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**Redox Behavior Of Europium In The Preyssler Heteropolyanion
[EuP₅W₃₀O₁₁₀]¹²⁻**

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Abstract

In aqueous, mineral-acid electrolytes, the cyclic voltammetry of the europium-exchanged Preyssler heteropolyanion, [Eu^{III}P₅W₃₀O₁₁₀]¹²⁻, is unique among all the other trivalent-lanthanide-exchanged anions, [Ln^{III}P₅W₃₀O₁₁₀]¹²⁻ for Ln ≡ Ce-Lu. All [LnP₅W₃₀O₁₁₀]¹²⁻, including Eu, form heteropoly blues upon reduction. In order to obtain insights about this issue, we conducted in situ Eu L₃-edge XANES (X-ray absorption near edge structure) spectroelectrochemical experiments on an aqueous solution of [EuP₅W₃₀O₁₁₀]¹²⁻ (5.5 mM) in a supporting electrolyte of 1 M H₂SO₄ at two extreme potentials. The results demonstrate that the Eu^{III} ion in the colorless Preyssler anion solution at open circuit potential (+0.21 V vs Ag/AgCl) is electroactive and is reduced to Eu^{II} in the resulting dark blue solution from constant-potential bulk electrolysis at -0.55 V vs Ag/AgCl. This unusual redox behavior of [EuP₅W₃₀O₁₁₀]¹²⁻ may be of technological importance in the area of oxidation catalysis.

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Introduction

The Preyssler heteropolytungstate anion, $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$, and its lanthanide-exchanged derivatives, $[\text{Ln}^{\text{III}}\text{P}_5\text{W}_{30}\text{O}_{110}]^{12-}$, are of practical interest as promising oxidation catalysts.^{1,2} The reactivity and selectivity of these anions results from a combination of their unique features—the most remarkable of which are their stability and reversible redox chemistry. Both $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ and $[\text{LnP}_5\text{W}_{30}\text{O}_{110}]^{12-}$ (for $\text{Ln}^{\text{III}} \equiv \text{Ce-Lu}$) are electrochemically-active and form heteropoly blues upon reduction.³⁻⁶ The intense blue color that develops from colorless solutions is evidence of electrons in W-O bands from the reduction of W^{VI} . The Ln^{III} ions are thought to be electrochemically inactive. Whereas $[\text{EuP}_5\text{W}_{30}\text{O}_{110}]^{12-}$ also undergoes a reversible, multielectron reduction, its cyclic voltammogram (CV) is different from those of the other Ln^{III} -exchanged anions^{4,6} and, curiously, is similar to that for $[\text{Ca}^{\text{II}}\text{P}_5\text{W}_{30}\text{O}_{110}]^{13-}$.^{3,4} In contrast to the other trivalent lanthanides, Eu^{III} is the most easily reduced to the divalent state.⁷ This suggests that some part of the redox behavior of $[\text{EuP}_5\text{W}_{30}\text{O}_{110}]^{12-}$ may arise from the reduction of europium. In order to investigate this possibility, we probed the valence of Eu in $[\text{EuP}_5\text{W}_{30}\text{O}_{110}]^{12-}$ at open circuit potential and at a significantly reducing potential, using in situ XANES (X-ray absorption near edge structure) spectroelectrochemistry.

Experimental Section

The Eu^{III} -exchanged Preyssler anion was prepared as previously described to provide a single substitution site.⁶ The $[\text{CaP}_5\text{W}_{30}\text{O}_{110}]^{13-}$ anion was prepared according to Creaser et al.⁴ In situ Eu L_3 -edge XANES was obtained at ambient temperature at the NSLS on beam line X-23A2 with a purpose-built spectroelectrochemical cell.⁸ 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 from a 5.5 mM solution of $[\text{EuP}_5\text{W}_{30}\text{O}_{110}]^{12-}$ in an aqueous 1 M H_2SO_4 supporting electrolyte. The XANES was first obtained at the open circuit 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 observable effect on either the current or potential in the cell. The XANES from the average of nine 40 min. scans at each potential was normalized to a unit edge jump according to standard procedures.⁹ 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 at open circuit potential and after bulk electrolysis with the electrode polarized at -0.7 V. These experiments provide trivalent and divalent europium reference spectra. Details are provided elsewhere.⁸

Results

The CVs for $[\text{CaP}_5\text{W}_{30}\text{O}_{110}]^{13-}$ and $[\text{EuP}_5\text{W}_{30}\text{O}_{110}]^{12-}$ are shown in Figure 1a. Both exhibit four reduction steps of 2, 2, 4, and 2 electrons each, in order of decreasing potential.^{3,4} Except for the difference in the redox peaks for the first reduction (at $1/2[E_{pc}+E_{pa}] = -0.15$ and -0.11 V, respectively), the voltammograms are similar at potentials more negative than about -0.2 V. The feature that distinguishes these two CVs from those for the other $[\text{LnP}_5\text{W}_{30}\text{O}_{110}]^{12-}$ (which exhibit five reduction waves of 2 electrons each) is the large and incompletely resolved wave at -0.32 V.^{4,6} This feature can almost be resolved into two steps through semi-differentiation of the primary data, as shown in Figure 1b. The normalized Eu L_3 -edge XANES for the colorless, deaerated solution of $[\text{EuP}_5\text{W}_{30}\text{O}_{110}]^{12-}$ at open circuit potential is shown in Figure 2. The intense edge resonance is the result of an electronic transition from the Eu $2p_{3/2}$ manifold to the empty 5d manifold. Its position (6982.3 eV) and shape are characteristic of Eu^{III} . In situ Eu L_3 -edge XANES was

recorded for the same solution after applying and maintaining a potential of -0.55 V. The XANES obtained from the resultant deep blue solution reveal a single edge resonance at 6974.1 eV as shown in Figure 2. The shape and position of this new resonance, which is 8.2 eV below the Eu^{III} resonance, is characteristic of the XANES of Eu^{II} .^{8,10-14}

Discussion

After exhaustive electrolysis at the applied potential of -0.55 V, the Eu XANES for the reduced, Eu-exchanged Preyssler heteropolyanion provides unequivocal evidence for divalent europium. Upon reoxidation of the reduced anion, the CV and the Eu XANES of the clear, colorless solution were identical to those observed prior to the reduction, suggesting that the Eu^{II} ion remains within the anion's cavity.^{3,4} This result is interesting in view of previous suggestions that the lighter lanthanides, such as La^{III} with an ionic radius of 1.16 Å (for CN=VIII),¹⁵ do not exchange for Na^+ (1.18 Å) because the central cavity in the Preyssler ion may not have the flexibility to expand beyond a well-defined size.^{4,5} Because Eu^{II} (1.25 Å) is larger than the lighter trivalent lanthanides and Ca^{2+} (1.12 Å), the results obtained here instead suggest that there is a kinetic problem with the exchange reaction rather than a stability (i.e., thermodynamic) problem with the exchange product.

The similarity of the CVs for $[\text{CaP}_5\text{W}_{30}\text{O}_{110}]^{13-}$ and $[\text{EuP}_5\text{W}_{30}\text{O}_{110}]^{12-}$ at potentials more negative than ca. -0.2 V (see Figure 1) suggests that the reduction of Eu^{III} occurs at a potential between ca. -0.2 V and the open circuit potential, ca. +0.2 V. This is where the two CVs are most different. Although the exact potential at which Eu^{III} reduction commences remains the subject of further experimentation, it is clear that the overall reduction chemistry of $[\text{EuP}_5\text{W}_{30}\text{O}_{110}]^{12-}$ involves *both the Eu^{III} ion and the $\text{W}^{\text{VI}}\text{-O}$ octahedra*. This is unusual in lanthanide heteropolyoxometalate electrochemistry wherein reduction typically involves just the $\text{W}^{\text{VI}}\text{-O}$ octahedra, such

as for $[\text{CaP}_5\text{W}_{30}\text{O}_{110}]^{13-}$. With the exception of $[\text{Eu}^{\text{III}}\text{W}_{10}\text{O}_{36}]^{9-,16}$ the Ln^{III} cations in other heteropoly complexes (e.g., $[\text{Ln}(\text{As}_2\text{W}_{17}\text{O}_{61})_2]^{17-}$ and $[\text{LnSb}_9\text{W}_{21}\text{O}_{86}]^{16-}$)^{17,18} are *not* reducible. The clear implications of this dual electroactivity concern catalysis.² The direct involvement of Eu 4f electrons and W 5d electrons might facilitate reactions of technological importance. For example, $[\text{EuP}_5\text{W}_{30}\text{O}_{110}]^{12-}$ may exhibit better properties than $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{12-}$ for oxidation catalysis, such as for the aerobic conversion of H_2S to sulfur.¹ Furthermore, the redox behavior of $[\text{EuP}_5\text{W}_{30}\text{O}_{110}]^{12-}$ is pertinent to the solid-state redox behavior of Eu^{III} -exchanged zeolites,^{10,19} which are well-known for their use as cracking catalysts in the petroleum industry. In this regard, the cavity through the Preyssler heteropolyanion bears some resemblance to the tunnels connecting cages in zeolites. Experiments to evaluate various catalytic reactions with $[\text{EuP}_5\text{W}_{30}\text{O}_{110}]^{12-}$ are underway.

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Figure Captions

Figure 1. (a) Cyclic voltammograms for 1.3 mM $[\text{CaP}_5\text{W}_{30}\text{O}_{110}]^{13-}$ (dashed line) and 1.2 mM $[\text{EuP}_5\text{W}_{30}\text{O}_{110}]^{12-}$ (solid line) in aqueous, 1M H_2SO_4 obtained with a BAS 100B/W electrochemical analyzer and a scan rate of -100 mV/s, and BAS electrodes: 3.0 mm dia. glassy carbon working electrode; platinum wire auxiliary electrode; Ag/AgCl reference electrode. The arrows *1* and *2* indicate the electrode potentials (+0.21 and -0.55 V, respectively) at which the in situ Eu L_3 -edge XANES for $[\text{EuP}_5\text{W}_{30}\text{O}_{110}]^{12-}$ was recorded. (b) Semi-derivatives of the CVs in (a) reveal considerable improvement in the resolution of the four closely spaced redox waves.

Figure 2. In situ Eu L_3 -edge XANES spectroelectrochemistry of $[\text{EuP}_5\text{W}_{30}\text{O}_{110}]^{12-}$ (5.5 mM) in an aqueous 1M H_2SO_4 supporting electrolyte using a BAS CV-27 potentiostat. The XANES obtained for the colorless solution at open circuit potential (+0.21 V) before electrolysis reveals Eu^{III} as shown by the solid line *1*. The XANES obtained for the corresponding blue solution at -0.55 V after exhaustive electrolysis reveals Eu^{II} as shown by the dashed line *2*.

References and Notes

- (1) Harrup, M. K.; Hill, C. L. *Inorg. Chem.* **1994**, *33*, 5448-5455.
- (2) Antonio, M. R.; Malinsky, J.; Soderholm, L. In *Synthesis and Properties of Advanced Catalytic Materials*; E. Iglesia, P. Lednor, D. Nagaki and L. Thompson, Eds.; Mat. Res. Soc. Symp. Proc.: Boston, MA, 1995; Vol. 368; pp 223-228.
- (3) Alizadeh, M. H.; Harmalkar, S. P.; Jeannin, Y.; Martin-Frere, J.; Pope, M. T. *J. Am. Chem. Soc.* **1985**, *107*, 2662-2669.
- (4) Creaser, I.; Heckel, M. C.; Neitz, R. J.; Pope, M. T. *Inorg. Chem.* **1993**, *32*, 1573-1578.
- (5) Antonio, M. R.; Soderholm, L. *Inorg. Chem.* **1994**, *33*, 5988-5993.
- (6) Soderholm, L.; Liu, G. K.; Muntean, J.; Malinsky, J.; Antonio, M. R. *J. Phys. Chem.* **1995**, *99*, 9611-9616.
- (7) Morss, L. R. In *Standard Potentials in Aqueous Solution*; A. J. Bard, R. Parsons and J. Jordan, Eds.; Marcel Dekker: New York, 1985; Ch. 20.
- (8) Antonio, M. R.; Soderholm, L.; Song, I. *Anal. Chem.* **1995**, *submitted for publication*,
- (9) Lytle, F. W. In *Applications of Synchrotron Radiation*; H. Winick, D. Xian, M. H. Ye and T. Huang, Eds.; Gordon and Breach: New York, 1989; Vol. 4; pp 135-223.
- (10) Berry, F. J.; Marco, J. F.; Steel, A. T. *Hyperfine Interactions* **1994**, *83*, 347-350.
- (11) Michels, G.; Junk, S.; Schlabitz, W.; Holland-Moritz, E.; Abd-Elmeguid, M. M.; Dünner, J.; Mewis, A. *J. Phys.: Condens. Matter* **1994**, *6*, 1769-1778.
- (12) Ravot, D.; Godart, C.; Achard, J. C.; Lagarde, P. In *Valence Fluctuations in Solids*; L. M. Falicov, W. Hanke and M. B. Maple, Eds.; North-Holland: Amsterdam, 1981; pp 423-426.
- (13) Wortmann, G. *Hyperfine Interactions* **1989**, *47*, 179-202.

- (14) Wortmann, G.; Nowik, I.; Perscheid, B.; Kaindl, G.; Felner, I. *Phys. Rev. B: Condens. Matter* **1991**, *43*, 5261-5268.
- (15) Shannon, R. D. *Acta Cryst.* **1976**, *A32*, 751-767.
- (16) Mulazzani, Q. G.; Venturi, M.; Ballardini, R.; Gandolfi, M. T.; Balzani, V. *Israel J. Chem.* **1985**, *25*, 183-188.
- (17) Xi, X.; Wang, G.; Liu, B.; Dong, S. *Electrochimica Acta* **1995**, *40*, 1025-1029.
- (18) Liu, J.; Liu, S.; Qu, L.; Pope, M. T.; Rong, C. *Transition Met. Chem.* **1992**, *17*, 311-313.
- (19) Arakawa, T.; Takata, T.; Takakuwa, M.; Adachi, G. Y.; Shiokawa, J. *Mat. Res. Bull.* **1982**, *17*, 171-177.

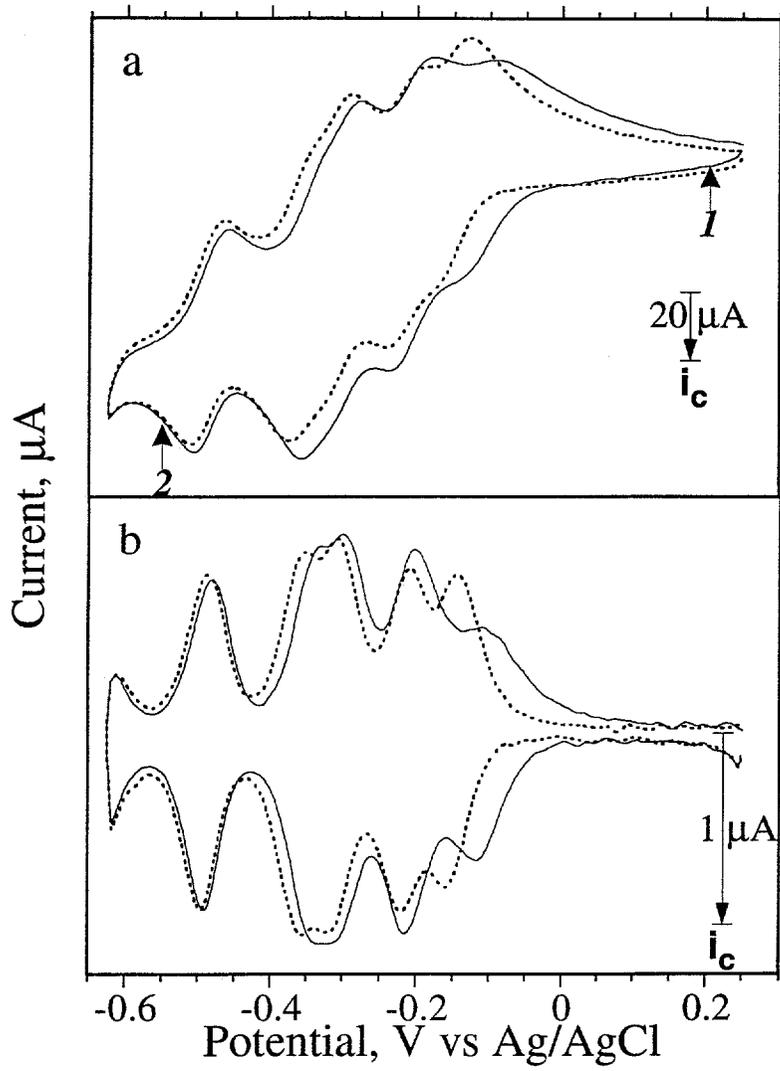


Figure 1
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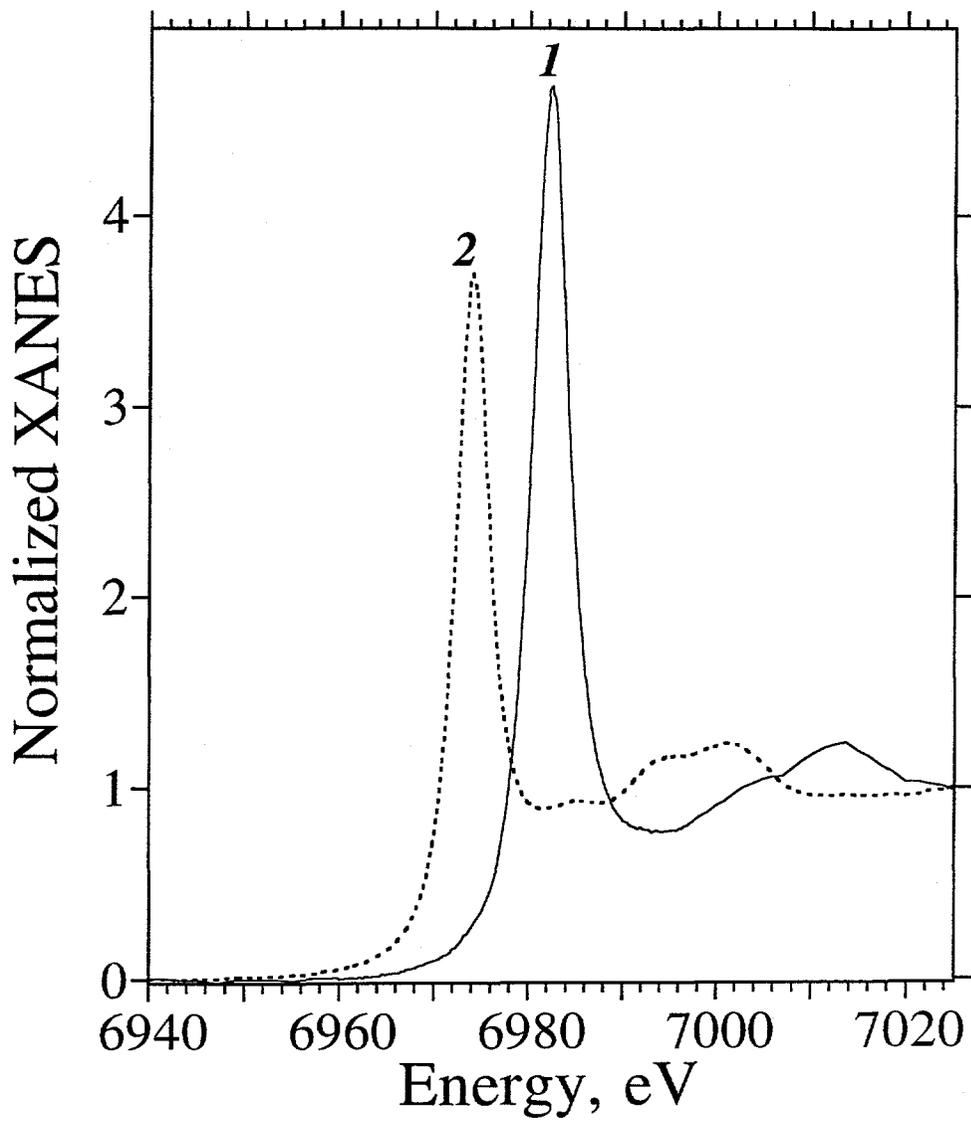


Figure 2
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