

Tetrathiorhenate(vi), ReS_4^{2-} . Spectroelectrochemical Characterization (UV–VIS–IR) of a Small New d^1 System and of its Tetrakis(2,2'-bipyridine)diruthenium(II) Complex (EPR)

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ReS_4^{2-} is the first d^1 tetrathiometalate persistent enough to be studied with respect to charge transfer, ligand field and IR vibrational spectra via spectroelectrochemistry; an EPR spectrum could only be detected of its trinuclear derivative $[(\text{bpy})_2\text{Ru}(\mu\text{-ReS}_4)\text{Ru}(\text{bpy})_2]^{2+}$ ($\text{bpy} = 2,2'$ -bipyridine) at 4 K.

The tetrathiometalates MS_4^{n-} with d^0 configuration have been intensively studied¹ for a variety of reasons. These relatively simple pentaatomic species have low lying unoccupied d orbitals which are responsible for the conspicuous colours due to ligand-to-metal charge transfer (LMCT) transitions, $p(\text{S}) \rightarrow d(\text{M})$. Furthermore, the negative charge and the presence of potentially bis-chelating sulfur atoms make these metal-containing anions useful as π accepting bridging ligands in the formation of homo- and heteropolynuclear systems,^{1–6} the electronic structures of which have been related to heterometallic sulfide clusters such as the Fe–Mo or Fe–V centres of nitrogenases.³ With respect to this latter aspect, the groups of Müller⁴ and Holm⁵ have recently drawn attention to the particular behaviour of the ReS_4^- ion as compared to MoS_4^{2-} or WS_4^{2-} . For instance, the lower lying unoccupied orbitals of ReS_4^- are believed to be responsible for an apparent electron transfer reaction with FeCl_2 to yield $[\text{Cl}_2\text{Fe}(\mu\text{-ReS}_4)\text{FeCl}_2]^{2-}$, with formally hexavalent rhenium, as a stable product.⁴

While the facilitated reduction of a bridging π acceptor system after twofold metal coordination is common with inorganic⁶ and organic⁷ bis(chelate) ligands (*vide infra*), the reduction behaviour of the 'free', *e.g.* merely ion-paired, tetrathiometalates of Mo^{VI} , W^{VI} and Re^{VII} has not been extensively studied because of the negative potentials and the high nucleophilicity of the species thus generated.

We have now used the possibility of (spectro)electrochemistry in a specially designed cell⁸ using very dry solvents to study the reduction of the tetraethylammonium salts of MoS_4^{2-} , WS_4^{2-} and ReS_4^- in dimethylformamide (DMF) or MeCN –0.1 mol dm^{-3} Bu_4NClO_4 . In contrast to previous statements on MoS_4^{2-} ^{4b} or WS_4^{2-} ,⁹ these ions can be reduced reversibly in very dry DMF at half-wave potentials of –2.94 and –3.16 V vs. ferrocene/ferrocenium (Fc/Fc^+), respectively; unfortunately, the persistence of the trianions is not sufficient for detailed spectroscopic studies.

ReS_4^- , on the other hand, is reduced in two reversible one-electron steps⁵ in acetonitrile at less negative half-wave potentials of –1.58 and –2.46 V vs. Fc/Fc^+ which enabled us to study the Re^{VI} intermediate with its comproportionation constant of $K_c = 10^{\Delta E/59 \text{ mV}} = 10^{15}$ by optical and vibrational

spectroelectrochemistry in the UV, visible, near-IR and IR regions (Figs. 1 and 2).

The two major LMCT bands¹ of purple ReS_4^- at 509 and 313 nm in acetonitrile exhibit shifts to 486 and 326 nm upon reduction to ReS_4^{2-} (Fig. 1). In addition to these intense bands (the small band at 589 nm is assigned to a triplet charge transfer transition typical for 5d systems¹⁰), there are now three weak ligand field (LF) bands in the long-wavelength region of that d^1 system at 1046, 950 and 874 nm (9560, 10 530 and 11 450 cm^{-1}), corresponding to $10 Dq = 10 520 \text{ cm}^{-1}$ and a splitting of about $2 \times 950 \text{ cm}^{-1}$ (Fig. 1). The number and approximate positions of these bands for ReS_4^{2-} corresponds closely to those of MnO_4^{2-} in various host crystals¹¹ (about 10 690, 11 030 and 11 370 cm^{-1} ; $10 Dq = 11 030 \text{ cm}^{-1}$, split by $2 \times 340 \text{ cm}^{-1}$) which suggests an analogous assignment $e \rightarrow t_2$ where the levels are split¹² by (Jahn–Teller) distortion and spin–orbit coupling:¹¹ $\xi(\text{Re}) \gg \xi(\text{Mn})$.

The IR vibrational spectrum measured in CD_3CN –0.1 mol dm^{-3} Bu_4NPF_6 shows that the typical ν_{as} band of tetrathiometalates¹ shifts from 490 to 439 cm^{-1} upon reduction to ReS_4^{2-} (Fig. 2). This confirms that the added electron is placed in a partly antibonding orbital³ and suggests a Re^{VI} formulation for $[\text{Cl}_2\text{Fe}(\mu\text{-ReS}_4)\text{FeCl}_2]^{2-}$ ($\nu_{\text{as}} = 446 \text{ cm}^{-1}$);⁴ for the size- and charge-related WS_4^{2-} ν_{as} is 455 cm^{-1} in Me_2SO .^{1b}

While EPR studies of the electrogenerated ReS_4^{2-} did not show a distinct signal at 4 K in frozen acetonitrile solution, perhaps owing to very short relaxation times, the less symmetrical trinuclear ion $[(\text{bpy})_2\text{Ru}(\mu\text{-ReS}_4)\text{Ru}(\text{bpy})_2]^{3+}$ ($\text{bpy} = 2,2'$ -bipyridine), obtained in analogy to Mo and W complexes,⁶ has a small frontier orbital gap ($\text{Ru}^{\text{II}} \rightarrow \text{Re}^{\text{VII}}$ transitions at 826 and 713 nm) and is reduced at a much less negative potential (–0.73 V vs. Fc/Fc^+ in acetonitrile) to a paramagnetic Re^{VI} species which gave a detectable EPR signal at 4 K. The values of $g_x = 1.73$, $A_x(\text{Re}) = 49 \text{ mT}$, $g_y = 1.78$, $A_y(\text{Re}) = 39.0 \text{ mT}$; $g_z = 2.08$ and $A_z(\text{Re}) < 6 \text{ mT}$ reflect the high spin–orbit coupling constant and the nuclear magnetic properties of rhenium ($\xi > 2000 \text{ cm}^{-1}$; ^{185,187}Re: $I = 5/2$). The results may be compared to those of a 'true' Re^{VI} species, *viz.*, tetragonally distorted ReO_4^{2-} in CaWO_4 ($g_{\perp} = 1.7164$, $A_{\perp}(\text{Re}) = 0.0324 \text{ cm}^{-1} = 40.4 \text{ mT}$, $g_{\parallel} = 1.8549$, $A_{\parallel} =$

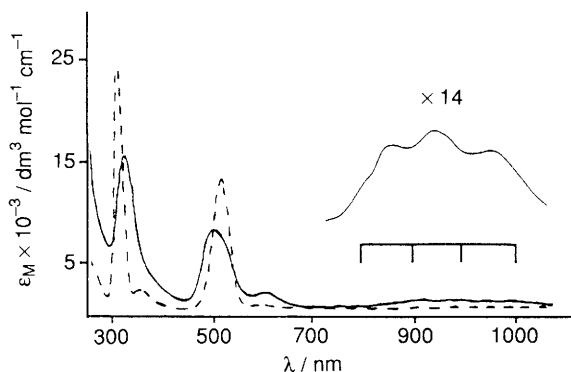


Fig. 1 UV–VIS–near IR absorption spectra of ReS_4^- (---) and ReS_4^{2-} (—) from spectroelectrochemistry in acetonitrile–0.1 mol dm^{-3} Bu_4NClO_4

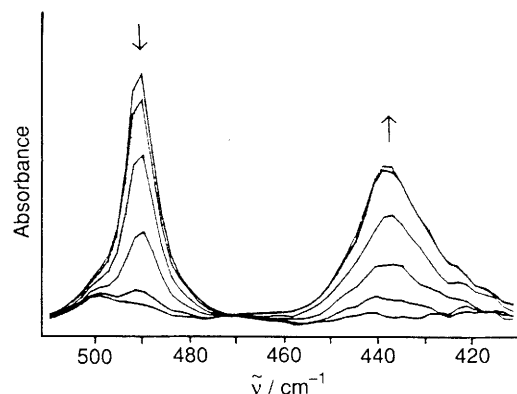


Fig. 2 IR vibrational spectra of ReS_4^- (↓) and ReS_4^{2-} (↑) from spectroelectrochemistry in CD_3CN –0.1 mol dm^{-3} Bu_4NPF_6

$0.0042 \text{ cm}^{-1} = 4.85 \text{ mT}$);¹² the $g_z > 2$ component of the trinuclear tetrathiorhenate(vi) complex indicates contributions from the ligand-based t_1 orbitals,¹³ *i.e.* considerable metal–ligand orbital mixing as was recently reported also for RuO_4^- .¹³

The striking correspondence in spectral data for MnO_4^{2-} and ReS_4^{2-} and the EPR results suggest a high degree of covalency of the metal–chalcogen bond, reducing the effective oxidation state of the metal. In fact, Müller and coworkers have deduced from XPS and XANES studies^{4b} that such a delocalization should be quite strong for the ReS_4^{2-} system, preventing it from being useful within artificial nitrogenase enzymes.

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