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UV–Vis-NIR spectroelectrochemical study of tetrathiorhenate-bridged diruthenium complexes

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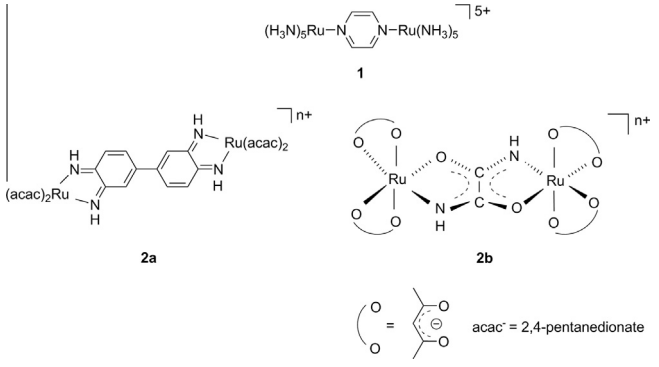
ABSTRACT

The new compound $(NEt_4)[(acac)_2RuS_2ReS_2Ru(acac)_2]$ was characterized by cyclic voltammetry to reveal reversible reduction and oxidation behavior. While the redox products proved EPR silent, the UV–Vis-NIR spectroelectrochemistry showed shifted charge-transfer absorptions and a typical near-infrared intervalence ($Ru^{II} \rightarrow Ru^{III}$) band at $\lambda_{max} = 1725$ nm ($\varepsilon = 1800\ M^{-1}\ cm^{-1}$) for the one-electron oxidized intermediate. The results are discussed in comparison to those obtained for $[(bpy)_2RuS_2ReS_2Ru(bpy)_2]Cl_3$.

1. Introduction

Tetrathiometallates have frequently served as building blocks for higher nuclear aggregations, e.g. with the aim of modeling hydrodesulfurization and other catalysts [1,2]. The rather facile reduction of ReS_4^- in particular [3,4] has stimulated our research in probing the properties of rhenium(VI) species based on ReS_4^{2-} [4,5]. The bis-bidentate chelating capacity of tetrathiometallates [6] as potentially redox-noninnocent bridging ligands has been employed to prepare dinuclear, trinuclear and higher nuclear arrangements [1,7]. Bridging components with low lying orbitals such as π^* orbitals of aromatic organic molecules can serve as mediators between two redox-active centers, such as transition metals [8]. The classical case in point is the Creutz–Taube ion **1** in which two ruthenium ions of formally different charge are effectively bridged by a potentially electron-accepting ligand [9]. Numerous studies of this and related systems such as the molecule-bridged dinuclear bis(acetylacetonato)ruthenium species **2a** and **2b** have been reported in attempts to understand the factors determining the equilibrium situation, the electronic interaction, and the magnetic coupling [8–10].



Inorganic bridged diruthenium redox systems without conventional planar π systems such as in **1**, **2a** or **2b** have been described e.g. with halide [11a] or N_2 bridges [11b]. Here we can report an effort using a tetrathiometallate bridge by presenting compound (NEt_4)**3** = $(NEt_4)[(acac)_2RuS_2ReS_2Ru(acac)_2]$ and describing its electron transfer behavior. The results will be compared to those obtained for $[(bpy)_2RuS_2ReS_2Ru(bpy)_2]Cl_3$ = **4**$(Cl)_3$, a compound referred to earlier [4].

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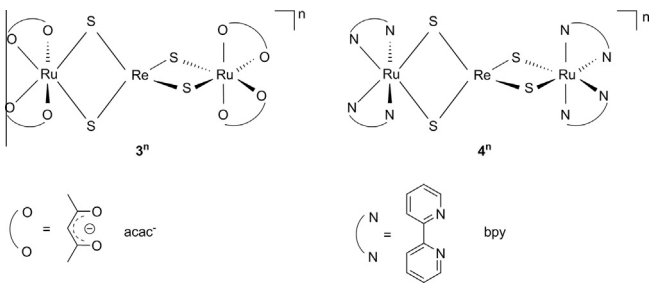

2. Results and discussion

The trinuclear complex ion $\mathbf{3}^-$ could be prepared as the tetraethylammonium salt by reacting the well known [12] precursor $[Ru(acac)_2(CH_3CN)_2]$ with the tetrathiorhenate(VII) ion [13]. Although the substance could not be crystallized for X-ray structure determination, its identity was established by elemental analysis and mass spectrometry, showing the calculated isotope combination pattern for $\mathbf{3}^-$ (Fig. 1). We therefore assume a structure $\mathbf{3}^- = [(acac)_2Ru(\mu\text{-}S)_2Re(\mu\text{-}S)_2Ru(acac)_2]^-$ as obtained before for related trinuclear tetrathiometallate-bridged systems [1,6]. The analogous $\mathbf{4}^{3+} = [(bpy)_2Ru(\mu\text{-}S)_2Re(\mu\text{-}S)_2Ru(bpy)_2]^{3+}$ was prepared as a trichloride, as described previously [4].

Both tetrathiorhenate-bridged diruthenium complex ions exhibit oxidation and reduction behavior (Fig. 2). According to the charge differences resulting from the different co-ligands (anionic $acac^-$ versus neutral bpy), the corresponding redox potentials of $\mathbf{3}^-$ and $\mathbf{4}^{3+}$ are shifted in rather different ways (Table 1). While the double coordination of dicationic $[Ru(bpy)_2]^{2+}$ to ReS_4^- yields the expected [4,5,14,15] effect of shifting both reduction waves of the tetrathiometallate to considerably *less* negative values, the twofold coordination of the neutral complex fragments $[Ru(acac)_2]$ causes a shift to *more* negative potentials. Apparently, the back-donation from two electron-rich ruthenium centers overcompensates the bonding polarization originating from the tetrathiometallate. Similar effects have been observed in complexes of $(\eta^n\text{-}C_nR_n)M$, M = Rh or Ir and $n = 5$, M = Ru or Os and $n = 6$, with α-diimine acceptor ligands [16]. As a consequence of the addition of two neutral $[Ru(acac)_2]$ fragments to ReS_4^- the oxidation is now facilitated (Table 1) because it involves the electron-rich ruthenium centers.

Both complexes $\mathbf{3}^-$ and $\mathbf{4}^{3+}$ display long-wavelength absorption bands between 700 and 1100 nm (Fig. 3). These can be attributed to bathochromically shifted ligand-to-metal charge transfer (LMCT) transitions ($S^{-II} \rightarrow$ Re or Ru) and to metal-to-metal charge transfer (MMCT) [5]. The shift of the LMCT band would correspond

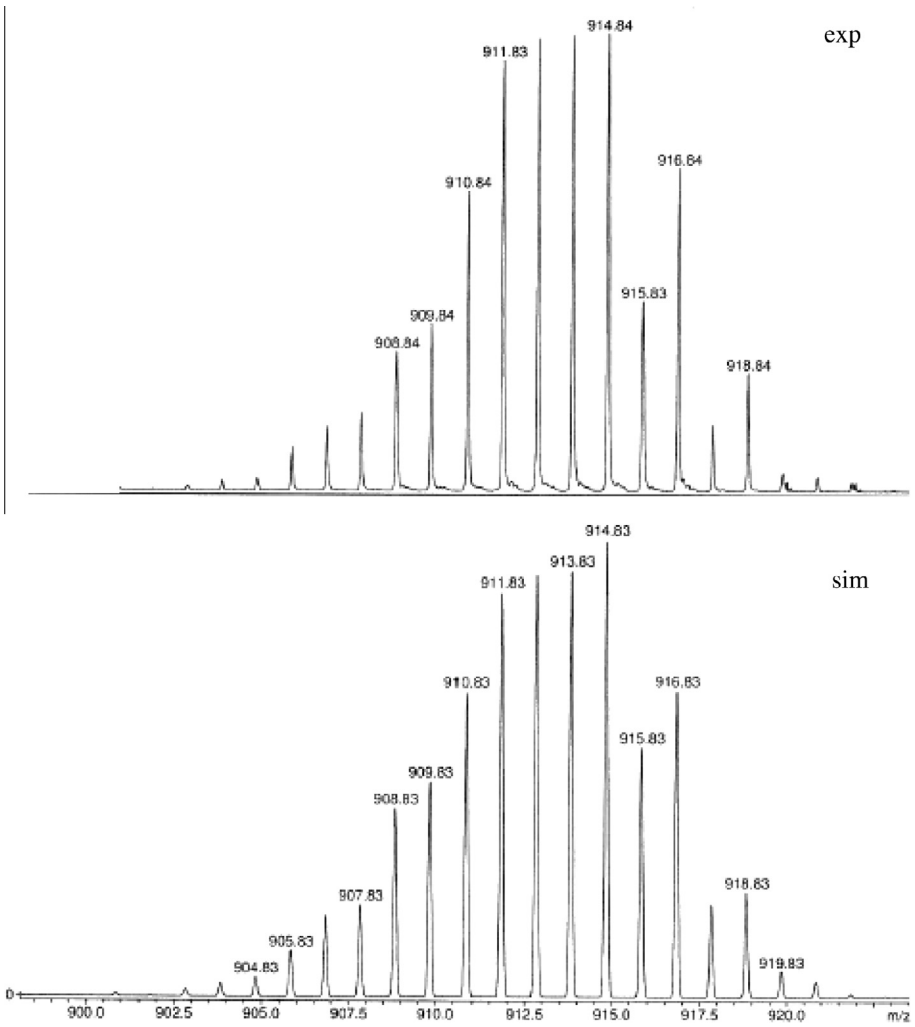

Fig. 1. Isotope pattern of $\mathbf{3}^-$ from ESI mass spectrometry: experimental (top) and simulated (bottom).