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Preparation, Structure, and Properties of Europium Ruthenium Hydride

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Eu_2RuH_6 is formed by allowing EuH_2 and Ru to react at 800° in approximately 1 atm of hydrogen. The ternary hydride is a dark red, air-stable crystalline solid which appears to be thermally stable to 900°. An analysis of X-ray powder diffraction data and density measurements suggests that the structure is consistent with the $Fm3m$ space group wherein the ruthenium atoms assume fourfold occupancy and europium atoms assume eightfold occupancy in a fluorite type lattice. Magnetic susceptibility measurements between 77 and 296°K show that Eu_2RuH_6 obeys a Weiss–Curie law with $\Theta = +43$°K indicative of ferromagnetic interactions. The measured effective magnetic moment for the europium ion in Eu_2RuH_6 is 7.82 BM assuming no contributions from the ruthenium and hydrogen. This suggests the europium ions are divalent based on a comparison with a calculated value of 7.94 BM for $S = {}^7/_2$. Electrical resistivity measurements indicate that Eu_2RuH_6 behaves as a semiconductor.

Introduction

Several studies describing the behavior of some intermetallic binary compounds composed of a rare earth metal and cobalt or nickel with hydrogen have been reported recently. Zijlstra and Westendorp[1] observed that $SmCo_5$ absorbs 2.5 mol of hydrogen at 20 atm of pressure accompanied by a transformation to an orthorhombic structure. van Vucht, Kuijpers, and Bruning[2] reported that $LaNi_5H_{6.7}$ is formed when $LaNi_5$ is exposed to hydrogen at 2.5 atm at room temperature and that $SmCo_5H_3$ is formed at room temperature when the hydrogen pressure is 4.5 atm. $PrCo_5D_{3.9}$ is formed by heating $PrCo_5$ in hydrogen at 4 atm of pressure at room temperature.[3] Two phases were reported for the $CeCo_5$–H system, i.e., a hydrogen-poor room temperature α phase with an estimated composition $CeCo_5H_{0.6}$ and a hydrogen-rich β phase with a stoichiometry believed to be $CeCoH_{2.05}$. Three phases were reported for $LaCo_5H_x$ where x is 0.17 for the α phase, 3.35 for the β phase, and 4.3 for the γ phase.[4] Takeshita, Wallace, and Craig[5] studied the behavior of YCo_5 and $ThCo_5$ with hydrogen and concluded that these systems absorb hydrogen reversibly resulting in a limiting composition of 3 H/mol of intermetallic alloy between 304.5 and 324.5°K. The maximum solubility of hydrogen in $DyCo_3$, $HoCo_3$, and $ErCo_3$ at 40 atm and at room temperature corresponds to RCo_3H_5 where R = Dy, Ho, or Er.[6]

A study of the synthesis, structure, and properties of several ternary hydrides of the general stoichiometry $M_2M'H_{4+z}$ has been reported where M is an alkaline earth metal, i.e., calcium or strontium, M' is a group 8 rarer platinum metal, i.e., rhodium, ruthenium, or iridium, and z is 1 when M' is Rh or Ir and 2 when M' is Ru.[7] There is ample evidence of similarity of crystal structure between divalent europium or ytterbium compounds and compounds of calcium, strontium, and barium. For example, Korst and Warf[8] discovered that the deuterides of ytterbium and europium were isostructural with the hydrides of calcium, strontium, and barium. Messer and Hardcastle[9] reported the formation of the inverse perovskite $LiEuH_3$ which was isostructural with $LiSrH_3$. Based on X-ray diffraction evidence, Moyer and Thompson[10] reported a structural similarity between ytterbium ruthenium hydride and calcium ruthenium hydride. We now wish to report the synthesis, structure, and properties of Eu_2RuH_6 which appears to be isostructural with Sr_2RuH_6.

Experimental Section

Europium ingot, presumably 99.9% pure, was purchased from A. D. Mackay, Inc., and Electronics Space Products, Inc. The europium was purified by vacuum distillation at approximately 800°. A thin molybdenum disk (0.005 in. thick) was inserted at the tip of the stainless steel cold finger onto which the distilled europium was collected. Deposition on the disk eliminated ferromagnetic contamination of the europium by the stainless steel cold finger. Ruthenium powder (325 mesh and 99.9% pure) was purchased from A. D. Mackay, Inc. Prepurified grade hydrogen (99.9% minimum) and prepurified argon (99.998% minimum) were purchased from Airco Industrial Gases. Tank hydrogen was purified further by passing the gas through a heated palladium tube filter, Model H-1-DH, purchased from Matthey Bishop, Inc.

Europium hydride was prepared by direct combination of the elements at approximately 500°. X-Ray diffraction data for europium hydride were consistent with data reported for europium deuteride.[8] Anal. Calcd for EuH_2: H, 1.31. Found: H, 1.28. The analytical procedure is described later in this paper.

Europium ruthenium hydride was prepared according to the following procedure. Europium hydride powder was combined with ruthenium powder in a 2:1 mole ratio and mixed for approximately 10 min. The powdered mixture was compressed into a pellet at 5000 psi. The pellet was loaded into a molybdenum boat; and the boat, in turn, was inserted into a quartz reaction tube. The tube was attached to a glass vacuum line, and the system was evacuated to a pressure of at least 10^{-5} mm. The reaction zone was filled with hydrogen to a pressure of approximately 700 mm. The reactants were heated to 800° for 18 hr and cooled by air quenching. Anal. Calcd for Eu_2RuH_6: Eu, 73.95; Ru, 24.58; H, 1.47. Found: Eu, 73.08; Ru, 26.73; H, 1.42. The procedures for the elemental determinations are presented later in this paper.

Europium metal was handled in a glove bag under a protective layer of argon. Binary and ternary hydrides were handled in an atmosphere of nitrogen.

Elemental chemical analysis of Eu_2RuH_6 for europium and ruthenium was performed by gravimetric methods. Europium ruthenium hydride was decomposed with 0.75 M HCl. Ruthenium remained as the metal and was retained on a sintered-glass crucible, dried at 110°, and weighed. Data obtained by X-ray diffraction qualitative analysis confirmed the presence of ruthenium, exclusively. Europium was precipitated from solution as the oxalate and converted analytically to europium oxide at 900° for 2 hr. Elemental hydrogen determinations for both binary and ternary hydrides were performed by thermally decomposing the sample. Initially, the hydride sample (0.1–0.5 mmol) in the form of a pellet was placed in a molybdenum container inside a quartz tube, and the tube was attached to the vacuum line. The system was evacuated to a pressure of at least 10^{-5} mm. The sample was heated to 925° and held at 925° for the duration of the hydrogen transfer. The evolved hydrogen was transferred with a Toepler pump to a calibrated gas buret.

X-Ray powder diffraction data for indexing purposes were obtained with a General Electric XRD-6 diffractometer using a Debye–Scherrer camera, 114.6 mm in diameter. Samples were sealed in glass capillaries (0.5-mm o.d.) and exposed to nickel-filtered Cu Kα radiation for 2 hr. X-Ray powder diffraction intensity data were obtained with a General Electric XRD-5 unit. Samples scanned with the General Electric XRD-5 were mixed with a protective coating of Vaseline, smeared on a glass slide, and exposed to nickel-filtered Cu Kα radiation. The intensities were determined by measuring the area under the peaks on the chart with a planimeter. Potassium chloride was used as an internal standard.

High-temperature differential thermal analyses were obtained with a Du Pont Model 1200 instrument. Samples were heated from room temperature to 950° at a rate of 20°/min in a slow stream of hydrogen

Table I. X-Ray Diffraction Data for Eu_2RuH_6

	$\sin^2\theta$			$\sin^2\theta$	
hkl	Obsd	Calcd	*hkl*	Obsd	Calcd
111	0.0310	0.0312	533	0.4463	0.4467
200	0.0413	0.0416	622	0.4554	0.4571
220	0.0827	0.0831	444	0.4993	0.4986
311	0.1135	0.1143	551, 711	0.5323	0.5298
222	0.1286	0.1247	640	0.5399	0.5402
400	0.1646	0.1662	642	0.5804	0.5817
331	0.1968	0.1974	800	0.6699	0.6648
420	0.2073	0.2078	733	0.6972	0.6960
422	0.2490	0.2493	644	0.7056	0.7064
333, 511	0.2790	0.2805	660, 644	0.7471	0.7479
440	0.3312	0.3324	751, 555	0.7801	0.7791
531	0.3626	0.3636	662	0.7887	0.7895
600, 442	0.3736	0.3740	840	0.8318	0.8310
620	0.4145	0.4155			

gas. Molybdenum cups were used to hold the sample and alumina reference. The instrument was calibrated with sodium chloride (mp 800°).

Density measurements of Eu_2RuH_6 were made according to the liquid buoyancy method using reagent grade carbon tetrachloride. The sample was compressed at 5000 psi into a pellet, weighed, submerged in carbon tetrachloride, deaerated, and weighed in carbon tetrachloride.

The magnetic susceptibility of the Eu_2RuH_6 sample was measured by the Faraday method[11] using an automatic analytical balance which was enclosed in a controlled helium atmosphere. The inhomogeneous magnetic field zone was calibrated with powdered recrystallized reagent grade $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$ (Mohr's salt) using the susceptibility data of Jackson.[12] The sample was contained in a thin-walled cylindrical Teflon boat with an internal volume of about 0.30 cm^3. The magnetic corrections due to the boat were determined in a separate run. The susceptibility was corrected for all the individual ion core diamagnetic contributions.[13] Measurements on the sample were made at field strengths of 3000, 4300, and 5700 Oe over the temperature range from 77 to 296°K. Temperatures were controlled by a heating coil wound on the lower half of a vacuum-insulated copper tube surrounding the sample. Temperatures were read with a copper–constantan thermocouple placed inside the tube, close to the sample boat. The accuracy of boat temperature was estimated to be ±0.5°K. The absolute accuracy of the susceptibility measurements was estimated to be ±2%.

The electrical resistivity of Eu_2RuH_6 was measured by the voltage–current method. A powder sample was compressed into a hard-packed cylindrical pellet under a pressure of 5000 psi and then held between two electrodes under compression. The electrical resistance was determined from measurements of the current through the sample and the potential difference across the sample. The resistivity was calculated from the pellet length and area which were 0.39 cm and 0.32 cm^2, respectively. Measurements were made at temperatures of 296, 209, 166, and 77°K.

Results and Discussion

Europium ruthenium hydride was formed by heating europium hydride and ruthenium in a hydrogen atmosphere at 800° according to the equation

$$2EuH_2(s) + Ru(s) + H_2(g) \rightarrow Eu_2RuH_6(s)$$

Eu_2RuH_6 is a brick red crystalline, nonvolatile solid which decomposes in acidic solutions. Unlike EuH_2, which is extremely reactive in air, Eu_2RuH_6 appears unreactive. For example, after exposing a sample of Eu_2RuH_6 to ambient air conditions for 2 weeks no apparent weight change was observed; and the X-ray powder diffraction pattern indicated the presence of the ternary hydride exclusively. The formation of Eu_2RuH_6 was accompanied by an approximately threefold expansion in the reaction pellet size and a decrease in the hydrogen pressure.

To establish initially the stoichiometry of this new ternary hydride phase, the products of several samples prepared from starting materials varying in composition, i.e., EuH_2:Ru mole ratios of 4:1 to 1:2, were studied by X-ray diffraction techniques. No reactants were observed in the product formed from the 2:1 mole ratio. Ruthenium was observed in products obtained from mole ratios less than 2:1, i.e., 1.5:1. No ruthenium was observed in products from compositions of 2:1 or greater.

Table II. Observed and Calculated X-Ray Diffraction Intensities for Eu_2RuH_6

hkl	I_o	I_c	*hkl*	I_o	I_c
111	19.8	16.1	422	32.0	30.0
200	23.7	31.4	511, 333	3.48	3.43
220	100	100	440	11.3	8.45
311	10.2	7.8	531	0.01	3.93
222	7.02	8.31	600, 442	0.03	4.34
400	18.4	16.3	620	12.4	10.8
331	5.44	2.89	642	11.3	12.4
420	7.00	10.9			

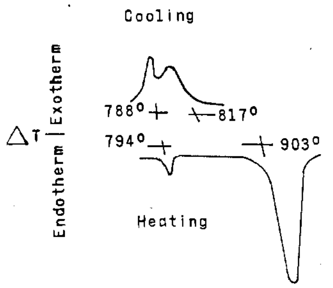

Figure 1. Schematic of a DTA plot for Eu_2RuH_6.

X-Ray powder diffraction data were indexed completely on a face-centered cubic basis and are shown in Table I. An extrapolation of the measured lattice parameters to $\sin^2\theta = 1.0$ by reducing the data with a least-squares analysis technique gave a unit cell dimension of 7.566 Å.

The average experimental density was 6.28 g/cm^3 with a range of ±0.23 g/cm^3. This value is consistent with four molecules of Eu_2RuH_6 per unit cell with a theoretical density of 6.28 g/cm^3.

A structure factor analysis indicated that Eu_2RuH_6 belonged to the *Fm*3*m* space group. Hydrogen atoms were not inserted in the trial structure calculations because of their very small scattering ability for X-rays compared to either europium or ruthenium. The most successful model can be viewed as a fluorite lattice with ruthenium atoms occupying the fourfold sites at the atomic coordinates (0, 0, 0), $(0, {}^1/_2, {}^1/_2)$, $({}^1/_2, 0, {}^1/_2)$, and $({}^1/_2, {}^1/_2, 0)$ and the europium atoms assuming eightfold occupancy with atomic coordinates at $({}^1/_4, {}^1/_4, {}^1/_4)$, $({}^3/_4, {}^1/_4, {}^1/_4)$, $({}^1/_4, {}^3/_4, {}^1/_4)$, $({}^3/_4, {}^3/_4, {}^3/_4)$, $({}^1/_4, {}^1/_4, {}^3/_4)$, $({}^3/_4, {}^1/_4, {}^3/_4)$, $({}^3/_4, {}^3/_4, {}^1/_4)$, and $({}^1/_4, {}^3/_4, {}^3/_4)$. The results are shown in Table II, where the calculated intensity values are temperature corrected. The reliability factor for the data in Table II, defined as $R = \sum|I_o - I_c|/\sum I_o$, was 0.15. Based on X-ray diffraction evidence, Eu_2RuH_6 appears to be isostructural with Sr_2RuH_6.[7] Results of the neutron diffraction study of Sr_2RuD_6 indicated that deuterium atoms occupy octahedral positions around the ruthenium atom, i.e., at (0, *x*, 0) where *x* is approximately 0.25.

The results of the differential thermal analyses are shown in Figure 1. No enthalpic changes were observed for Eu_2RuH_6 when first heated from room temperature to 903°, the temperature at which a large endotherm was noted. Upon cooling, two exotherms were observed, one at 817° and a slightly more intense and sharper exotherm at 788°. The sample was exposed to three subsequent heating and cooling cycles. The endotherm at 903° as well as the exotherm at 788° persisted, but the exotherm at 817° became progressively broader and weaker. Furthermore, a weak endotherm at 794° appeared upon heating for all subsequent cycles after the initial one. The intensity of all enthalpic changes decreased with succeeding cycles. A small sample pellet containing a 2:1 mole

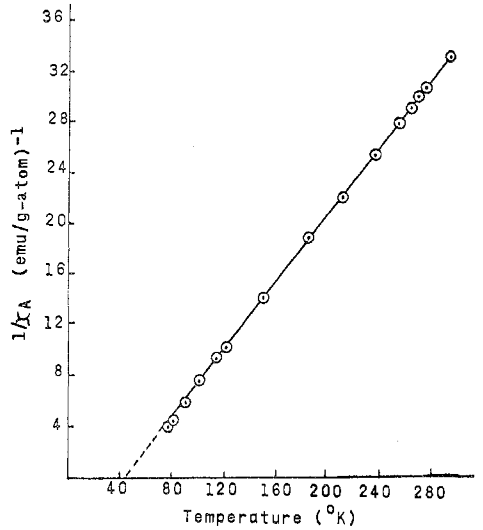

Figure 2. Graph of $1/\chi_A$ (emu/g-atom)$^{-1}$ vs. T (°K) for Eu_2RuH_6.

ratio of europium hydride and ruthenium was scanned for three cycles under conditions similar to Eu_2RuH_6. With the exception of the response at 817°, the other enthalpic responses observed for Eu_2RuH_6 at 794, 903, and 788° were found in the thermogram for the sample of reactants. Also, ruthenium and europium hydride were scanned independently under similar experimental conditions. No enthalpic change was observed for ruthenium; but a small, broad exotherm at 790° was noted upon cooling for europium hydride.

An experiment simulating DTA instrumental conditions as closely as possible with a reaction tube furnace and under a static hydrogen atmosphere was run in order to examine a much larger sample. A sample of Eu_2RuH_6 was heated to 925° in a hydrogen atmosphere and cycled four times between 775 and 925°. When the sample was finally cooled to room temperature, the hydrogen pressure in the system was found to have increased, the reaction tube next to the hot zone in the furnace had become discolored, and the sample pellet, originally brick red, had developed a gray shell retaining a brick red core. Separate X-ray diffraction patterns of the shell and core indicated that the shell was composed essentially of ruthenium while the core was Eu_2RuH_6. The reaction tube discoloration was due probably to the evolution of some europium and its subsequent reaction with the quartz tube.

An interpretation of the differential thermal analyses follows. The endotherm at 903° is due almost certainly to the decomposition of Eu_2RuH_6. The exotherm at 788° probably represents the formation of europium hydride, an assignment consistent with the thermogram for europium hydride where an exotherm was observed upon cooling at approximately 790°. The source of europium is presumably one of the decomposition products of Eu_2RuH_6. It can be argued that the endotherm seen at 794° on the later heating cycles is probably due to the formation of Eu_2RuH_6 by the reaction of europium hydride, ruthenium, and hydrogen. The following reasons are given for this assignment. On the original heating cycle, starting with the intact Eu_2RuH_6 sample no formation would be expected at 794°; and none was observed. The subsequent appearances of an Eu_2RuH_6 formation endotherm at 794° are explained by saying that after the first complete heating cycle, components for its formation have become available. The association of the 794° endotherm with the Eu_2RuH_6 formation is further supported by the results of the experiment in which a mixture of europium hydride and ruthenium was thermally scanned and an endotherm observed. The exotherm at 817° is more difficult to assign. Hence, it is cautiously proposed that this exotherm might arise from the formation of a hydride by a route involving the reaction between some intermetallic compound of europium and ruthenium with hydrogen or by the chemical combination of europium, ruthenium, and hydrogen.

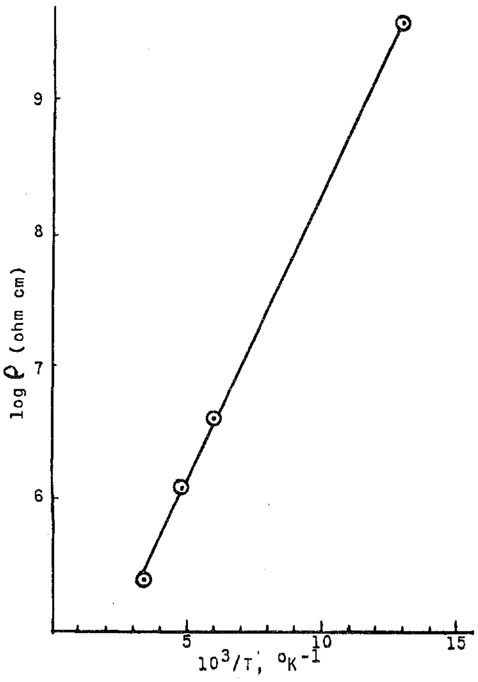

Figure 3. Graph of log ρ (ohm cm) vs. T (°K) for Eu_2RuH_6.

Figure 2 is a plot of the reciprocal of χ_A, the corrected magnetic susceptibility per gram-atom of europium, vs. T, the absolute temperature of the Eu_2RuH_6 sample. A straight line fits the experimental points from 85 to 296°K. The temperature dependence of χ_A above 85°K, as determined from a least-squares fit to the Weiss–Curie law of the form $\chi_A = C_A/(T \pm \Theta)$, is given by $\chi_A = 7.58/(T - 43)$. The constant $C_A = 7.58$ corresponds to $\mu_{eff} = 7.82$ BM. The value of the Weiss–Curie Θ is 43 ± 1°K and suggests that the compound becomes ferromagnetic at some temperature below 77°K.

Results of the magnetic susceptibility measurements are most consistent with oxidation state assignments of II for europium and ruthenium. Divalent europium has a half-filled 4f shell with a spin quantum number of $S = {}^7/_2$ and a zero oribtal angular momentum quantum number. This yields a calculated μ_{eff} of 7.94 BM which agrees well with the experimental result if it is assumed the europium accounts for all of the observed paramagnetic moment of the sample. It can be argued that divalent ruthenium contributes zero paramagnetic moment for the following reason. Hydrogen atoms are tentatively proposed to form an octahedral environment around each ruthenium atom as in the case of Sr_2RuH_6, thereby invoking d^2sp^3 hybridization. If the t_{2g} and e_g orbitals are sufficiently separated energetically, then it is highly probable that the six 4d electrons of the divalent ruthenium would occupy completely the three t_{2g} orbitals and hence not be expected to contribute paramagnetically to the bulk susceptibility.

Less attractive alternatives would be to assign europium to a +3 oxidation state or to a mixed oxidation state. Compared with other lanthanide elements, europium is unique in terms of its trivalent binary hydride chemistry. Hardcastle and Warf[14] tried unsuccessfully to synthesize a higher hydride of europium with maximum hydrogen pressures of 33 atm at 400° and 41 atm at 500°, respectively. The range of theoretical permanent magnetic moments for trivalent europium is reported to be 3.40–3.51 BM.[15] Hence, the magnetic moment per paramagnetic atom would be expected to be 4.37 BM for

Table III. Electrical Resistivity for Eu_2RuH_6

T, °K	ρ, ohm cm	T, °K	ρ, ohm cm
294	2.5×10^5	167	4.1×10^6
209	1.2×10^6	77	4.0×10^9

a $Eu^{II}Eu^{III}Ru^{I}H_6$ model and 3.24 BM for a $Eu^{III}{}_2Ru^{0}H_6$ model. These values are based on a consideration that one electron is occupying an e_g ruthenium orbital in the mixed-valence model and two unpaired electrons are in the e_g ruthenium orbitals for the trivalent model.

No field dependence within experimental limits was observed for Eu_2RuH_6 between 77 and 296°K from 3000 to 5700 Oe. A small but significant deviation from linearity in the curve of $\chi_A{}^{-1}$ vs. T below 85°K was observed. It is possible that this deviation may be due to a small quantity of EuO impurity. EuO is ferromagnetic with a Curie temperature of 77°K.[16]

The results of the resistivity measurements are displayed in Table III.

Because of the possibility of fairly high contact and grain boundary resistances the indicated values of the resistivity are undoubtedly somewhat higher than the actual values. Nonetheless the order of magnitude and behavior with temperature strongly suggests that Eu_2RuH_6 is a semiconductor. The data could be fitted to the equation $\rho = \rho_0 e^{\Delta E/2kT}$ which describes semiconductors characterized by an activation energy ΔE. The results in Figure 3 show the plot of log ρ as a function of $1/T$. The value of ΔE was determined to be 0.15 eV.

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Registry No. Eu_2RuH_6, 55450-40-3; EuH_2, 13814-78-3; Ru, 7440-18-8.

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Electrochemical Studies of Vanadium(III), -(IV), and -(V) Complexes of 8-Quinolinol in Acetonitrile. Formation of a Binuclear Mixed-Valence (IV,V) Complex

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The electrochemistry of VQ_3, VOQ_2, $VO(OCH_3)Q_2$, and $VO(OH)Q_2$ (Q = 8-quinolinol anion) has been studied by cyclic voltammetry and controlled-potential coulometry in acetonitrile, dimethyl sulfoxide, and dimethylformamide at a platinum electrode. The complexes have been further characterized by infrared, uv-visible, and ESR spectroscopy and by magnetic susceptibility measurements. In acetonitrile VQ_3 is reversibly reduced by a one-electron process at −1.475 V vs. SCE and is irreversibly oxidized at +0.475 V. $VO(OCH_3)Q_2$ undergoes a half-electron reduction at −0.45 V to form a mixed oxidation state oxo-bridged dimer $[(V^{V}OQ_2){-}O{-}(V^{IV}OQ_2)]^-$. This dimer is reversibly oxidized at +0.025 V to give $[(V^{V}OQ_2){-}O{-}(V^{V}OQ_2)]$.

In recent years there has been increasing evidence for the biological importance of vanadium.[1] Several types of marine life contain vanadium, including the Ascidians[2] where it may function as an oxygen carrier.[3] Oxovanadium(IV) porphyrins commonly are found in petroleum, although their origins are unknown.[4] Recently vanadium also has been shown to be an essential nutrient in higher life forms.[1,5] It is involved in phospholipid oxidation, sulfur metabolism, and cholesterol biosynthesis[6] and probably plays a role in other biochemical processes.

The chemistry of vanadium also is of interest because of its similarity to molybdenum. The latter is an essential cofactor in a number of oxidation–reduction enzymes including xanthine oxidase, aldehyde oxidase, nitrate reductase, and nitrogenase.[7,8] The function of the molybdenum-containing enzyme, xanthine oxidase, is thought to be electron transport with the molybdenum associated with FAD–FADH· (flavine adenine dinucleotide–protonated radical of FAD).[7] Electrochemical studies of riboflavine (Rib)[9] have shown that the one-electron reduction product (Rib·⁻ or HRib·) complexes with metal ions, while the oxidized form does not. A similar electrochemical study of the molybdenum–riboflavine system also has been made.[10]

Because of the complexity of molybdenum–flavine systems, studies of model systems are an attractive simplification. 8-Quinolinol is structurally similar to the flavine radical, HRib·, when the isoalloxazine nucleus is in the enol form. Several complexes of molybdenum and 8-quinolinol are known[11] with the ligand bonded as an anion. This is similar to the enol form of the riboflavine radical anion. These model systems have been the basis for electrochemical studies of molybdenum(V) and -(VI)[12] and for NMR studies of molybdenum(V) and -(VI) and vanadium(V).[7] The present paper summarizes the results of an electrochemical and ESR investigation of va-