

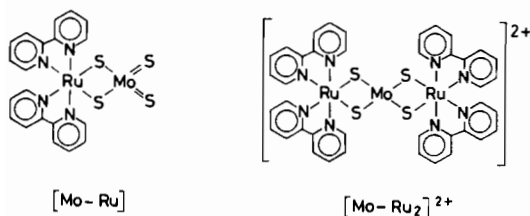
Synthesis of some Molybdenum–Ruthenium Clusters and their Catalytic Behavior Toward Acetylene Reduction

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Much attention has been paid to the coordination geometry around the molybdenum atom of nitrogenase. Recently, the extended X-ray absorption fine structure (EXAFS) studies on the Mo–Fe cofactors extracted from *Clostridium pasteurianum* [1] and *Azotobacter vinelandii* [2] have suggested that the molybdenum atoms in their reduced forms are both surrounded by three or four bridging sulfides, one or two terminal cysteine sulfurs, and two or three sulfide-bridged irons. This result has provided the impetus for synthesizing various molybdenum–sulfur–iron clusters [3–7]. On the other hand, it seems to be of interest to compare the catalytic activities of molybdenum–sulfur–ruthenium clusters with those of molybdenum–sulfur–iron clusters [8]. This letter reports the synthesis of two molybdenum–sulfur–ruthenium clusters, bis(2,2'-bipyridine)ruthenium(II) tetrathiomolybdate(VI) ([Mo–Ru]) and bis[bis(2,2'-bipyridine)ruthenium(II)] tetrathiomolybdate(VI) ([Mo–Ru₂]²⁺), and the electrochemical reduction of acetylene in MeOH/DMF containing [Mo–Ru] or [Mo–Ru₂]²⁺ as catalysts.



A filtered solution of (NH₄)₂MoS₄ [9] (0.26 g, 1.0 mmol) in ethanol/water (4:1 v/v, 100 cm³) was added to a solution of (bpy)₂RuCl₂·2H₂O [10] (bpy; 2,2'-bipyridine) (0.52 g, 1.0 mmol) in the same solvent (200 cm³). After being stirred for 18 hr at room temperature, the resulting precipitate was collected by filtration and washed with ethanol, water, and diethylether, and dried *in vacuo* to give a dark green powder of [Mo–Ru] in a 87% yield, mp > 300 °C. *Anal.* Found: C, 37.23; H, 2.55; N, 8.59%. Calcd for C₂₀H₁₆N₄MoRuS₄: C, 37.67; H,

2.53; N, 8.79%. The [Mo–Ru₂]²⁺ cation was isolated as hexafluorophosphate as follows; a mixture of (bpy)₂RuCl₂·2H₂O (0.13 g, 0.25 mmol) and [Mo–Ru] (0.16 g, 0.25 mmol) in ethanol/water (4:1 v/v, 50 cm³) was refluxed for 4 hr. After being cooled to room temperature, the solution was concentrated to the volume of ca. 15 cm³ under reduced pressure, followed by filtration. To the filtrate was added an aqueous solution (20 cm³) of excess NH₄PF₆ (0.16 g, 1.0 mmol) to give an air-sensitive brown precipitate, which was collected by filtration, washed with water and dried *in vacuo*, 70% yield, mp 280 °C (decomp.). *Anal.* Found: C, 35.06; H, 2.46; N, 8.12%. Calcd for C₄₀F₁₂H₃₂N₈MoP₂Ru₂S₄: C, 35.35; H, 2.52, N, 8.25%.

The electronic spectra of [Mo–Ru] and [Mo–Ru₂]²⁺ show three strong absorption bands in the 330–800 nm region (Fig. 1), of which the band with an intermediate wavenumber in each complex (425 or 480 nm) may be assigned to the charge transfer (CT) transition from sulfur to molybdenum, since a strong ligand to metal CT band of various clusters involving the MoS₄ moiety has been observed in the 400–500 nm range [3, 4, 11]. The remaining two bands, 580 and 346 nm for [Mo–Ru] and 692 and 410 nm for [Mo–Ru₂]²⁺, may be associated with metal to ligand CT transitions; π₁^{*}(bpy) ← dπ(Ru) and π₂^{*}(bpy) ← dπ(Ru), respectively, by reference to the assignments for the absorption spectrum of Ru(bpy)₂(SCN)₂ [12].

Figure 2 shows the cyclic voltammogram of [Mo–Ru] and [Mo–Ru₂]²⁺ in DMF containing (n-Bu)₄NClO₄ (0.1 mol dm⁻³) as a supporting electrolyte by the use of a Pt electrode. The [Mo–Ru] complex displays an irreversible anodic and two quasi-reversible cathodic waves, as confirmed from the peak separations shown in Table I. Formal oxidation states of the molybdenum and ruthenium atoms of [Mo–Ru] are six and two, respectively. The irreversible anodic wave is, therefore, reasonably associated with the oxidation process of Ru(II) to Ru(III). The two

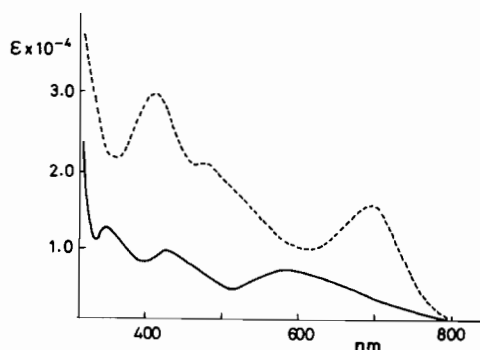


Fig. 1. Electronic absorption spectra of [Mo–Ru] (—) and [Mo–Ru₂]²⁺ (---) in DMSO.

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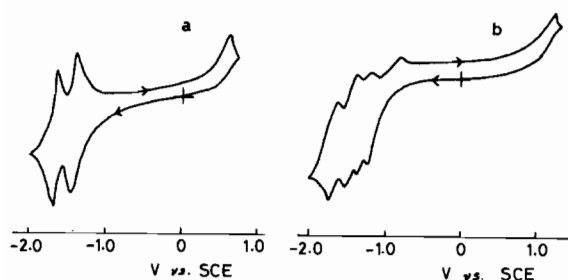


Fig. 2. Cyclic voltammograms of [Mo-Ru] (a) and [Mo-Ru₂]²⁺ (b) (1.0×10^{-3} mol dm⁻³) in DMF (0.1 mol dm⁻³, n-Bu₄NClO₄); scan rate 0.2 V s⁻¹.

TABLE I. Cyclic Voltammetry in DMF at the Sweep Rate of 0.2 V s⁻¹.

	Reduction		Oxidation
	E _{pc} ^a	ΔE _p ^b	E _{pa} ^c
[Mo-Ru]	-1.50 -1.75	80 80	+0.54
[Mo-Ru ₂] ²⁺	-1.24 -1.39 -1.54 -1.75	390 160 100 100	+0.90

^aCathodic peak potentials vs. SCE, V. ^bPeak separations between the cathodic and anodic waves. ^cAnodic peak potentials vs. SCE, V.

successive cathodic waves may be assigned to the reduction of the bipyridine moiety coordinated to Ru(II) judging from the peak potentials, which are almost the same as those of complexes of the [Ru^{II}-(bpy)₂L]X type (L = S₂CN(CH₃)₂, S₂P(C₆H₅)₂, and S₂P(OC₂H₅)₂; X = PF₆) [13]. On the other hand, the cyclic voltammogram of [Mo-Ru₂]²⁺ shows four successive cathodic waves, as well as an irreversible anodic wave (Fig. 3, Table I). The controlled potential electrolysis at -1.90 V revealed that the number of electrons required in the reduction of [Mo-Ru₂]²⁺ at this potential were $n = 3.8 \pm 0.1$. This result suggests that each cathodic wave is consistent with one electron reduction process of [Mo-Ru₂]²⁺, though it is not evident whether four cathodic waves result only from the reduction of bipyridine moieties, or whether some result from the reduction of Mo(VI).

Although no reaction occurred between [Mo-Ru] or [Mo-Ru₂]²⁺ and acetylene in the presence of MeOH as a proton source, the reduced species of [Mo-Ru] or [Mo-Ru₂]²⁺ can react with acetylene in the same condition to afford ethylene and ethane. Controlled potential electrolysis was carried out for an acetylene saturated MeOH/DMF (1:3 v/v,

40 cm³) solution containing [Mo-Ru] or [Mo-Ru₂]²⁺ (24 μmol) and LiCl (9.6 mmol) as a supporting electrolyte at -1.70 V. At this potential, the Mo-Ru clusters may be reduced to [Mo-Ru]²⁻ and [Mo-Ru₂]²⁻ respectively. The electrolysis cell consists of three compartments; a working electrode of Hg, an auxiliary electrode separated from the working electrode by a glass frit, and an SCE reference electrode. Figure 3 shows the amounts of ethylene and ethane produced in the course of controlled potential electrolysis. The slopes found became gradually more gentle, suggesting that both [Mo-Ru]²⁻ and [Mo-Ru₂]²⁻ slowly lose their activities for acetylene reduction with time. These species, however, still reduce acetylene over 400 min, and the reduction proceeds, catalytically at least with [Mo-Ru₂]²⁻. In addition, the rate of acetylene reduction by [Mo-Ru₂]²⁻ is about twice that of [Mo-Ru]²⁻ and the ratios of ethane to ethylene produced for the initial 300 min were 0.26 and 0.32 for the reactions catalyzed by [Mo-Ru]²⁻ and [Mo-Ru₂]²⁻ respectively. These reactions were accompanied also by H₂ evolution. Although the ratios of ethane to ethylene were not so different between [Mo-Ru]²⁻ and [Mo-Ru₂]²⁻, the concomitant H₂ evolution was quite different in the amount, the ratios of H₂ to ethylene produced were 1.2 and 13.6 in the reactions catalyzed by [Mo-Ru]²⁻ and [Mo-Ru₂]²⁻ respectively. This result indicates that 44 and 89% of electrons transferred from the Hg electrode to [Mo-Ru]²⁻ and [Mo-Ru₂]²⁻ respectively were consumed by H₂ evolution. In the previous paper [8], we have reported that [Fe₄S₄(SPh)₄]³⁻ (or [Mo₂Fe₆S₉(SPh)₈]⁵⁻) reduces protons to H₂ in the absence of acetylene in MeOH/THF, but that in the solution saturated with acetylene it catalytically reduces acetylene to give only ethylene without H₂ evolution, as is the case with nitrogenase [14]. The difference in catalytic activities between [Mo-Ru]²⁻ or [Mo-Ru₂]²⁻ and [Fe₄S₄(SPh)₄]³⁻, or [Mo₂Fe₆S₉(SPh)₈]⁵⁻, may be explained by the assumption that the interaction of the former species with acetylene is weaker,

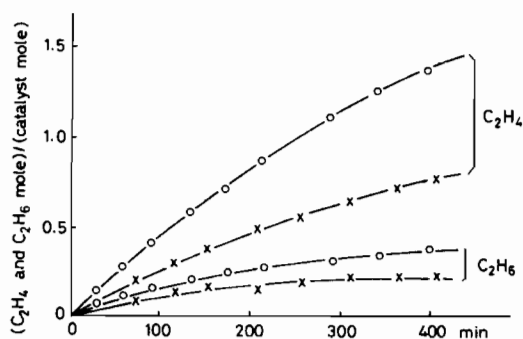


Fig. 3. Plots of (C₂H₄ and C₂H₆ mole)/(catalyst mole) vs. time in the presence of [Mo-Ru]²⁻ (x) or [Mo-Ru₂]²⁻ (o).

and that with ethylene is stronger, than those with the latter species respectively.

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