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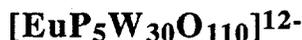
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Implications of the Unusual Redox Behavior Exhibited by the Heteropolyanion



Mark R. Antonio and L. Soderholm

Chemistry Division, Argonne National Laboratory,

Argonne IL 60439-4831 U.S.A.

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Abstract

We report on the novel electrochemical behavior of the heteropolyanion $[\text{EuP}_5\text{W}_{30}\text{O}_{110}]^{12-}$, with specific emphasis on the valence of Eu in both the oxidized and reduced forms of the anion. In aqueous electrolytes, the P-W-O framework is electroactive, and can reversibly accept up to 10 electrons before the potential becomes reducing enough for H_2 evolution. Europium L₃-edge X-ray absorption near edge structure (XANES) results demonstrate that Eu is also electroactive under the same conditions. The implications of this work will be discussed in terms of their contribution to long-standing questions about intermediate-valent materials.

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Introduction

Materials containing more than one electroactive species may exhibit a variety of unusual properties, including intermediate valence, and related phenomena [1-4]. Intermediate valence arises when localized states, notably valence f-states, interact in a bonding fashion with delocalized, molecular orbitals in the same material. Electrons are viewed to be rapidly hopping between these two very different kinds of states, and it is their relative residence times that are interpreted as a non-integral valence. Whereas there have been considerable efforts expended to understand this unusual behavior, these efforts have not proven successful, largely because the problem is many-bodied and is usually studied on infinite band states, often in chemically complex systems. We report here on the novel electrochemical behavior of the heteropolyanion $[\text{EuP}_5\text{W}_{30}\text{O}_{110}]^{12-}$ [5,6], and examine the valence of Eu in both the oxidized and reduced form of the anion, as determined from Eu L₃-edge X-ray absorption near edge structure (XANES). The results demonstrate that, with careful electrochemical control, Eu in this ion may become intermediate valent. Such a result would provide an entirely new and unique approach to long-standing questions related to the phenomenon of intermediate valence.

Intermediate valence occurs when the chemical potential of localized, valence f orbitals is degenerate with that of the extended-molecular orbitals, in this case the W-O orbitals of the cluster. This degeneracy may permit some bonding interactions that can lead to a range of unusual behaviors. There are three common methods used to move the energies of the localized f orbitals relative to the extended molecular orbitals in a solid, in order to create an intermediate-valent material: (1) the application of external pressure, (2) the application of internal pressure through chemical substitutions, (substituting a chemically similar ion with a different ionic radius) and

(3) the addition or subtraction of electrons to the band states through chemical doping (substituting an ion with another with a higher or lower charge state).

The heteropolytungstates $[\text{RP}_5\text{W}_3\text{O}_{110}]^{n-}$ are a series of electroactive clusters in which the P-W-O network forms a donut-shaped, well-defined framework that effectively encapsulates the R ion [5,7,8]. The cluster is initially formed with $\text{R}=\text{Na}$, but the Na^+ can be exchanged for a variety of ions, including Y and all the rare earths, except La. The redox behaviors of most of the $[\text{RP}_5\text{W}_3\text{O}_{110}]^{n-}$ ions, for which R is a trivalent rare earth, are the same, as typified by the Y data presented in Figure 1a. In aqueous solution, these anions will accept reversibly up to 10 electrons, in a multistep process, before the potential becomes reducing enough to evolve H_2 . The intense blue color that develops from the colorless solution upon reduction is used as evidence that the electrons reside in W-O bands within the cluster. The R ion is thought to be electrochemically inactive. Whereas the Eu analog also undergoes a reversible, multielectron reduction, details of the cyclic voltammogram (CV) are different from those of the other R [5,7,8], as shown in Figure 1a, and indicate a different reduction process. In contrast to the other rare earths, Eu^{III} is easily reduced to the divalent state [9], a fact suggesting that the unique reduction behavior of $[\text{EuP}_5\text{W}_3\text{O}_{110}]^{12-}$ may arise from a concurrent, reversible reduction of Eu. If Eu reduction does occur between reduction waves of the tungstate cluster, the clear implication is that the energy of the localized 4f-valence states crossed the chemical potential of the molecular orbitals. In order to investigate this possibility, we probed the valence of Eu in the $[\text{EuP}_5\text{W}_3\text{O}_{110}]^{12-}$ cluster at open circuit, and at a significantly reducing potential, using XANES.

Experiments

A single site $[\text{EuP}_5\text{W}_{30}\text{O}_{110}]^{12-}$ sample was prepared as previously described, and a 5.5 mM aqueous solution was used for the experiments [6]. In situ Eu L_3 -edge XANES were obtained at ambient temperature at the NSLS on beam line X-23A2 with a purpose-built spectroelectrochemical cell, as previously described [10]. For exhaustive electrolysis, the working electrode was a 6.15 mm dia. carbon graphite rod (Alfa, Grade AGKSP). An identical rod was used as the auxiliary electrode, and the reference electrode was Ag/AgCl (BAS, MF-2063)—all quoted potentials are vs Ag/AgCl. The Eu fluorescence signal was collected first at the solution rest potential (0.21 V) and, then, after bulk electrolysis with the electrode polarized at -0.55 V. The illumination of the spectroelectrochemical cell with the X-ray beam had no effect on either the current or potential in the cell. The primary XANES from the average of nine 40 min. scans at each potential was normalized according to standard procedures [11]. For calibration and comparison, in situ Eu L_3 -edge fluorescence XANES was also recorded for a 14.2 mM solution of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ in 1 M H_2SO_4 . These experiments were done both at open circuit, and at -0.55 V, and provide divalent and trivalent standard spectra. Details of these results are outlined elsewhere [10].

Results and Discussion

The normalized Eu L_3 -edge XANES for the colorless, deaerated solution of $[\text{EuP}_5\text{W}_{30}\text{O}_{110}]^{12-}$ at rest potential is shown in Figure 1b. The edge resonance, the result of a Eu $2p_{3/2} \rightarrow 5d$ transition, is at 6982 eV. Both the energy and the appearance of a single-line transition are characteristic of Eu^{III} . Intermediate valence manifests itself as a two-line resonance, shifted to somewhat lower energy [12]. In situ, Eu L_3 -edge XANES was recorded on the same sample after applying, and maintaining a potential of -0.55V. The Eu XANES spectra obtained from the resultant

deep blue solution reveal a single edge resonance at 6974 eV, as shown in Figure 1b. The observation of a single line with an absolute edge-energy shifted to about 8 eV below the Eu^{III} resonance together are characteristic of Eu^{II} [13,14]. These data provide unequivocal evidence that Eu is divalent at an applied potential of -0.55 V. After reoxidation of the reduced Eu heteropolyanion, the CV and the Eu XANES of the clear, colorless solution were identical to those observed prior to the reduction, indicating that the Eu ion remains encapsulated upon reduction.

Intermediate-valence theories suggest that some bonding occurs when there is a coincidence in energies of the 4f-local state and the chemical potential of the molecular orbitals which effectively pins their chemical potentials [1]. This effect is observed in pressure studies, where increasing the pressure past the onset of an intermediate-valent phase does not fully oxidize the rare earth [12]. The situation here appears different, in that if an intermediate valent system was created at some point during the electrochemical reduction process, it was destroyed upon further reduction. Conversely, because of our unusually versatile, dynamic method of moving the band states relative to the 4f states, we can cover a much greater energy range than is possible with either pressure or chemical doping. For this reason alone it is important to investigate further the electronic behavior of the two electronically active subspecies at applied potentials near that at which they are energetically equivalent.

A requirement for the reductive formation of an intermediate-valent material is the ability of the host to accept a relatively large change in ionic size. The Eu^{III} reduction outlined herein clearly demonstrates that the heteropolyanion can accept the larger Eu^{II} ion without decomposition. The valence stability of this system, after the removal of electrochemical control, is certainly open to question. Whether crystals grown electrochemically are stable, or whether there is any structural phase

modification, which may serve to stabilize the intermediate valent state, remain to be determined. Even without this added stability, the rewards to be gained from creating an intermediate-valent state in a heteropolyanion framework would be significant both from a fundamental science perspective, as well as from a technological standpoint.

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FIGURE CAPTIONS

Figure 1. (a) Cyclic voltammograms obtained from a 1.3 mM solution of $[\text{YP}_5\text{W}_{30}\text{O}_{110}]^{12-}$ (dashed line) and a 1.2 mM solution of $[\text{EuP}_5\text{W}_{30}\text{O}_{110}]^{12-}$ (solid line) in aqueous 1M H_2SO_4 with a glassy carbon working electrode (3 mm diam.), Pt wire auxiliary electrode, and Ag/AgCl reference electrode. The arrows (1 and 2) indicate the electrode potentials at which the in situ Eu L_3 -edge XANES for $[\text{EuP}_5\text{W}_{30}\text{O}_{110}]^{n-}$ were recorded; (b) In situ Eu L_3 -edge XANES spectroelectrochemistry in aqueous 1M H_2SO_4 electrolyte of $[\text{EuP}_5\text{W}_{30}\text{O}_{110}]^{n-}$ (5.5 mM) obtained at rest potential (solid line) and after bulk electrolysis with the electrode polarized at -0.55 V vs Ag/AgCl (dashed line).

