_3CN	$\Gamma_8(^2T_{1g})$	1380	7200	0.04	c

[a] Phosphorescence wavelengths and energies represent 0–0 transitions (for ReX_6^{2-} in single-crystal hosts) or band maxima (for $(Bu_4N)_2[ReX_6]$ in CH_3CN). [b] Measured in K_2SnCl_6. [c] This work.

Table II. Half-Wave Potentials from Cyclic Voltammetry[a]

couple	CH_3CN	CH_2Cl_2	couple	CH_3CN	CH_2Cl_2
$ReCl_6^{2-/-}$	0.77	0.70	$TCNE^{0/-}$	-0.16[c]	-0.25
$ReBr_6^{2-/-}$	0.78	0.75[b]	$DDQ^{0/-}$	0.14	0.19
$Chl^{0/-}$	-0.36	-0.45			

[a] V vs Fc/Fc$^+$; 0.1 M $(Bu_4N)(O_3SCF_3)$ or $(Bu_4N)(BF_4)$; 100 mV s^{-1}. See text for abbreviations. [b] Irreversible; value quoted is the anodic peak potential (E_{pa}). [c] Reference 2.

internal conversion rate constant is only ca. 6×10^4 s^{-1}. Flint and Black showed further that the Γ_7 and Γ_8 phosphorescences in $ReBr_6^{2-}$ have different excitation spectra and significant risetimes.[18]

We have reported that $ReCl_6^{2-}$ phosphoresces in the near-infrared region in solution at room temperature.[3] The electronic absorption and emission spectra for $ReCl_6^{2-}$ and $ReBr_6^{2-}$ are included in Figures 1 and 2, respectively. (Although the data for $ReCl_6^{2-}$ were published previously, the present spectrum includes the high-energy LMCT absorptions; also, the present phosphorescence spectra are corrected for Ge detector response and for reabsorption of the emitted light due to CH_3CN vibrational overtone bands.) These $\Gamma_8(^2T_{1g})$ phosphorescences are similar to those reported by Flint and Paulusz[12,13] for doped single crystals, except that the resolution in our spectrum is considerably poorer. These phosphorescences can be induced by irradiating either the other intraconfigurational bands or the higher energy LMCT bands. We observe no luminescence from $^2T_{2g}$ in $ReCl_6^{2-}$ or $ReBr_6^{2-}$, either at room temperature (pure solids or fluid solutions) or at 77 K (pure solids or glassy solutions).

The phosphorescences of the two rhenium complexes overlap substantially with the corresponding absorption bands. This is to be expected: because the ground and excited states both arise from the $(t_{2g})^3$ electronic configuration, their geometries are very similar, and the Stokes shift is likely to be very small. As a result of this overlap between the lowest energy absorption and emission transitions, reabsorption of the emitted light by the complex can lead to significant errors.[19] Therefore, the emission spectra in Figures 1 and 2 were recorded in dilute solutions ($ReCl_6^{2-}$, 2×10^{-3} M; $ReBr_6^{2-}$, 1×10^{-3} M) so as to minimize this problem.

Transient Spectra and Lifetimes. A transient difference spectrum produced by Nd:YAG-pumped dye-laser irradiation of $(Bu_4N)_2[ReCl_6]$ in CH_3CN was also recorded. This signal decays exponentially with a lifetime very similar to that observed for phosphorescence decay under comparable conditions. Transient signals observed with $ReBr_6^{2-}$ under comparable conditions also show an excited-state lifetime well below 100 ns. Phosphorescence data for the two ions in solution and in several single-crystal hosts are summarized in Table I. (The lifetime for $ReCl_6^{2-}$ is shorter than the value we reported previously.[3] This is because our previous measurements did not take the detector response time into account.)

One-Electron Photooxidation. Davison and co-workers showed that the two Re(IV) complexes could be oxidized reversibly by one electron in CH_3CN.[20] We repeated these measurements in

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(17) Independent phosphorescence from upper excited states in solution has been observed in Eu^{3+} and Tb^{3+} and in the copper(I) cluster Cu$_4$I$_4$-(pyridine)$_4$: Watson, W. M.; Zerger, R. P.; Yardley, J. T.; Stucky, G. D. *Inorg. Chem.* **1975**, *14*, 2675–2680. Goldschmidt, C. R.; Stein, G.; Würzberg, E. *Chem. Phys. Lett.* **1975**, *34*, 408–413. Kyle, K. R.; Ford, P. C. *J. Am. Chem. Soc.* **1989**, *111*, 5005–5006. There do not appear to be any well-documented examples of phosphorescence from upper excited states in organic compounds; for a discussion, see: Turro, N. J. *Chem. Rev.* **1978**, *78*, 125–145.

(18) Flint, C. D.; Black, A. M. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 767–774.
(19) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991–1024. We found previously[3] that the apparent phosphorescence maximum for $ReCl_6^{2-}$ is red-shifted by ca. 10 nm in 0.1 M $(Bu_4N)_2[ReCl_6]$.

order to determine the potentials relative to the Fc/Fc$^+$ (Fc = ferrocene) reference redox couple. We also found that ReCl$_6{}^{2-}$ exhibits a reversible one-electron oxidation wave in CH$_2$Cl$_2$; ReBr$_6{}^{2-}$, on the other hand, undergoes only irreversible oxidation. The results of these experiments are summarized in Table II.

We have studied the photochemical reactions of the hexahalorhenates(IV) with several reversible one-electron acceptors. Powerful electron acceptors are required to react with ReCl$_6{}^{2-}$ or ReBr$_6{}^{2-}$ even in excited states. For example, outer-sphere oxidation of the lowest energy excited state of ReCl$_6{}^{2-}$ by an electron acceptor A

$$ReCl_6{}^{2-} \ (\Gamma_8(^2T_{1g})) + A \rightarrow ReCl_6{}^- + A^- \qquad (1)$$
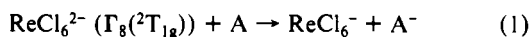
is expected to be fastest when the A/A$^-$ electrode potential is at least −0.16 V vs Fc/Fc$^+$. Tetracyanoethylene (ethenetetracarbonitrile, or TCNE) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; see Table II) satisfy this requirement; we also studied chloranil (2,3,5,6-tetrachloro-1,4-benzoquinone, or Chl).

Mixing solutions of (Bu$_4$N)$_2$[ReCl$_6$] (pale yellow-green) and TCNE (colorless) in CH$_3$CN immediately produces a deep violet color. We attribute this color to a charge-transfer transition within a ReCl$_6{}^{2-}$–TCNE electron donor–acceptor complex. This system was therefore not used for photochemical experiments.

The electron acceptors DDQ and Chl produce much smaller effects on electronic spectra. Although there is some additional absorption with both of these acceptors attributable to charge transfer within donor–acceptor complexes, the additional absorption is primarily at high energy, and it is possible to irradiate the solutions in regions where essentially the only absorption is due to ReCl$_6{}^{2-}$. The best results were obtained in CH$_2$Cl$_2$. Transient absorption signals associated with the radical anions DDQ$^-$ (λ_{max} 585 nm[21]) and Chl$^-$ (450 nm[22]) are observed in flash kinetic experiments. These transients decay with second-order kinetics; rate constants determined from the decay kinetics are (4.6 ± 0.5) × 10^9 M^{-1} s^{-1} (Chl$^-$) and (2.1 ± 0.6) × 10^9 M^{-1} s^{-1} (DDQ$^-$). Thus, the back-electron-transfer reactions are essentially diffusion-controlled, as expected because of their large driving forces.

ReBr$_6{}^{2-}$ also undergoes photochemical oxidation in CH$_3$CN and CH$_2$Cl$_2$ on flash irradiation in the presence of DDQ. However, the signals observed in these experiments are too small to analyze kinetically. Also, the solutions of ReBr$_6{}^{2-}$ and DDQ in CH$_2$Cl$_2$ were stable only for a small number of flashes. This behavior is consistent with our observations that solutions of (Bu$_4$N)$_2$[ReBr$_6$] decompose under laser irradiation and that the oxidation of ReBr$_6{}^{2-}$ is electrochemically irreversible.

Irreversible Photooxidation. The transient signals discussed above are associated with the organic radical anions generated in the photochemical electron-transfer reactions. In an attempt to identify spectral features due to the rhenium-containing products, and in order to explore permanent photooxidation reactions of the ReX$_6{}^{2-}$ ions, we also utilized CCl$_4$ and tetranitromethane (C(NO$_2$)$_4$). These are well-known for their ability to function as irreversible electron acceptors,[23,24] as follows:

$$CCl_4 + e^- \rightarrow CCl_3 + Cl^- \qquad (2)$$

$$C(NO_2)_4 + e^- \rightarrow C(NO_2)_3{}^- + NO_2 \qquad (3)$$
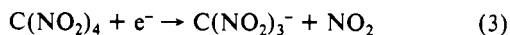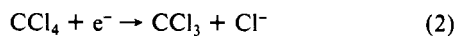
Neither CCl$_4$ nor C(NO$_2$)$_4$ reacts with ReCl$_6{}^{2-}$ in the dark. Also, no changes occur on irradiation of mixtures of (Bu$_4$N)$_2$[ReCl$_6$] with CCl$_4$ in CH$_3$CN or CH$_2$Cl$_2$. With C(NO$_2$)$_4$ as acceptor (0.03 M (Bu$_4$N)$_2$[ReCl$_6$], 0.035 M C(NO$_2$)$_4$), on the other hand, the solutions turn brown when irradiated. These experiments were performed at first with a 550-nm cutoff filter

in the excitation beam, ensuring that only ReCl$_6{}^{2-}$ was irradiated. However, the same spectral changes occur when Pyrex-filtered light from a xenon arc lamp is used for irradiation. Because this higher energy irradiation results in more rapid reaction, most of the remaining experiments were performed with Pyrex-filtered light.

The only readily discernible new spectral feature in the brown solutions produced by irradiation of (Bu$_4$N)$_2$[ReCl$_6$] with C(NO$_2$)$_4$ in CH$_2$Cl$_2$ is a shoulder at 457 nm. (Similar results are obtained in CH$_3$CN.) This shoulder is unlikely to be due to a photogenerated rhenium complex, because it disappears when the irradiated solutions are evaporated. It is also not due to NO$_2$, which should be produced according to eq 3: solutions of NO$_2$ in CH$_2$Cl$_2$ exhibit an absorption maximum at 342 nm and broad decreasing absorption in the 400–500-nm region. Instead, we attribute it to NOCl, whose solutions in organic solvents show well-defined maxima in the 450–470-nm region.[25] NO$_2$ is known to react with a variety of chloride salts to produce NOCl and NO$_3{}^-$.[26] To confirm this assignment, we passed NO$_2$(g) into a solution of (Bu$_4$N)$_2$[ReCl$_6$] in CH$_2$Cl$_2$. The pale green solution of ReCl$_6{}^{2-}$ turned brown (λ_{max} 458 nm) within a few minutes. Thus, the NOCl is probably formed by reaction of NO$_2$ (produced via reaction 3) with ReCl$_6{}^{2-}$ or with chloride ion formed in the photochemical reaction.

We found no electronic absorption bands attributable to rhenium-containing photoproducts in these irradiated solutions. However, we isolated two other materials from the residue that remains when the solvent is removed. Extraction of the residue with ethyl acetate produces a yellow solution and leaves behind pale green unreacted (Bu$_4$N)$_2$[ReCl$_6$], which is readily identified by its absorption spectrum in CH$_3$CN. We attribute the yellow color of the ethyl acetate solution (λ_{max} 350 nm) to the trinitromethanide ion, C(NO$_2$)$_3{}^-$,[27] the other product of reaction 3. Evaporation of this yellow solution leaves a yellow solid, as expected, but also colorless crystals. These were identified as (Bu$_4$N)[ReO$_4$], both by X-ray crystallography and by their IR spectrum ($\bar{\nu}_{Re=O}$ 906 cm^{-1}).[28,29] Thus, the final product of photooxidation of ReCl$_6{}^{2-}$ by C(NO$_2$)$_4$ is the perrhenate ion, ReO$_4{}^-$.

Incorporation of H$_2$O into Photogenerated ReO$_4{}^-$. We also repeated these experiments in mixtures to which water had been deliberately added. (Bu$_4$N)[ReO$_4$] and (Bu$_4$N)[C(NO$_2$)$_3$] were still observed as final products, but the brown color of NOCl was not produced in the intermediate stages. Irradiation in the presence of H$_2{}^{18}$O (10 atom %) produced some ^{18}O-labeled perrhenate ion, as judged by the appearance of a new band in the infrared spectrum at 865 cm^{-1} (thin film on NaCl plate).[30]

Murmann has reported a study of the exchange of ^{18}O between water and perrhenate ion.[31] Although this exchange is quite slow

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(28) Crystal data for (C$_4$H$_9$)$_4$NReO$_4$: orthorhombic, space group *Pnma* (No. 62); *a* = 15.417 (2), *b* = 9.927 (2), *c* = 13.856 (1) Å; *V* = 2120.6 Å^3; *Z* = 4; λ = 0.71073 Å (Mo Kα); *R* = 0.051, *R$_w$* = 0.054 for 71 parameters and 1157 reflections with *I* > 3σ(*I*). Both the anion and the cation in this structure lie on crystallographic mirror planes perpendicular to *b*. Two of the C$_4$H$_9$ groups in the cation are disordered about the mirror plane. Also, the displacement parameters for the O atoms in the anion refined to very large values, suggesting that ReO$_4{}^-$ is undergoing a large amount of rotational motion. Thus, it was not possible to complete the structure refinement. The infrared spectrum of ReO$_4{}^-$ is discussed briefly in ref 29; our spectrum matched that of (C$_4$H$_9$)$_4$NReO$_4$ prepared separately from (C$_4$H$_9$)$_4$NHSO$_4$ and HReO$_4$ in water.

(29) Fergusson, J. E.; Love, J. L. *Aust. J. Chem.* **1971**, *24*, 2689–2693.

(30) Our red shift of ca. 40 cm^{-1} on substitution of ^{18}O is consistent with data for aqueous solutions (Re^{16}O$_4{}^-$, 918 cm^{-1}; Re^{18}O^{16}O$_3{}^-$, 880 cm^{-1}): Müller, A.; Königer, F.; Weinstock, N. *Spectrochim. Acta, Part A* **1974**, *30A*, 641–649.
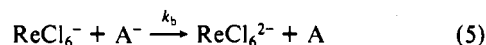
in neutral solution, it is much faster at low pH: the exchange lifetime is ca. 50 s at pH 2, a value that is reached quickly when unbuffered solutions are irradiated. In order to minimize the role of acid-catalyzed ^{18}O exchange, we also conducted the irradiation in the presence of excess 2,4,6-trimethylpyridine (pK_a = 7.43[32]) and $H_2{}^{18}O$. This time, although the pH remained near 7 (exchange lifetime ca. 7 × 10^7 s) throughout irradiation, labeled perrhenate ion was still formed.

Discussion

Photophysics. The major change observed in the spectral properties of the hexahalorhenates(IV) between the doped-single-crystal environment and that of the pure solids or solutions is the absence of phosphorescence from the upper ($^2T_{2g}$) excited states. The occurrence of intense phosphorescence from the $^2T_{2g}$ levels in the crystalline hosts has been attributed to the lack of high-energy vibrational modes for efficient deactivation to lower excited states. Flint and Black also noted that the $^2T_{2g}$ phosphorescence becomes weaker as the rhenium concentration in the crystals is increased above ca. 1%.[6] This suggests that ground-state quenching of $^2T_{2g}$ is very rapid. Both of these deactivation processes, ground-state quenching and vibrational deactivation, are likely to compete effectively with the higher energy emissions in our pure solids and solutions.

The phosphorescence of the lowest energy $\Gamma_8(^2T_{1g})$ state is also much weaker under our conditions than in the single-crystal experiments. Assuming the radiative rate constants are the same in solution and in the solid state, a comparison of the lifetimes for ReCl$_6{}^{2-}$ in CH$_3$CN and in K$_2$SnCl$_6$ suggests that the phosphorescence quantum yield in solution can be no larger than ca. 2 × 10^{-4}. This is similar to the case of chromium(III) complexes, few of which show solution phosphorescence quantum yields as high as 10^{-3}.[33]

Reversible Photooxidation. In our microsecond flash-photolysis experiments with ReCl$_6{}^{2-}$ and the acceptors DDQ and Chl, we observed transient signals attributable to the reduced electron acceptors that decayed with second-order kinetics. These observations are consistent with the following scheme:

$$\text{ReCl}_6{}^{2-*} + A \xrightarrow{k_q} \text{ReCl}_6{}^- + A^- \qquad (4)$$

$$\text{ReCl}_6{}^- + A^- \xrightarrow{k_b} \text{ReCl}_6{}^{2-} + A \qquad (5)$$

The lowest energy excited state of ReCl$_6{}^{2-}$, $\Gamma_8(^2T_{1g})$, is a sufficiently powerful reductant for quenching by DDQ. However, for Chl, electron transfer from this excited state is thermodynamically unfavorable: on the basis of half-wave potentials for ReCl$_6{}^{2-}$ and Chl and the energy of $\Gamma_8(^2T_{1g})$, ΔG_4 is ca. 0.20 eV (19 kJ mol^{-1}). Electron transfer to Chl could occur via $\Gamma_8(^2T_{1g})$, but with a small rate constant k_q; alternatively, an upper excited state of ReCl$_6{}^{2-}$ could be responsible for reaction with Chl.

Electron-transfer reactions with positive ΔG values have been studied by a number of authors.[34] Quenching data for Ru(bpy)$_3{}^{2+}$ with neutral donors and acceptors,[35] for example, suggest that, if $\Delta E°$ for reaction 4 is −0.2 V, k_q can be expected to be ca. 1 × 10^8 M^{-1} s^{-1}. Such a quenching rate constant might still permit detection of Chl$^-$ in our experiments, without causing a measurable difference in the observed lifetime of $\Gamma_8(^2T_{1g})$.[36]

We have reported previously that Mo(NCS)$_6{}^{3-}$ reacts photochemically with 1,3-dinitrobenzene, a reaction that is unfavorable by ca. 0.36 eV for the lowest energy Mo excited state.[2] This observation is consistent with the involvement of an upper excited state in the reaction. In the present case, although a variety of higher excited states of ReCl$_6{}^{2-}$ would have sufficient energy for reaction with Chl, the previously published spectroscopic studies suggest that only $\Gamma_7(^2T_{2g})$ is likely to have a significant lifetime. However, this appears to be true only in doped single crystals: we find no luminescence from $^2T_{2g}$ in either ReCl$_6{}^{2-}$ or ReBr$_6{}^{2-}$, either at room temperature or at 77 K, in fluid or glassy solution or in pure solids. Assuming its radiative rate constant under these conditions is comparable to that in K$_2$SnCl$_6$:Re^{4+}, the $^2T_{2g}$ lifetime must be extremely short, possibly 1 ns or less, in solution.

A lifetime of 1 ns for $^2T_{2g}$ would limit the efficiency of any photochemical reactions of ReCl$_6{}^{2-}$ requiring the participation of an upper excited state. However, we have previously shown that the vanadium(II) complexes of 2,2′-bipyridine and 1,10-phenanthroline, both of which have excited-state lifetimes less than 2 ns in solution at room temperature,[37] undergo photochemical reactions with electron acceptors.[38] Thus, even if it is extremely short-lived, the higher energy $^2T_{2g}$ level in ReCl$_6{}^{2-}$ may be responsible for the photochemical electron-transfer reactions we observe with chloranil as electron acceptor.

Our data do not show conclusively that an upper excited state of ReCl$_6{}^{2-}$ is redox-active. Unfortunately, there are few other electron acceptors with electrode potentials and absorption spectra that are appropriate for photoredox studies with ReCl$_6{}^{2-}$, so that this question is likely to be difficult to resolve.

Photooxidation with Tetranitromethane. Our irreversible photooxidation experiments utilized CCl$_4$ and C(NO$_2$)$_4$ as electron acceptors. Because the reduction of the electron acceptors (eqs 2 and 3) is irreversible, the corresponding electrode potentials are not readily available. However, solutions of CCl$_4$ and C(NO$_2$)$_4$ in aqueous-organic solvent mixtures undergo reduction at −0.34[39] and 0.45 V vs SCE.[40] These potentials are consistent with our photochemical experiments, in which we observe reaction only with C(NO$_2$)$_4$.

The initial reaction of a ReCl$_6{}^{2-}$ excited state with C(NO$_2$)$_4$ probably involves one-electron outer-sphere oxidation of ReCl$_6{}^{2-}$. (One-electron oxidation was observed by Kochi and co-workers in the photochemical reaction of C(NO$_2$)$_4$ with anthracenes.[24] Also, in our previous photochemical study of Mo(NCS)$_6{}^{3-}$, irreversible photooxidation by CCl$_4$ produced Mo(NCS)$_6{}^{2-}$.[2]) The likely product in the present case, ReCl$_6{}^-$, has been reported only in solids such as red-brown (Bu$_4$N)[ReCl$_6$].[41] No spectral properties have been reported for ReCl$_6{}^-$; therefore, it is difficult to determine directly whether it is produced in our photochemical experiments. ReCl$_6{}^-$ should show intense LMCT absorptions. For example, the lowest energy LMCT transition in a related d^0 complex, NbCl$_6{}^-$, occurs near 360 nm.[42] However, competing intense absorption from NOCl and C(NO$_2$)$_3{}^-$ in this region obscures any new bands attributable to ReCl$_6{}^-$.

A photogenerated rhenium(V) species such as ReCl$_6{}^-$ might also hydrolyze readily to form an oxo complex. We were especially interested in this reaction because the resulting oxorhenium(V) species might in turn be photoactive. For example, dioxo-

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(36) In our preliminary report of the photochemistry of ReCl$_6{}^{2-}$, we found that its excited-state lifetime is reduced in the presence of DDQ but not Chl.[3] However, as a reviewer has pointed out, it would be difficult to measure the change in phosphorescence lifetime with our detector even if as much as 10% of the excited states were quenched by electron transfer.

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rhenium(V) complexes such as $ReO_2(py)_4{}^+$ (py = pyridine) are diamagnetic, with the $(d_{xy}{}^2)$ ground-state configuration; the lowest lying ${}^3E_g$ $((d_{xy})^1(d_{xz,yz})^1)$ excited states of these complexes are relatively long-lived.[43] A regular octahedral rhenium(V) species such as $ReCl_6{}^-$ would have a triplet ground state. However, Fergusson and Love showed that $ReOCl_5{}^{2-}$ is diamagnetic;[29] thus, it is likely to be electronically similar to $ReO_2(py)_4{}^+$. The present rhenium system therefore presents an unusual example of two adjacent oxidation states both of which are potentially photoactive.

In our photochemical oxidations, however, the only identifiable rhenium-containing product is $ReO_4{}^-$. (We observe no UV/ visible[29,44,45] or infrared[29,46] absorption bands attributable to $Re^VOCl_5{}^{2-}$ or $Re^{VI}OCl_5{}^-$.) Our failure to observe these possible intermediates is consistent with the relatively small extinction coefficients for these species, especially compared to those of the other products, NOCl and $C(NO_2)_3{}^-$. Nevertheless, this makes it difficult to determine a detailed mechanism for the reaction following the initial photooxidation (reaction 6) and disproportionation of NO_2 (reaction 7). Instead, on the basis of our results

$$ReCl_6{}^{2-*} + C(NO_2)_4 \rightarrow ReCl_6{}^- + C(NO_2)_3{}^- + NO_2 \quad (6)$$

$$2NO_2 + [Cl^-] \rightarrow NOCl + NO_3{}^- \quad (7)$$

and on the known chemistry of NO_2 and NOCl, we can outline the most likely steps. After reactions 6 and 7, two additional types of reactions are required: further oxidation to Re(VII) and replacement of the coordinated Cl atoms by O.

Several oxidants are present in these solutions that could react with the rhenium-containing intermediate species. The reagent present in highest concentration is $C(NO_2)_4$. Although it does not react spontaneously with $ReCl_6{}^{2-}$, other species may be easier to oxidize. Other potentially oxidizing species include NO_2 and NOCl. NO_2 has been studied as an outer-sphere one-electron oxidant with iron(II) complexes.[47] For NOCl, the reaction is a one-electron transfer accompanied by chloride loss (NOCl + $e^- \rightarrow$ NO + Cl^-);[48] NOCl has been used to prepare highly oxidizing metal chloro complexes.[49] NOCl is also known to produce NO and Cl_2 on irradiation;[50] this could account for further oxidation following the initial energy transfer. And, finally, $Re^VOCl_5{}^{2-}$ is known to disproportionate under certain conditions, producing $ReCl_6{}^{2-}$ and $ReO_4{}^-$.[29]

We have proposed above that $ReCl_6{}^-$, when produced photochemically, would hydrolyze readily to form $Re^VOCl_5{}^{2-}$. If enough water is present, similar hydrolysis steps, especially if oxidation were occurring simultaneously, could remove all of the coordinated chloride ions and add the other oxygen atoms required for for-

mation of perrhenate. Many of our photooxidation experiments were conducted in dichloromethane solutions open to the atmosphere; these solutions may contain significant quantities of water.

Our experiments with $H_2{}^{18}O$ show that, when water is present, its O atoms are incorporated into the final $ReO_4{}^-$ product. This must occur during the oxidation, because (as demonstrated by irradiation in buffered solution) the formation of labeled perrhenate ion is much faster than its expected rate of exchange with $H_2{}^{18}O$. In order to explore the scope of the photochemical reaction, we also irradiated solutions prepared in an inert-atmosphere glovebox so as to minimize the concentration of water. The final products, $C(NO_2)_3{}^-$ and $(Bu_4N)[ReO_4]$, are the same in all cases, and the reactions proceed at similar rates.[51] Thus, although water is consumed if it is available, other materials in these solutions can carry out similar transformations as well.[52] In the absence of water, likely alternative sources of oxygen atoms are NO_2, and $NO_3{}^-$ produced from it by disproportionation. NO_2 has been shown to react with a variety of high-valent halides to produce oxo complexes,[53] and nitrate ion can donate O atoms to transition-metal complexes such as $Ru(bpy)_2(py)(H_2O)^{2+}$.[54]

Thus, although a definite mechanism for the photooxidation of $ReCl_6{}^{2-}$ to $ReO_4{}^-$ is difficult to establish, several reagents are available for the primary transformations of oxidation and oxo complex formation. Oxidation routes include reaction with $C(NO_2)_4$, NO_2, and NOCl as well as disproportionation of $Re^VOCl_5{}^{2-}$; for forming oxo complexes, the most likely reagents are H_2O, NO_2, and $NO_3{}^-$.

Summary

Hexachlororhenate(IV) and hexabromorhenate(IV) phosphoresce in solution at room temperature, and their excited states are oxidized by several electron acceptors in both reversible and irreversible reactions. Extended photolysis of $ReCl_6{}^{2-}$ in the presence of $C(NO_2)_4$ leads to three-electron oxidation, producing $ReO_4{}^-$. We are now exploring the reactivity of rhenium complexes in the V, VI, and VII oxidation states with other inorganic and organic species, so that these photooxidations can be adapted to sensitized multielectron transformations in substrate molecules.

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(51) The most noticeable effect of water concentration in these experiments is on the persistence of the brown color of NOCl: it is longest lived in the dry solution, and the wet mixture produces no brown color at all. This suggests that the photogenerated NO_2 reacts with water (forming $NO_3{}^-$ and HNO_2) more rapidly than with Cl^-; alternatively, any NOCl formed according to reaction 7 hydrolyzes readily, producing HCl(aq) and HNO_2(aq) (Schmid, H.; Maschka, A. *Z. Phys. Chem. (Leipzig)* **1941**, *B49*, 171–186).
(52) Traces of water may still be present even in the "dry" solutions. For example, in a typical experiment, 0.036 g of $(Bu_4N)[ReO_4]$ was isolated from 20 mL of irradiated solution. A water concentrated of 0.02% by weight in the original solution would be sufficient to produce all of the perrhenate ion that was isolated in this experiment.
(53) MF_5 (M = P, As, Sb): Peacock, R. D.; Wilson, I. L. *J. Chem. Soc. A* **1969**, 2030–2036. MoF_6, WF_6: Geichman, J. R.; Smith, E. A.; Swaney, L. R.; Ogle, P. R. *U.S.A.E.C., Rep. GAT-T-970* **1962**. WCl_6, $WOCl_4$, WO_2Cl_2: Zelikman, A. N.; Leonova, L. M.; Myakisheva, L. V. *Tsvetn. Met. (Moscow)* **1984**, 59–62 (*Chem. Abstr.* **1985**, *102*, 223915c).
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