is clearly within the range associated with polymeric structures.[19,25–27]

SnCl$_2$BrCN(THF). Figure 4 shows the Mössbauer spectrum of SnCl$_2$BrCN(THF) at liquid-nitrogen temperature. The IS and QS values for this compound (Table I) are practically constant in the temperature range $77 \leqslant T \leqslant 189$ K. SnCl$_2$BrCN(THF) gives a poor Mössbauer effect at room temperature (0.4% absorption), and although its spectra are unresolved quadrupole doublets, their computer fitting indicate a line asymmetry, which seems to be temperature-dependent (Figure 2) and might be due to the Goldanskii–Karyagin effect.

The plot of ln A vs. temperature for SnCl$_2$BrCN(THF) (Figure 3) shows a small downward curvature over the entire range of temperatures studied (77–189 K); however, the experimental points can be fitted to a straight line ($r = 0.997$) with a slope -1.32×10^{-2} K^{-1}, which allows us to propose a polymeric structure for this compound,[19,20,28] similar to the one of SnCl$_3$CN(Me$_3$SiCN).[29]

SnCl$_2$ICN(THF). The Mössbauer spectrum of SnCl$_2$ICN(THF) at liquid-nitrogen temperature (Figure 4) cannot be satisfactorily adjusted with only one quadupole doublet; this is even more evident, bearing in mind that $\chi^2 = 2105$,[30] and shows that more than one resonant species are present. We have fitted the seven registered spectra in the temperature range $77 \leqslant T \leqslant 187$ K with only a quadrupole doublet in order to study their evolution with temperature, because of the difficulties in fitting them with all the present species. The IS and QS values (Table I) display little changes with temperature, and the computed line asymmetry in the spectra is temperature insensitive ($I-/I+$ ranges between 1.07 and 1.09), showing no evidence of the Goldanskii–Karyagin effect. No ambient-temperature spectrum can be resolved for SnCl$_2$ICN(THF). Although the plot of ln A. vs. temperature also shows some downward curvature (Figure 3), a regression straight line ($r = 0.996$) can be obtained with a slope, $\mathrm{d}(\ln A)/\mathrm{d}T = -1.59 \times 10^{-2}$ K^{-1}. Similar temperature coefficients have been found for solids comprising noninteracting molecules,[19,28,31] so that an oligomeric structure would be possible for SnCl$_2$ICN(THF). On the other hand, cryoscopic measurements in nitrobenzene indicate a greater association degree than the one corresponding to a dimer.

"SnCl$_2$BrCN(THF)$_{1.5}$". By reaction of SnCl$_2$ with BrCN in THF solution we initially isolated a solid of approximate composition SnCl$_2$BrCN(THF)$_{1.5}$, whose Mössbauer spectrum (Figure 4) indicates the presence of more than one species and can be explained as a mixture of SnCl$_2$BrCN(THF) and SnCl$_2$BrCN(THF)$_2$. According to this interpretation, the initial product of the reaction is SnCl$_2$BrCN(THF)$_2$, which afterward loses a molecule of THF, giving rise to SnCl$_2$BrCN(THF). In fact, when "SnCl$_2$BrCN(THF)$_{1.5}$" is kept in vacuo, at a moderate temperature, the final product is exclusively SnCl$_2$BrCN(THF). Both "SnCl$_2$BrCN(THF)$_{1.5}$" and SnCl$_2$BrCN(THF) have practically the same IR spectra. The lack of νCN corresponding to SnCl$_2$BrCN(THF)$_2$ could be due to the fact that, although CN terminal groups display νCN at lower frequencies than the bridging ones,[18] its intensity is generally weaker[32] and could be masked by the band at 2210 cm^{-1} of SnCl$_2$BrCN(THF). The Mössbauer spectra of "SnCl$_2$BrCN(THF)$_{1.5}$" were fitted with two quadrupole doublets; for the one corresponding to SnCl$_2$BrCN(THF), the IS, QS, and intensity ratio were constrained to the previously found values. In this way, the parameters shown in Table I were obtained. Due to the overlapping nature of the spectra the intensities corresponding to each species are subject to considerable error, thus precluding the determination of the temperature dependence of ln A for SnCl$_2$BrCN(THF)$_2$. However, Table I shows the temperature dependence of the total area under the spectra, and considering the value previously found for SnCl$_2$BrCN(THF) (1.32×10^{-2} K^{-1}), the temperature coefficient for SnCl$_2$BrCN(THF)$_2$ must be higher than 1.56×10^{-2} K^{-1}. That agrees[19,28,31] with the monomeric structure that was expected because the tin atom is hexacoordinated without the need of using cyanide bridges. The IS and QS for SnCl$_2$BrCN(THF)$_2$ resemble those measured for SnCl$_2$Br$_2$(THF)$_2$,[13] corresponding to the similarity between both compounds, which implies that the THF groups coordinate in the trans position.

Registry No. SnCl$_3$CN(Me$_3$SiCN), 98586-97-1; SnCl$_2$BrCN(THF), 98586-98-2; SnCl$_2$ICN(THF), 98586-99-3; SnCl$_2$BrCN(THF)$_2$, 98587-00-9; SnCl$_2$, 7772-99-8; BrCN, 506-68-3; ICN, 506-78-5.

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(29) An approximate point charge model calculation suggests that SnCl$_3$CN(Me$_3$SiCN) and SnCl$_2$BrCN(THF) might have a different sign of the quadrupole splitting. This fact could explain the different behavior in line asymmetry, which can be seen in Figure 2.

(30) With 192 degrees of freedom; for the other compounds χ^2 ranges between 237 and 330 under the same conditions.

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Pulse-Radiolysis Study of Mixed-Valence Mo^{IV,V} Complexes of EDTA, L-Cysteine, and Oxalate

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The molybdenum(IV,V) mixed-valence complexes Mo^{IV}Mo^{V}O$_4$L$_n$$^{2-}$, where L$_n$ = (EDTA), (L-cyst)$_2$, or (ox)$_2$(H$_2$O)$_2$, were obtained by pulse-radiolytic reduction of the corresponding Mo^{V} complexes with the hydrated electron, e$_{aq}^-$. The rates of reduction for the various complexes were found to be similar; $k_4 = k_5 = (1.5 \pm 0.5) \times 10^{10}$ M^{-1} s^{-1}. The mixed-valence complexes can also be generated by reduction of the parent complexes with Zn$^+$ ($k_6 \sim k_7 \simeq 5 \times 10^9$ M^{-1} s^{-1}). The Mo(IV,V) mixed-valence complexes absorb weakly in the visible range ($\epsilon \sim 300$–500 M^{-1} cm^{-1}). While in the absence of oxygen their decay is relatively slow ($t_{1/2} \sim 5$–10 s) and does not result in Mo(III) product formation, in the presence of O$_2$ they undergo rapid second-order oxidation ($k \sim 10^8$ M^{-1} s^{-1}) back to the Mo(V) complexes. The latter observation suggests that the driving force for regeneration of the Mo$^{V}_2$O$_4$$^{2+}$ unit is sufficient to cause reduction of the ligands in the reduced complex. Substitution of the bridging oxides in the EDTA complex with sulfide does not significantly change the stability of the mixed-valence complex.

Introduction

The aqueous chemistry of molybdenum in its higher oxidation states (IV, V, VI) is characterized by the formation of polymeric species, and the structures of numerous complexes of molybdenum(V) and -(VI) have been determined.[1,2] Interest in these complexes has been partly due to the importance of molybdenum

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as a component of active sites in enzymes[3] that catalyze nitrogen fixation and reduction of nitrate ion.

The cysteine complex of molybdenum(IV) has been described as a species effective in reducing acetylene in some model fixation experiments.[4] Solutions of the Mo(IV) aquo ion (which investigations have shown to be a trimer[5]) are relatively stable to disproportionation and air oxidation. However, there is evidence that in smaller units it is highly reactive[6] and that it may be the active valence state in molybdenum-containing enzymes.

The reduction of dinuclear Mo(V) complexes with μ-sulfido bridges by electrochemical methods has been reported to result in the formation of mixed-valence Mo(V,IV) species in nonaqueous solvents,[7] and mixed-valence intermediates have been postulated in redox reactions of dimeric Mo(III) complexes. In aqueous solution, however, electrochemical reductions of the μ-oxo- and μ-sulfido-bridged dinuclear Mo(V) complexes with EDTA and cysteine, e.g. $[Mo_2O_4(EDTA)]^{2-}$ and $[Mo_2O_4(cyst)]^{2-}$ are reduced to the Mo(III) analogues (usually at potentials less than −1.0 V vs. SCE) without observable intermediate states.[8]

The present study uses the reaction between binuclear Mo(V) complexes and the aquated electron (e_{aq}^-) to generate the Mo(V,IV) mixed-valence species from the parent complexes $[Mo_2O_4(EDTA)]^{2-}$, $[Mo_2O_2S_2(EDTA)]^{2-}$, $[Mo_2O_4(ox)_2(H_2O)_2]^{2-}$, and $[Mo_2O_4(cyst)_2]^{2-}$.

Experimental Section

The sodium bis(μ-oxo)(ethylenediaminetetraacetato)bis[oxomolybdate(V)] trihydrate complex ($Na_2[Mo_2O_4(EDTA)]\cdot 3H_2O$), was prepared according to the method of Pecsok and Sawyer.[9] After repeated recrystallizations from ethanol–water, the electronic spectrum of the complex was in agreement with that of the literature (ϵ_{296} = 12 000 M^{-1} cm^{-1}, ϵ_{385} = 350 M^{-1} cm^{-1}).

Preparation of Potassium Bis(μ-oxo)bis[aquo(oxalato)oxomolybdate(V)] ($K_2[Mo_2O_4(C_2O_4)_2(H_2O)_2]$). A literature method of preparation[10] was used, and the complex had a spectrum in agreement with the literature values.

The sodium bis(μ-oxo)bis[(L-cysteinato)oxomolybdate(V)] pentahydrate complex ($Na_2[Mo_2O(\text{L-cyst})_2]\cdot 5H_2O$) was prepared by a literature method[11] using sodium dithionite as reductant. The spectrum was in agreement with literature values (ϵ_{308} = 12 000 M^{-1} cm^{-1} per dimer) after two recrystallizations from ethanol–water.

Conversion to Sodium Bis(μ-sulfido)bis[(L-cysteinato)oxomolybdate(V)] Trihydrate ($Na_2[Mo_2O_2S_2(\text{L-cyst})_2]\cdot 3H_2O$). The μ-oxo complex was bubbled with hydrogen sulfide as described by Kay and Mitchell.[11] The crude complex was separated as an amorphous material from the reaction mixture and used without further purification in the following synthesis.

Preparation of a Solution of Bis(μ-sulfido)bis[triaquooxomolybdenum(V)] ($Mo_2O_2S_2(H_2O)_6^{2+}$). A 1-g sample of the dried μ-sulfido cysteinate complex was worked up as described by Armstrong et al.[12] After the reaction mixture was eluted with 1.0 M $HClO_4$ through a Sephadex G10 column, free cysteine was removed and the aquo ion in 1.0 M $HClO_4$ was obtained. The shape of the electronic spectrum agreed with that in ref 12.

Preparation of a Solution of the Bis(μ-sulfido)(ethylenediaminetetraacetato)bis[oxomolybdate(V)] Complex ($[Mo_2O_2S_2(EDTA)]^{2-}$). To a 1 × 10^{-4} M solution of the aquo complex was added an equivalent amount of EDTA. The solution was brought to pH 6 by the addition of NaOH. The spectrum of the complex in solution corresponded to the one reported in the literature.[8]

Pulse-Radiolysis Experiments. The pulse-radiolysis experiments were carried out with a 2-MeV Van de Graaff generator. The experimental arrangement consists of an interface between the photomultiplier tube of the optical assembly and a PDP-11 computer. Solutions to be irradiated are contained in a reservoir where they are saturated/purged with a desired gas and from which they are transferred to the optical sample cell with the aid of a computer-controlled solenoid valve. Optical path lengths were 2.0 or 6.1 cm as required, and solutions were thermostated at 25 °C. The pulse typically generated from 5–10 μM of aquated electrons (e_{aq}^-).

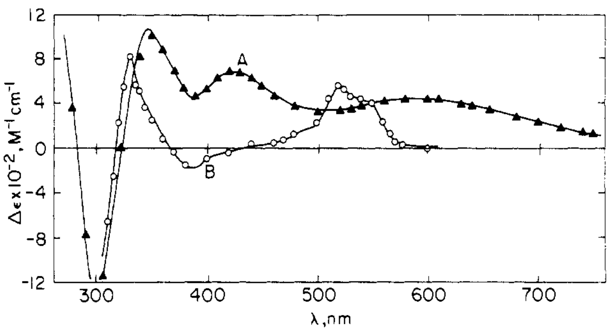

Figure 1. Difference spectra obtained for the mixed-valence complexes relative to Mo^V parent species in 0.1 M *tert*-butyl alcohol, pH 6: A, $[Mo^{IV}Mo^{V}O_4(ox)_2(H_2O)_2]^{3-}$; B, $[Mo^{IV}Mo^{V}O_4(EDTA)]^{3-}$.

All solutions were prepared with water that had been distilled and passed through a millipore ultrapurification system. Nitrogen (Matheson 99.999% UHP grade) or argon (passed through a Cu_2O catalyst to remove traces of O_2) was used as a blanket gas for most solutions. The *tert*-butyl alcohol used as a hydroxyl scavenger was purified by repeated recrystallization of a Fisher C.P. grade. Sodium formate (Baker) was of reagent grade, and the zinc sulfate used was of Puratronics grade.

Results

The radiolysis of water yields primary radicals and molecular species according to eq 1, where the numbers in parentheses indicate *G* values or the number of free radicals formed per 100 eV of energy absorbed by the medium.[13] Hydroxyl radicals were

$$H_2O \rightsquigarrow OH\ (2.75) + e_{aq}^-\ (2.65) + H\ (0.65) + H_2O_2\ (0.70) + H_2\ (0.45) \quad (1)$$

scavenged by either 0.1 M *tert*-butyl alcohol or 0.1 M sodium formate according to reactions 2 or 3. The *tert*-butyl radical

$$OH + (CH_3)_3COH \rightarrow \cdot CH_2(CH_3)_2OH + H_2O \quad (2)$$

$$OH + HCOO^- \rightarrow CO_2^- + H_2O \quad (3)$$

formed in reaction 2 is unreactive and decays by dimerization whereas CO_2^- is a strong reductant. At pH less than ~3.5 most of the e_{aq}^- are converted to H atoms by reaction with protons. H atoms abstract hydrogen from *tert*-butyl alcohol to form H_2 at relatively rapid rates but, in general, are poorer reductants than e_{aq}^- unless bond formation with the substrate can occur; e_{aq}^- reacts with Zn^{2+} to form Zn^+, a facile reductant[14] that does not require an inner-sphere pathway for reaction.

Reaction of e_{aq}^- with the Molybdenum(V) Complexes. The second-order rate constants for the reaction of pulse radiolytically generated e_{aq}^- with $[Mo_2O_4(EDTA)]^{2-}$ and $[Mo_2O_4(cryst)_2]^{2-}$ were measured at 25 °C in solutions of the respective complexes (2 × 10^{-5} M < [complex] < 2 × 10^{-4} M). A final pH ~6 was obtained in both cases, and the reaction was monitored near the absorbance maximum of the hydrated electron (720 nm). Pseudo-first-order rates for the decay of e_{aq}^- were first order in $[Mo_2^V]$ over the range 1 × 10^{-5} M ≤ $[Mo^V_2]$ ≤ 1 × 10^{-4} M and the second-order rate constants for reactions 4 and 5 were, within experimental error, similar ($k_4 \sim k_5 = 1.5\ (\pm 0.5) \times 10^{10}\ M^{-1}\ s^{-1}$).

$$[Mo_2O_4(EDTA)]^{2-} + e_{aq}^- \xrightarrow{k_4} [Mo^{IV}Mo^{V}O_4(EDTA)]^{3-} \quad (4)$$

$$[Mo_2O_4(cyst)_2]^{2-} + e_{aq}^- \xrightarrow{k_5} [Mo^{IV}Mo^{V}O_4(cyst)_2]^{3-} \quad (5)$$

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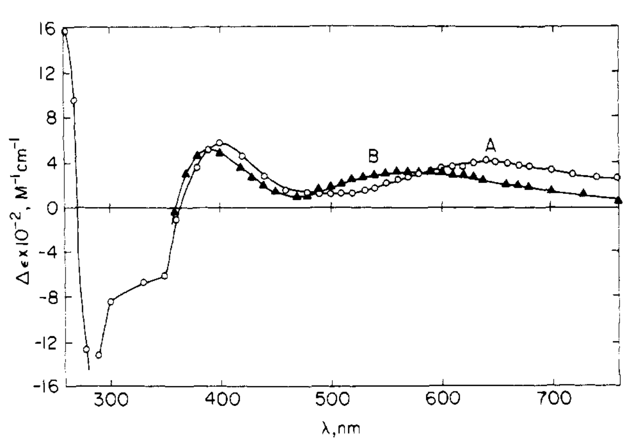

Figure 2. Difference spectra of the mixed-valence complexes relative to the Mo^V parent species in 0.1 M *tert*-butyl alcohol, pH 6: A, [Mo^{IV}Mo^{V}O$_2$S$_2$(EDTA)]$^{3-}$; B, [Mo^{IV}Mo^{V}O$_4$(L-cyst)$_2$]$^{3-}$.

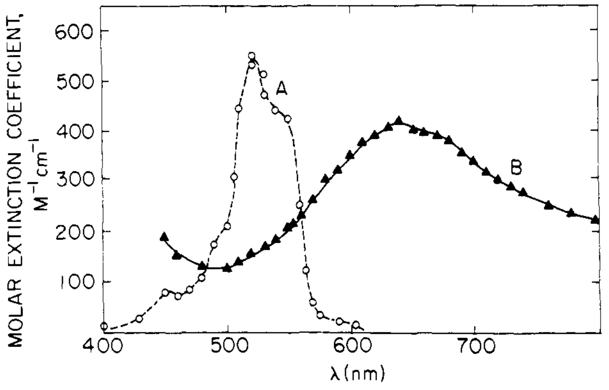

Figure 3. Electronic spectra of the mixed-valence complexes: A, [Mo^{IV}Mo^{V}O$_4$(EDTA)]$^{3-}$; B, [Mo^{IV}Mo^{V}O$_2$S$_2$(EDTA)]$^{3-}$.

Although a change in charge on these species occurs (eq 4 and 5), one can assume that the (Mo$_2$O$_4$) moiety remains intact; this is supported by the observed stability of Mo$^V{}_2$O$_4{}^{2+}$ [15] and the absence of any changes during the short observation times used in these experiments. The spectra of the products of reactions 4 and 5 and those corresponding to [Mo$_2$O$_4$(ox)$_2$(H$_2$O)$_2$]$^{2-}$ and [Mo$_2$O$_2$S$_2$(EDTA)]$^{2-}$ were measured ~3 μs after the pulse. The difference spectra are shown in Figures 1 and 2. The intense bands in the UV spectra of the parent complexes are shifted, and bleaching of the weaker bands near ~385 nm (these bands are characteristic of the Mo$_2{}^V$O$_4{}^{2+}$ moiety and are relatively independent of the ligand)[16] occurs in the mixed-valence complexes. The true absorption spectra of the mixed-valence transients [Mo^{IV}Mo^{V}O$_4$(EDTA)]$^{3-}$ and [Mo^{IV}Mo^{V}O$_2$S$_2$(EDTA)]$^{3-}$ are shown in Figure 3. The spectrum of the former complex is independent of [H$^+$] in the range from pH 4 to 10. At pH 3, *G*(Mo(IV,V)) ≃ 0, indicating that H atoms react slowly, if at all, with these complexes.

The reaction of e$_{aq}{}^-$ with [Mo$_2$O$_4$(cyst)$_2$]$^{2-}$ initiates a sequence of first-order processes. A slow ($t_{1/2}$ ~ 0.05 s) increase in absorbance following the pulse precedes the final decay of the complex and may indicate a partial dissociation of the cysteine moiety.

Reactions of [Mo$_2$O$_4$(EDTA)] with CO$_2{}^-$ and Zn$^+$. The reaction of CO$_2{}^-$ with [Mo$_2$O$_4$(EDTA)]$^{2-}$ was investigated to see if higher yields could be obtained when formate was substituted for *tert*-butyl alcohol as an OH scavenger. In pulse experiments at pH 6, *G*(Mo(IV,V)) was unchanged, and it is concluded that CO$_2{}^-$ is unreactive toward [Mo$_2$O$_4$(EDTA)]$^{2-}$. The reactivity of Zn$^+$ was determined in a 1 × 10^{-4} M solution of the complex at pH 6 to which ZnSO$_4$ was added (0.1 M) with *tert*-butyl alcohol as the OH radical scavenger. Under these conditions e$_{aq}{}^-$ reacts exclusively with Zn^{2+} to form Zn$^+$ (k = 1.5 × 10^9 M^{-1} s^{-1}).[17] In the presence of Mo$^V{}_2$(EDTA) and Mo$^V{}_2$(cyst)$_2$ the disappearance of Zn$^+$ (measured at 320 nm) is pseudo first order. A plot of k_{obsd} vs. [complex] was linear over the range 2 × 10^{-5} M ≤ [complex] ≤ 2 × 10^{-4} M that yielded second-order rate constants k_6 = (5.0 ± 0.5) × 10^9 M^{-1} s^{-1} and k_7 = (4.5 ± 1.0) × 10^9 M^{-1} s^{-1}, respectively:

$$[\mathrm{Mo_2O_4(EDTA)}]^{2-} + \mathrm{Zn}^+ \rightarrow [\mathrm{Mo^{IV}Mo^{V}O_4(EDTA)}]^{3-} + \mathrm{Zn}^{2+} \qquad (6)$$

$$[\mathrm{Mo_2O_4(cyst)_2}]^{2-} + \mathrm{Zn}^+ \rightarrow [\mathrm{Mo^{IV}Mo^{V}O_4(cyst)_2}]^{3-} + \mathrm{Zn}^{2+} \qquad (7)$$

Reactions and Decay of Transients. A fast, pH-independent reaction between traces of oxygen and the mixed-valence complexes was observed. The oxygen was reduced to levels of (1–5) × 10^{-6} M by near-exhaustive bubbling with argon, and the dose was adjusted to yield (1.0 ± 0.1) × 10^{-5} M solutions of the mixed valence dimers. The dimers of the EDTA and oxalate complexes were oxidized with observed rate constants of ~2 × 10^3 s^{-1} and ~1 × 10^3 s^{-1}, respectively. Assuming that oxidation occurs by a simple second-order reaction, second-order rate constants (k_{obsd}/[complex]) of ~2 × 10^8 M^{-1} s^{-1} and 1 × 10^8 M^{-1} s^{-1}, respectively, were calculated.

In all cases the transient mixed-valence complexes disappeared with no overall change in the optical absorption spectrum, which indicated that these transients were reoxidized to the Mo^V states. Their decays were not a simple process subject to either a first-order or second-order rate-determining step. It was not possible to resolve these kinetics, but decay, in all cases, was complete within 5–10 s. Variation of the pH from 4 to 10 in the EDTA system did not substantially affect the lifetime of the mixed-valence species. Although intermediate states are involved, we were unable to resolve these spectrally as they are not sufficiently stable under our conditions. A possible scheme for the process is given by reactions 8 and 9; L = ligand. It is clear that disproportionation

$$2\mathrm{Mo^{IV,V}L} \rightarrow \mathrm{Mo^{IV}{}_2L} + \mathrm{Mo^{V}{}_2L} \qquad (8)$$

$$\mathrm{Mo^{IV}{}_2L} \rightarrow \mathrm{Mo^{V}{}_2L(red)} \qquad (9)$$

cannot be rate-determining, but must be preceded by other reactions. The validity of reaction 9 is difficult to measure spectrally since complexes containing the Mo$^V{}_2$O$_4{}^{2+}$ moiety are spectrally similar and changes in the absorption spectrum due to the reduction of, e.g., a carboxylate group might not be resolvable.

In order to determine whether reoxidation of the mixed-valence state might be occurring via reduction of the solvent or through reaction with oxidizing impurities, a series of ^{60}Co radiolysis experiments were carried out.

^{60}Co Radiolysis: ^{60}Co radiolysis of the (μ-oxo)molybdenum(V) EDTA, cysteine, and oxalate complexes in 0.1 M *tert*-butyl alcohol (neutral pH) produced no changes in the starting material spectrum after 30 min of exposure (~6 × 10^4 rad absorbed dose). The absence of any apparent net loss of the Mo(V) complex was found not to be a result of solvent reduction. Values of *G*(hydrogen) for *tert*-butyl alcohol solutions of the EDTA and cysteine complexes were 0.48 and 0.69, respectively, as determined by gas chromatography. Therefore H$_2$ production is about equivalent to primary processes plus some contribution from the reaction of H atoms with *tert*-butyl alcohol.

Discussion

The visible spectra of the mixed-valence species show absorbances of moderate intensity in the 500–700-nm range. The visible spectrum of the EDTA mixed-valence dimer shows four or five separate transitions. Both monomeric Mo(V) and trimeric Mo(IV) have bands in this region, and it is not possible to tell whether they are characteristic of a particular oxidation state. The intense

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bands ($\epsilon > 10\,000$ M^{-1} cm^{-1}) seen in certain sulfur-containing Mo(IV,V) systems, which have been interpreted to indicate electron delocalization over the binuclear unit, are absent. However, some recent examples of oxo-bridged vanadium(IV)–vanadium(V) systems, in which delocalization has been demonstrated by EPR, show relatively weak visible absorptions.[18]

Substitution of bridging oxides by sulfide in the EDTA complexes results in broadening of these transitions and their displacement toward longer wavelengths (Figure 3) although the similar intensities of the absorption bands of the μ-oxo- and μ-sulfido-bridged complexes suggest that the same transitions are involved. However, all the complexes studied have similar stabilities with respect to reoxidation and are highly reactive toward oxygen. The decomposition mechanism of the mixed-valence complex is unclear. The reduction of a liganded carboxylate group might occur in any of the systems studied. However, the relative insensitivity of the absorption spectrum of the $Mo^{V}{}_2O_4{}^{2+}$ unit to its ligands prevented the confirmation of this possibility. The reducing strength of Mo(IV) in these mixed-valence systems undoubtedly results from the tendency to re-form the strong covalent bonding between Mo(V) atoms[16] in the $Mo_2O_4{}^{2+}$ or $Mo_2O_2S_2{}^{2+}$ moieties. The presence of bridging sulfides in the EDTA system does not appear to result in significant stabilization of the Mo(IV)–Mo(V) state.

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Nitrosyl Complexes of Rhenium. 2.[1] Neutral and Cationic Monohydride Complexes of Rhenium(I) Resulting from the Reaction of $ReH_2(NO)(PPh_3)_3$ with Perchloric Acid

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The rhenium dihydride complex $ReH_2(NO)(PPh_3)_3$ reacts with $HClO_4$ in the presence of CO with the cleavage of only one hydride ligand. Careful control of the degree of acidity and the solvent system leads to isolation of compounds such as $ReH(OR)(CO)(NO)(PPh_3)_2$ (R = Me, Et) and $[ReH(CO)(NO)(PPh_3)_3]ClO_4$. The alkoxide complexes are protonated by $HClO_4$ at the alkoxide oxygen to yield alcohol complexes $ReH(ROH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$, in which the perchlorate counterion is hydrogen bound to the coordinated alcohol. Heating $ReH(MeOH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$ in methanol results in the formal 1,2-elimination of dihydrogen with concomitant formation of $Re(OMe)(OClO_3)(CO)(NO)(PPh_3)_2$. A similar elimination reaction occurs when the alcohol complexes are reacted with halide ions to give $ReX(OR)(CO)(NO)(PPh_3)_2$ (X = Cl, Br, I). Reacting the alcohol complexes with base or $NaBH_4$, however, regenerates $ReH(OR)(CO)(NO)(PPh_3)_2$. The perchlorate complex, $Re(OMe)(OClO_3)(CO)(NO)(PPh_3)_2$, while reacting with halide ions merely with displacement of the perchlorate group, reacts with $NaBH_4$ to give $ReH_2(CO)(NO)(PPh_3)_2$ via a putative borohydride complex. The chloro–alkoxy complexes $ReCl(OR)(CO)(NO)(PPh_3)_2$ also react with $HClO_4$ to give alcohol complexes, which are considerably more labile than their hydride analogues. All structural assignments have been made on the basis of elemental analysis, infrared spectroscopy, ^1H NMR spectroscopy, and, where appropriate, deuteration studies.

Introduction

In a recent publication,[1] we described the reaction of $ReH_2(NO)(PPh_3)_3$ with HBF_4 in the presence of carbon monoxide to yield $[ReF(CO)(NO)(PPh_3)_3]BF_4$. The isoelectronic complex $OsH_2(CO)(PPh_3)_3$ behaves quite differently, affording $[OsH(CO)_2(PPh_3)_3]BF_4$ under the same conditions.[2] In the same publication we also described $ReH_2(NO)(PPh_3)_3$ as reacting with $HClO_4$ and CO with apparent decomposition. We have had cause to reinvestigate this system and have found that provided the conditions are carefully controlled, a wealth of chemistry can be obtained. In particular, we have found that in the absence of a source of good coordinating anions, cleavage of only one hydride ligand occurs, leading to a series of monohydride–nitrosyl complexes of rhenium(I). In this paper we describe a number of these complexes including $ReH(MeOH{\cdot}OClO_3)(CO)(NO)(PPh_3)_2$, which, on heating, undergoes an unusual elimination of dihydrogen.

Experimental Section

Caution! These compounds should be treated with the extreme caution normally afforded organometallic perchlorate salts, which are potentially explosive.[3] In particular, complexes **4**, **5**, **14**, and **15** described below have decomposed violently and without warning. To minimize the hazard we recommend the following precautions be taken when handling these complexes: (i) keep reaction scales to <0.5 g, (ii) avoid the use of metal spatulas since the decomposition appears to be catalyzed by finally divided metal particles, and (iii) use complexes when prepared and refrain from storing them in a sealed container.

Except where otherwise stated, all reactions were performed under an atmosphere of prepurified nitrogen (O_2 < 3 ppm). All solvents were appropriately dried, distilled, and stored over Linde type 4A molecular sieves prior to use. Infrared spectra were recorded on a Perkin-Elmer 283B spectrophotometer and calibrated against polystyrene. ^1H NMR spectra were recorded either on a Varian Associates CFT 20 spectrometer or the Nicolet 360-MHz instrument of the Atlantic Regional Magnetic Resonance Centre as CD_2Cl_2 solutions with either the $CHDCl_2$ triplet at 5.32 ppm or Me_4Si used as internal reference. ^{31}P NMR spectra were obtained on the Varian Associates XL100 spectrometer of the Atlantic Regional Laboratory of the NRC, whose services are gratefully acknowledged. Melting points were recorded on a Fisher-Johns apparatus and are uncorrected. Conductivity measurements were performed by using a conductivity bridge of local manufacture with ca. 10^{-3} M solutions in dichloromethane or nitromethane. The cell constant was determined by using a 0.0100 M aqueous KCl solution. Elemental analyses were performed by the Canadian Microanalytical Service Ltd.

Reaction of $ReH_2(NO)(PPh_3)_3$ with $HClO_4$ and CO. Synthesis of $ReH(OCH_3)(CO)(NO)(PPh_3)_2$ (1). $ReH_2(NO)(PPh_3)_3$[1] (1.00 g, 1.00 mmol) was suspended in dichloromethane–methanol (40 mL, 1:1 v/v) and the suspension degassed by rapidly bubbling carbon monoxide through for 20 min. Upon the addition of perchloric acid (0.20 mL, 70% w/v) immediate dissolution of the solid was observed with effervescence. Once dissolution was complete, 0.5 M sodium methoxide solution was added dropwise until the bright yellow solution became just slightly basic (Fisher Alkacid test paper). The passage of carbon monoxide was continued for a further 5 min after which the dichloromethane was removed slowly under reduced pressure. Pale yellow crystals were deposited from a small volume of solution and were generally sufficiently pure for further

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[1] Part 1: Cameron, T. S.; Grundy, K. R.; Robertson, K. N. *Inorg. Chem.* **1982**, *21*, 4149.

[2] Collins, T. J.; Grundy, K. R.; Roper, W. R. *J. Organomet. Chem.* **1982**, *231*, 161.

[3] Raymond, K. N. *Chem. Eng. News* **1983**, *61* (Dec 5), 4. Wolsey, W. C. *J. Chem. Educ.*, **1978**, *55*, A355; *Chem. Eng. News* **1963**, *41* (July 8), 47.

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