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Coordination and valence of europium in $[Eu(\alpha\text{-}2\text{-}As_2W_{17}O_{61})_2]^{17-}$ and $[Eu(W_5O_{18})_2]^{9-}$

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Abstract

Europium L_3 edge X-ray absorption fine structure (XAFS) spectroelectrochemistry was used to determine the valence of europium in $[Eu(\alpha\text{-}2\text{-}As_2W_{17}O_{61})_2]^{17-}$ and $[Eu(W_5O_{18})_2]^{9-}$. Dilute solutions of these anions in aqueous supporting electrolytes were examined at ambient temperature and at extreme potentials. In situ XANES (X-ray absorption near edge structure) data revealed that Eu is trivalent in both $[Eu(\alpha\text{-}2\text{-}As_2W_{17}O_{61})_2]^{17-}$ and $[Eu(W_5O_{18})_2]^{9-}$ at rest potential. Furthermore, it was not reduced to Eu^{2+} by constant-potential bulk electrolysis at significantly reducing potentials under the electrochemical conditions used herein. These results stand in obvious contrast to the redox behavior of $[EuP_5W_{30}O_{110}]^{12-}$, in which Eu^{3+} is reduced to Eu^{2+} under similar electrochemical conditions. © 1998 Elsevier Science S.A.

Keywords: Europium; L_3 edge; X-ray absorption fine structure; Spectroelectrochemistry; Valency; Polyoxometalate; Heteropolyanion

1. Introduction

Lanthanide chemistry is dominated by reactions of the trivalent state, which is the most stable valence for all of the 4f elements, Ce–Lu [1]. In many solids and solutions, the lanthanide (Ln) elements generally behave as classical, non-interacting tripositive ions. There are exceptions, of course, and one of the most notable ones is europium. Europium(III) is readily reduced to Eu^{2+}. The stability of Eu^{2+} is partially attributed to its formal electronic configuration with a half-filled 4f shell, $[Xe]4f^7 5d^0 6s^0$. The standard potential of −0.55 V vs. Ag/AgCl for the one-electron reduction $Eu^{3+} + e^- \rightarrow Eu^{2+}$ is attainable in aqueous, noncomplexing supporting electrolytes [2]. In addition, the europium(III,II) system has a simple and well-understood potential–pH diagram [3], and its aqueous redox equilibria have received considerable attention [4–8]. As the potential indicates, Eu^{2+} is a good reducing agent.

Heteropolyoxometalates such as the Wells–Dawson anion, $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$, are electroactive and good oxidizing agents [9]. Like the well-known Keggin, $[PW_{12}O_{40}]^{3-}$, and Preyssler, $[NaP_5W_{30}O_{110}]^{14-}$, heteropolyanions, the Wells–Dawson anion turns blue upon reduction to form a so-called 'heteropoly blue' [10]. The blue color arises from the distribution of electrons in the W–O band [11,12]. Heteropolyanions like the Wells–Dawson anion that are deficient in one $[W{=}O]^{4+}$ unit (e.g. $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$) are known as monovacant, lacunary anions. These lacunary anions bind metal ions to form coordination complexes [13–19]. The first lanthanide(III) complexes of the monovacant anions $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ and $[W_5O_{18}]^{6-}$ were reported in 1971 by Peacock and Weakley [20]. Since then, there has been a great deal of research activity, both practical and theoretical, on other f element complexes of $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ as well as its arsenic analog $[\alpha\text{-}2\text{-}As_2W_{17}O_{61}]^{10-}$ and $[W_5O_{18}]^{6-}$ [21–36].

The series of rare-earth arsenotungstate heteropolyanions, $[Ln(\alpha\text{-}2\text{-}As_2W_{17}O_{61})_2]^{17-}$, where Ln=La–Yb, has recently come to our attention because of subtle differences in the potentials of the reduction waves for different Ln [28]. The apparent shift to more positive reduction potentials, relative to those obtained from the neighboring Ln ions, of the three redox waves of the Eu analog is particularly interesting because the scans were over an applied potential of 0.0 to −1.1 V vs. Ag/AgCl. This potential range includes the standard reduction potential of Eu^{3+} itself, and raises the question of whether or not Eu is redox active in $[Eu(\alpha\text{-}2\text{-}As_2W_{17}O_{61})_2]^{17-}$. Indeed, Eu has

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previously been found to be redox active under similar conditions in the Preyssler anion $[EuP_5W_{30}O_{110}]^{12-}$ [37]. In contrast, the cyclic voltammetry of $[Eu(W_5O_{18})_2]^{9-}$ is reported to be featureless with applied potentials to −1.5 V vs. Ag/AgCl [30]. From this result alone, it is unclear if either the W–O framework or the Eu ion are electrochemically active in aqueous solution.

Herein we report our efforts to clarify any valence ambiguities of Eu in both $[Eu(\alpha\text{-}2\text{-}As_2W_{17}O_{61})_2]^{17-}$ and $[Eu(W_5O_{18})_2]^{9-}$ at rest potential and under reducing conditions through Eu X-ray absorption fine structure (XAFS) spectroelectrochemistry. In situ XANES (X-ray absorption near edge structure) data were collected at ambient temperature on dilute aqueous solutions of both anions at their rest potentials and at applied potentials of −1.0 and −1.5 V vs. Ag/AgCl for $[Eu(\alpha\text{-}2\text{-}As_2W_{17}O_{61})_2]^{17-}$ and $[Eu(W_5O_{18})_2]^{9-}$, respectively. Our XANES results are compared with previous experiments on $[EuP_5W_{30}O_{110}]^{12-}$.

2. Experiments

$K_{17}[Eu(As_2W_{17}O_{61})_2]\cdot nH_2O$ was prepared from $EuCl_3\cdot 6H_2O$ and the α-isomer of $K_6[As_2W_{18}O_{62}]$, which was synthesized according to Contant and Thouvenot [38], according to the methods of Bartis et al. [23] for the synthesis of $K_{17}[Eu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]\cdot nH_2O$. $Na_9[Eu(W_5O_{18})_2]\cdot 32H_2O$ was prepared according to the published method of Sugeta and Yamase [34].

Solution XAFS data were obtained at ambient temperature at the Stanford Synchrotron Radiation Laboratory on wiggler beam line 4-3 using a Si⟨220⟩ double-crystal monochromator and a 0.6-mm vertical pre-monochromator slit in a spectroelectrochemical cell of published design [39]. The fluorescence XAFS was accumulated with a flow-type ion chamber detector (The EXAFS Co.) [40]. Helium was used to purge the cell box; nitrogen was used to monitor the incident X-ray intensity, I_0, and argon was used to monitor the Eu L_α fluorescent X-ray intensity, I_f, in the conventional 45°-incident/45°-exit configuration through a Cr filter. At the Eu L_3 edge energy (6,977 eV), the total energy resolution was estimated to be 1 eV, which is less than the natural linewidth (3.91 eV [41]) of the Eu L_3 core hole. As a result, the Eu L_3 edge XANES shown here is not significantly broadened by instrumental factors. A BAS 100B/W electrochemical workstation was used to monitor and control the potential for the in situ electrochemical reduction with graphite rods for the working and auxiliary electrodes and a Ag/AgCl (3 M NaCl) reference electrode [39]. The aqueous supporting electrolytes were vigorously sparged with He prior to and throughout the XAFS data collection and the course of the bulk electrolysis experiments.

3. Results and discussion

The Eu L_3 edge XANES data for the clear and colorless 3 mM solution of $[Eu(\alpha\text{-}2\text{-}As_2W_{17}O_{61})_2]^{17-}$ at rest potential are shown in Fig. 1 as the dashed line. The Eu L_3 edge XANES data for the clear, colorless, 4.8 mM solution of $[Eu(W_5O_{19})_2]^{9-}$ at rest potential are shown in Fig. 2 as the dashed line. These data reveal intense edge resonances at 6,983.5 eV, which are typical of the Eu^{3+} L_3 edge XANES observed for the solid reference materials EuF_3, $EuCl_3\cdot 6H_2O$, and Eu_2O_3. The XANES shown in Figs. 1 and 2 provide clear evidence that Eu is trivalent in the two aqueous electrolytes at rest potential. The presence of divalent or intermediate-valent Eu would manifest itself through the appearance of an additional peak shifted approximately 8 eV to the low energy side of Eu^{3+} resonance [37,39,42].

The $[Eu(\alpha\text{-}2\text{-}As_2W_{17}O_{61})_2]^{17-}$ complex was reduced through constant-potential electrolysis at −1.0 V vs. Ag/AgCl. The applied potential was chosen to effect a deep, ca. five-electron reduction of the heteropolyanion. The in situ XANES obtained for the resulting inky-blue, electrochemically reduced solution is shown in Fig. 1 as the solid line. The spectrum is nearly indistinguishable from the XANES obtained at rest potential, shown in Fig. 1 as the dashed line. Because there is no evidence for a low energy resonance attributable to Eu^{2+}, we conclude that europium is trivalent in the reduced anion. The data of Fig. 1 demonstrate that Eu^{3+} in $[Eu(\alpha\text{-}2\text{-}As_2W_{17}O_{61})_2]^{17-}$ is not

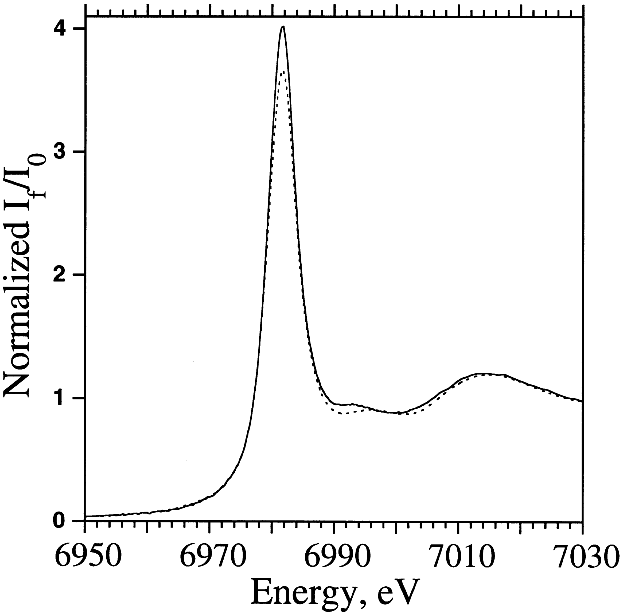

Fig. 1. In situ Eu L_3 edge fluorescence XANES obtained at ambient temperature for a 3 mM solution of $[Eu(\alpha\text{-}2\text{-}As_2W_{17}O_{61})_2]^{17-}$ in an aqueous supporting electrolyte of 0.1 M CH_3CO_2Na+0.1 M $NaClO_4$ at pH 5.0, at the open circuit potential of +0.15 V (dashed line) and after bulk electrolysis with the electrode polarized at −1.0 V (solid line).

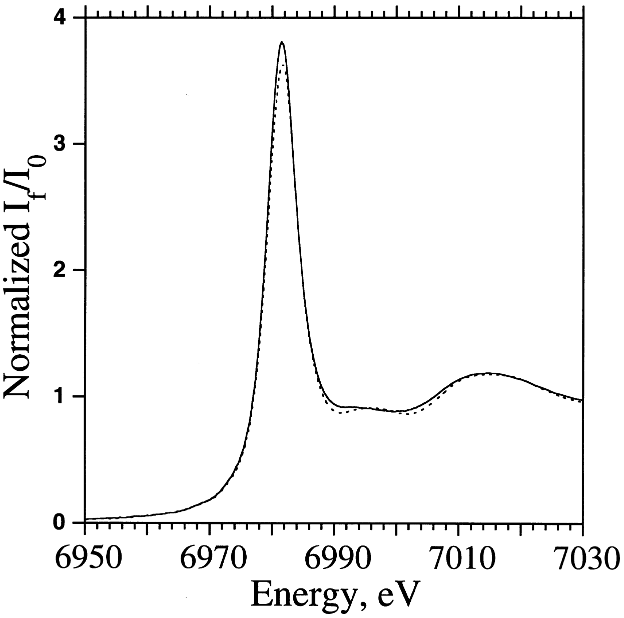

Fig. 2. In situ Eu L_3 edge fluorescence XANES of a 4.8 mM solution of $[Eu(W_5O_{18})_2]^{9-}$ at ambient temperature in an aqueous supporting electrolyte of 0.5 M NaCl, at the open circuit potential of +0.6 V (dashed line) and after bulk electrolysis with the electrode polarized at −1.5 V (solid line).

reducible to Eu^{2+} by constant-potential electrolysis under the electrochemical conditions used herein. From this result, it follows that europium does not contribute to the redox behavior of $[Eu(\alpha\text{-}2\text{-}As_2W_{17}O_{61})_2]^{17-}$. This direct result obtained from in situ Eu L_3 edge XAFS spectroelectrochemistry is consistent with the electrochemical studies of Xi et al. [28], who suggest that the reduction of $[Eu(\alpha\text{-}2\text{-}As_2W_{17}O_{61})_2]^{17-}$ involves the addition of electrons to predominantly non-bonding orbitals of the W^{6+}–O framework.

The in situ XANES for the colorless $[Eu(W_5O_{18})_2]^{9-}$ solution with the electrode polarized at −1.5 V vs. Ag/AgCl is shown in Fig. 2 as the solid line. These data are virtually identical to those obtained at rest potential, shown in Fig. 2 as the dashed line. The solution remains colorless, therefore there is no indication of electron transfer to the W–O framework. Nor is there evidence for the reduction of Eu^{3+} to Eu^{2+} under the electrochemical conditions employed herein. This is an interesting result in light of the fact that pulse and continuous radiolysis experiments show that Eu^{3+} can be reduced by e^-_{aq} to form $[Eu^{2+}(W_5O_{18})_2]^{10-}$ [30]. The hydrated electron has a standard reduction potential of about −3 V vs. Ag/AgCl [43].

The resistance of Eu^{3+} to reduction in $[Eu(\alpha\text{-}2\text{-}As_2W_{17}O_{61})_2]^{17-}$ is somewhat unexpected. Precedence for the electrochemical reduction of Eu^{3+} complexed to an electroactive phosphotungstate framework comes from our study of the Eu-exchanged Preyssler anion $[EuP_5W_{30}O_{110}]^{12-}$ [37]. XANES spectroelectrochemical experiments reveal the presence of Eu^{2+} after constant-potential electrolysis at −0.55 V in a 1 M H_2SO_4 aqueous electrolyte [37]. Indeed, there is evidence that the Eu^{3+} is reducible at applied potentials as high as −0.2 V (M.R. Antonio, L. Soderholm, unpublished results, 1997). The difference in reduction potentials of Eu in $[Eu(\alpha\text{-}2\text{-}As_2W_{17}O_{61})_2]^{17-}$ and $[EuP_5W_{30}O_{110}]^{12-}$ may be the result of large differences in the relative chemical potentials of the W–O framework orbitals that accept electrons during the reduction and the Eu 4f states. It should be noted that the mechanism of electron transfer from the W–O framework to the Eu is not understood at this time. The difference may also be due to orbital symmetry mismatches, or to differences in details of the two experiments. For example, the electrochemistry of the Preyssler anion was carried out at a much lower pH than were the experiments on the Wells–Dawson anion, because of the limited range of stability of the latter anion as a function of pH [20,31]. The inability to reduce Eu^{3+} in $[Eu(W_5O_{18})_2]^{9-}$ is somewhat less surprising because this complex is not a heteropoly blue.

To date, there is no understanding of the mechanism(s) of electron transfer within the Preyssler or any other heteropolyanion that govern the reduction of Eu. Therefore, further work is necessary to quantify the reduction behavior as a function of the anion, as well as of the chemical conditions used to affect the electrochemical reductions, such as pH and the choice of electrode. These topics remain the subject of further experimentation.

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