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# Di- and Trinuclear Complexes with Sulfide-Bridged Rhenium in Very Different Oxidation States ($Re^{I}Re^{VII}$, $Re^{I}Re^{VI}Re^{I}$, $Re^{I}Re^{VII}Re^{I}$). The $d^0/d^1$ Transition in Tetrathiometalates

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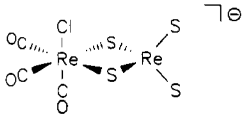
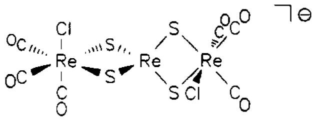
Tetrathiometalates $MS_4^{n-}$ (M = V, Nb, Ta, $n$ = 3; M = Mo, W, $n$ = 2; M = Re, $n$ = 1) have received attention in inorganic,[1-3] organometallic,[4] and bioinorganic chemistry[1a,5] and in catalysis.[6] The presence of relatively low-lying unoccupied d orbitals ($d^0$ configuration) and high-lying sulfur-based molecular orbitals[1a] results in intense ligand-to-metal charge-transfer (LMCT) transitions in the visible region.[1a,3] Despite relatively narrow HOMO–LUMO gaps the reversible electrochemical reduction to $d^1$ species occurs at rather negative potentials.[7] The potentials for the reduction $d^0 \rightarrow d^1$ are least negative for the rhenium system $ReS_4^{-/2-}$ with its rather small negative charges.[1c,3b,7] Chelate coordination of additional metal electrophiles to $ReS_4^-$ should shift the potential for $Re^{VII}/Re^{VI}$ to even less negative values. Trinuclear sulfido-bridged complexes $[L_nM(\mu\text{-}S)_2Re(\mu\text{-}S)_2ML_n]^n$ with the $ReS_4^{2-}$ bridge were reported for $ML_n$ = $Fe^{II}Cl_2$[1b] and $[Ru^{II}(bpy)_2]^{2+}$.[7]

In order to effect a less negative reduction potential for the $Re^{VII/VI}$ couple, we have been coordinating the strongly polarizing[8] $Re(CO)_3Cl$ complex fragments ($Re^I$, $d^6$) to $ReS_4^-$ to yield dinuclear $[Cl(CO)_3Re(\mu\text{-}S)_2ReS_2]^-$ ($I^-$) and trinuclear $[Cl(CO)_3Re(\mu\text{-}S)_2Re(\mu\text{-}S)_2Re(CO)_3Cl]^-$ ($II^-$) with the rhenium centers in very different oxidation states.



$I^{\ominus}$



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## Experimental Section

All reactions were carried out under an atmosphere of dry argon.

**$(NEt_4)[Cl(CO)_3Re(\mu\text{-}S)_2ReS_2]$, $(NEt_4)$(I).** A mixture of 0.224 g (0.5 mmol) of $(NEt_4)(ReS_4)$[9] and 0.18 g (0.5 mmol) of $Re(CO)_5Cl$[10] was heated to reflux for 3–4 h in 25 mL of acetonitrile. The color change from purple to blue-green was accompanied by precipitation of a small amount of dark material. Filtration from the precipitate, concentration of the remaining solution to about 5 mL, and column chromatography on silica/acetonitrile gave a solution from which pure $(NEt_4)$(I) could be obtained as blue-green microcrystals in 74% yield (270 mg) after evaporation and drying.

Anal. Calcd for $C_{11}H_{20}ClNO_3Re_2S_4$ (750.39): C, 17.61; H, 2.69; N, 1.87. Found: C, 17.62; H, 2.47; N, 1.68. IR: MeCN, 2038 (vs), 1936 (s), 1912 (s) $cm^{-1}$; $Me_2CO$, 2040 (vs), 1930 (s, br) $cm^{-1}$; $Me_2CHOH$, 2032 (vs), 1914 (s, br) $cm^{-1}$.

**$(NEt_4)[Cl(CO)_3Re(\mu\text{-}S)_2Re(\mu\text{-}S)_2Re(CO)_3Cl]$, $(NEt_4)$(II).** A mixture of 0.112 g (0.25 mmol) of $(NEt_4)(ReS_4)$ and 0.18 g (0.5 mmol) of $Re(CO)_5Cl$ was heated to reflux for 3 h in 25 mL of 1,2-dichloroethane. The color change from purple to green was accompanied by precipitation of a small amount of dark material. Following filtration and removal of the solvent the crude product was chromatographed on a silica column using acetonitrile as eluent. After eluation of the clearly separable dinuclear ion $I^-$, fractions of pure $II^-$ were collected, the solvent was removed, and the dark-green product was recrystallized from 2-propanol to afford 100 mg (37%) of the tetraethylammonium salt.

Anal. Calcd for $C_{14}H_{20}Cl_2NO_6Re_3S_4$ (1056.08): C, 15.92; H, 1.91; N, 1.33. Found: C, 16.02; H, 1.90; N, 1.22. IR: MeCN, 2040 (vs), 1937 (s), 1909 (s), 1880 (w) $cm^{-1}$; 1,2-dichloroethane, 2040 (vs), 1940 (s, br) $cm^{-1}$; $Me_2CHOH$, 2040 (vs), 1940 (s, br) $cm^{-1}$. IR spectroelectrochemistry (MeCN/0.1 M $Bu_4NPF_6$): isosbestic points at 2016, 1996, 1942, and 1930 $cm^{-1}$; absorption maxima for $II^{2-}$ at 2013 (s), 1934 (m), 1903 (m), and 1880 (sh) $cm^{-1}$.

Instrumentation and spectroscopic and spectroelectrochemical procedures were described previously.[7,11]

## Results

The compounds $(NEt_4)$(I) and $(NEt_4)$(II) were characterized analytically as summarized in the Experimental Section and in Table I. Figure 1 shows the electronic absorption spectra.

Both complexes undergo reduction to a dianion; however, UV/vis and IR spectroelectrochemistry showed that the less symmetrical complex $I^-$ is slowly decomposing after the first one-electron reduction on the time scale of about 1 min. The second reduction steps were found irreversible for both $I^-$ and $II^-$.

The persistent reduced form $II^{2-}$ was studied by UV/vis, IR, and EPR spectroelectrochemistry. Reduction of $II^-$ in 0.1 M $Bu_4NClO_4$ solutions of acetonitrile, acetone, or 1,2-dichloroethane in an EPR capillary did not produce a signal, even after cooling to 3 K. The UV/vis spectrum of $II^{2-}$ shows slightly shifted absorption bands in relation to those of $II^-$; IR vibrational spectra show similarly small changes on reduction of $II^-$ (Table I).

## Discussion

The typical *fac* configuration at the $Re(CO)_3$ centers in $I^-$ and $II^{n-}$ is apparent from the carbonyl vibrational pattern ($A_1$, split E due to lowered symmetry);[8b] the trinuclear ions are chiral.

Successive coordination of $Re(CO)_3Cl$ to $ReS_4^-$ in complexes $I^-$ and $II^-$ leads to the expected[4a,8b] systematic shift of the potentials for reversible reduction to the dianions from −1.58 via −1.16 ($I^{n-}$) to −0.74 V vs $FeCp_2^{0/+}$ for $II^{n-}$ (Table I). The second reduction which is still fairly reversible[3b,7] for $ReS_4^{-/2-}$ becomes strongly irreversible for the rhenium(I) chloride complexes because of the

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**Table I.** Electrochemical and Spectroscopic Data for Rhenium(VII) [and Rhenium(VI)] Complexes

| | $ReS_4^-$ [$ReS_4^{2-}$][a] | $I^-$ | $II^-$ [$II^{2-}$] |
|---|---|---|---|
| | Cyclic Voltammetry[b] | | |
| $E$(ox) | +0.17 (ir) | +0.77 (ir) | +0.85 (ir) |
| $E$(red$_1$) | −1.58 (70; 0.96) | −1.16 (83; 0.82) | −0.74 (70; 0.94) |
| $E$(red$_2$) | −2.46 (95; 1.00) | −1.65 (ir) | −1.40 (ir) |
| | Spectrophotometry[c] | | |
| λ(LMCT$_1$) | 509[d] [486][e] | 611[f] | 730[g,h] [630] |
| ε(LMCT$_1$) | 12700 [7900] | 5300 | 5000 [4400] |
| $\Delta\tilde{\nu}_{1/2}$(LMCT$_1$) | 1360 [2500] | 2600 | 2240 |
| λ(MMCT) | | 500 sh | 600 sh |
| λ(LMCT$_2$) | 313 [326] | 382 | 387[i] [370 sh] |
| ε(LMCT$_2$) | 24300 [14 900] | 9700 | 9200 |
| | Infrared Spectroscopy[j] | | |
| $\tilde{\nu}_{as}$ | 490 [439][k] | 457<br>435 | 456 [421][l] |

[a] From ref 7. [b] From cyclic voltammetry in acetonitrile/0.1 M $Bu_4NClO_4$ at 100 mV/s scan rate. Potentials in V vs $FeCp_2^{0/+}$; peak potentials (in mV) and peak current ratios $i_a/i_c$ in parentheses. ir: irreversible process, peak potential given. [c] In acetonitrile solution. Wavelengths λ (in nm) and molar extinction coefficients ε (in $M^{-1}$ $cm^{-1}$) at the absorption maximum, band widths at half-height $\Delta\tilde{\nu}_{1/2}$ in $cm^{-1}$. [d] Isosbestic points at 540, 497, 322, and 301 nm. [e] Additional bands at 589 nm (ε 2000) (triplet LMCT) and at 874 (1100), 950 (1300), and 1046 nm (950): (ligand-field transitions (d → d; ref 7)). [f] 590 nm in 2-propanol. [g] 719 nm in 2-propanol. [h] Isosbestic points at 671, 596, 540, and 422 nm. [i] Additional band at 346 nm (ε 10 900). [j] In $d_3$-acetonitrile solution. [k] Isosbestic point at 471 nm. [l] Isosbestic point at 434 nm.

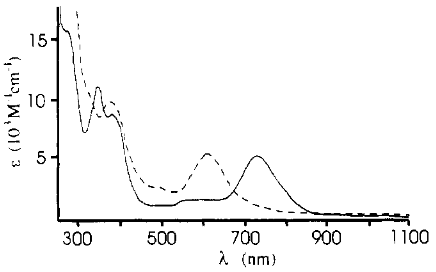

**Figure 1.** Absorption spectra of $(NEt_4)$(I) (- - -) and $(NEt_4)$(II) (—) in acetonitrile.

characteristic loss of $Cl^-$,[8b] indicating some ground-state charge shift from $ReS_4^{n-}$ to the $Re^I$ center.

Electrochemical oxidations of the complexes occur irreversibly for all three complexes (Table I). Although irreversible oxidation processes around +0.8 V vs $FeCp_2^{0/+}$ may be expected both for the Re(I) center of bound $Re(CO)_3Cl$[8b] and for the sulfido ligands of $ReS_4^-$, the sequence in Table I suggests that the sulfide oxidation occurs more easily.

In agreement with the relatively small difference of about 1.5 V between the oxidation and reduction potentials of $II^-$, the LMCT transitions p(S) → d($Re^{VII}$) and the now possible MMCT transitions $Re^I \rightarrow Re^{VII}$ should occur at rather long wavelengths. Complexes $I^-$ and $II^-$ show the familiar[1a,4a] long-wavelength LMCT transition LMCT$_1$ ($t_1 \rightarrow e$) shifted by about 3300 $cm^{-1}$ ($I^-$) and 6000 $cm^{-1}$ ($II^-$) relative to $ReS_4^-$ (Table I), in agreement with the anodic shifts of the reduction potentials and corresponding to a successive stabilization of the unoccupied d orbitals of $Re^{VII}$. The small monoanionic $ReS_4^-$ exhibits the narrowest band and thus a rather large ε value at the band maximum (Table I). The spectra of both $I^-$ and $II^-$ are clearly accompanied (Figure 1) by broad low-intensity features at slightly higher energies than the LMCT$_1$ band; we tentatively attribute these bands to the MMCT transition ($Re^I \rightarrow Re^{VII}$) occurring between nonbonded and very differently ligated metal centers.

In comparison to the rhenium complexes, the previously reported $d^6/d^0$ and $d^6/d^0/d^6$ di- and trinuclear complexes $[(CO)_4Mo(\mu\text{-}S)_2MoS_2]^{2-}$ and $[(CO)_4Mo(\mu\text{-}S)_2Mo(\mu\text{-}S)_2Mo(CO)_4]^{2-}$ show much more negative reduction potentials, less positive oxidation potentials, and slightly higher energies of the long-wavelength absorptions in acetonitrile (565 and 675 nm).[4a]

The second intense LMCT transitions LMCT$_2$ ($t_2 \rightarrow e$)[1a,12] in the near-UV region of the rhenium complexes shift less uniformly in the series of Table I. The complex $II^-$ shows two intense bands in that spectral region the assignments of which are not yet clear (Figure 1).

The absorption spectrum of $II^{2-}$ shows a slight hypsochromic shift of the long-wavelength LMCT band relative to nonreduced $II^-$, an effect which was observed similarly for the parent couple $ReS_4^{-/2-}$ (Table I).[7] Unfortunately, both the low-intensity ligand-field (d → d) transitions of the $d^1$ system and the expected triplet charge-transfer transitions are not as clearly visible for $II^{2-}$ as for the small, pentaatomic parent ion $ReS_4^{2-}$.[7]

IR spectroelectrochemical results lend further evidence to the notion that the central $ReS_4$ group of $II^{n-}$ is the primary site of electron addition. For the peripheral tricarbonylrhenium(I) groups there are only small low-energy shifts of the CO stretching bands which affect mainly the high-energy feature. Such small shifts of 27 $cm^{-1}$ or less (see Experimental Section) are typical for "remote reduction".[8b] In contrast to these small effects for the carbonyl groups, the $Re^{VII,VI}$–S stretching frequencies are shifted to a stronger extent (Table I), viz., by 51 $cm^{-1}$ in $ReS_4^{-/2-}$ [7] and by 35 $cm^{-1}$ in $II^{-/2-}$, where the coordination-induced shift and the effect of reduction combine to weaken the central Re–S bonds.

The failure to obtain an EPR signal of $II^{2-}$ even at 3 K is not unexpected. Whereas $[(bpy)_2Ru(\mu\text{-}S)_2Re(\mu\text{-}S)_2Ru(bpy)_2]^{2+}$ showed an EPR spectrum typical for hexavalent rhenium at low temperatures, the parent $ReS_4^{2-}$ was EPR silent.[7] Rapid relaxation is quite likely for an approximately tetrahedral $d^1$ center with a Jahn–Teller state,[13] especially in the case of a $5d^1$ system with large spin–orbit coupling constants of the contributing atoms.

The chemical persistence of the Re(VI) tetrathiometalate oxidation state at less negative potentials and the large electrochemical stability constant[15] $K_c(ReS_4^{2-}) = 10\exp(\Delta E/0.059\text{ V}) = 10^{14.9}$ raise the question whether other tetrathiometalates with a $d^1$ configuration can be obtained. Since we have recently reported for the first time that $WS_4^{2-}$ is reducible (as is $MoS_4^{2-}$),[7,14] albeit at the very negative potential of $E[WS_4^{2-/3-}] = -3.16$ V vs $FeCp_2^{0/+}$ in dry DMF,[7] we can extrapolate in the $5d^1$ series via $E[ReS_4^{-/2-}] = -1.58$ V (Table I) that the as yet unknown $OsS_4^-$ should exist below $E \approx 0$ V vs $FeCp_2^{0/+}$; i.e., the paramagnetic Os(VII) form may be a stable oxidation state.[16]

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(15) Stability toward disproportionation $2Re^{VI} \rightleftharpoons Re^{VII} + Re^V$.

(16) $OsS_4^{2-}$ was recently proposed as a conceivably stable new tetrathiometalate.[3a]