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Synthesis and characterization of actinide-exchanged Preyssler heteropolyanions $[AnP_5W_{30}O_{110}]^{n-}$ (An≡Th, Am, Cm)

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Abstract

Interest in the use of heteropolyoxometalate clusters as actinide complexants motivates our studies of the Preyssler heteropolytungstate anion, $[NaP_5W_{30}O_{110}]^{14-}$, and its actinide-exchanged derivatives, $[AnP_5W_{30}O_{110}]^{n-}$. Under specific conditions, substitution of Na^+ is possible by La^{3+} and Th^{4+} as well as by U^{4+} and the transuranics Am^{3+} and Cm^{3+}. Both $[AnP_5W_{30}O_{110}]^{11-}$ (for An≡Th^{4+}, U^{4+}) and $[AnP_5W_{30}O_{110}]^{12-}$ (for An≡Am^{3+}, Cm^{3+}) as well as $[LaP_5W_{30}O_{110}]^{12-}$ exhibit remarkable redox properties and form heteropoly blues. Although similar, the electrochemistry of the An^{3+}/La^{3+}- and An^{4+}-exchanged anions are different and distinguishable by cyclic voltammetry in aqueous mineral acid electrolytes. The synthesis of the new Preyssler anion complexes of La^{3+}, Th^{4+}, Am^{3+}, and Cm^{3+} will be described along with results from cyclic voltammetry measurements. © 1998 Elsevier Science S.A.

Keywords: Heteropolyoxometalate clusters; Actinide complexants; Preyssler heteropolytungstate anion; Actinide exchange; Cyclic voltammetry

1. Introduction

The class of large, water-soluble clusters of phosphorus–tungsten–oxygen known as heteropolytungstate anions show promise as complexants of rare-earth (RE) cations [1–11]. Our research [10–14] as well as that by Pope and co-workers [4,15] with the 145-atom Preyssler heteropolyanion, $[P_5W_{30}O_{110}]^{15-}$, demonstrates its ability to encrypt RE ions. The Preyssler molecule consists of a cyclic arrangement of five $-PW_6O_{22}-$ units forming a central tunnel through the anion. The encrypted RE ion is within the tunnel on the principal C_5 axis—displaced from the equatorial plane toward one end of the tunnel [15]. Ten oxygen atoms from the inner tunnel surface of the P–W–O framework serve to bind the RE ion [15]. Results from optical fluorescence measurements [14,16] reveal that the RE ion is also coordinated to water molecules, at least one of which is within the tunnel [15].

As yet, it has not been possible to synthesize directly—in one step—the $[REP_5W_{30}O_{110}]^{n-}$ cluster anions from $[WO_4]^{2-}$, $[PO_4]^{3-}$, and selected RE salts. Rather, first the Na^+ form of the Preyssler anion, $[NaP_5W_{30}O_{110}]^{14-}$, is prepared, then, under relatively rigorous conditions, Na^+ is exchanged with RE^{3+} (for RE≡Ce–Lu) and U^{4+}. Except for uranium(IV), the complexation chemistry of $[P_5W_{30}O_{110}]^{15-}$ is dominated by Na^+-exchange reactions with trivalent RE ions to form $[REP_5W_{30}O_{110}]^{12-}$. Despite reported attempts, the La^{3+}- and Th^{4+}-Preyssler anions have eluded preparation [4,10]. Moreover, until now, there have been no reports of transuranic complexes of the Preyssler heteropolyanion. We describe the successful preparation of four new RE-Preyssler heteropolyanions containing lanthanum, thorium, americium, and curium.

The only cations of La and Th that exist in aqueous solution are La^{3+} and Th^{4+}, and these are not redox active. In contrast, the electrochemistry of Eu is quite different. Both Eu^{2+} and Eu^{3+} are stable and electroactive in aqueous solutions. Our XANES (X-ray absorption near-edge structure) spectroelectrochemical studies of the redox behavior of the Eu-encrypted Preyssler anion reveal that Eu^{3+} in $[EuP_5W_{30}O_{110}]^{12-}$ in an aqueous mineral acid electrolyte is readily reducible to Eu^{2+} [12]. This result serves to explain its unique cyclic voltammetry, which involves both the P–W–O framework and the Eu ion. Our ongoing work with $[EuP_5W_{30}O_{110}]^{12-}$ suggests that the $Eu^{3+} \rightarrow Eu^{2+}$ reduction occurs at a potential that is more positive than the standard reduction potential of -0.55 V vs. Ag/AgCl [17]. This observation suggests the possibility that $[P_5W_{30}O_{110}]^{15-}$ stabilizes encrypted divalent europium.

Although americium ($5f^6$) is the 5f electronic analog of europium ($4f^6$), their chemistries are considerably different. Whereas Am^{2+} has been reported in solid phases, such as the binary halides [18,19], it has only been generated by pulsed radiolysis as a transitory species in aqueous solution

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[20]. Am^{2+} has been shown to oxidize by contact with water. The standard reduction potential of Am^{3+} has been estimated between −1.3 and −2.1 V vs. Ag/AgCl [21], which is consistent with its ability to reduce water. We wondered if the encapsulation of Am in the Preyssler heteropolyanion might afford an opportunity to study its divalent state in solution through the electrochemical reduction of $[AmP_5W_{30}O_{110}]^{12-}$. There are two reasons that Am^{2+} might be stabilized in the $[P_5W_{30}O_{110}]^{15-}$ anion. First, encapsulation limits its exposure to free water [14]. Second, the reduction potential of Eu^{3+} upon encapsulation with $[P_5W_{30}O_{110}]^{15-}$ is more positive (i.e. Eu^{3+} is more easily reduced) than in a noncomplexing medium [12]. The same might be true for Am^{3+}.

The aqueous solution chemistry of Cm is almost exclusively that of the tripositive ion [22]. An intriguing report by Kosyakov et al. [23] suggests that Cm^{4+} can be stabilized in aqueous solution by complexation with the monovacant Wells–Dawson heteropolyanion, $[P_2W_{17}O_{61}]^{10-}$. Similar work [24,25] suggests that Am^{4+} is stabilized with the lacunary Wells–Dawson anion in the complex $[Am(P_2W_{17}O_{61})_2]^{16-}$. We prepared $[CmP_5W_{30}O_{110}]^{12-}$ in order to compare its cyclic voltammetry with that of $[AmP_5W_{30}O_{110}]^{12-}$ and, thereby, to gain insights about the redox behavior of both of these transuranic heteropolyanions. The results of our cyclic voltammetry studies are presented here.

2. Experiments

2.1. Synthesis

The actinides ^{243}Am and ^{248}Cm are man-made, radioactive isotopes with limited availability—Na^+-exchange reactions were restricted to milligram-scale preparations based upon previously published methods for lanthanides [4,10,11]. A solution of $^{243}AmCl_3$ (634 μl, 3.01 mg) was added to a solution of $K_{12.5}Na_{1.5}[NaP_5W_{30}O_{110}]\cdot 15H_2O$ (1.2 ml, 100.3 mg), which was sealed in a Parr 4746 high pressure bomb and heated at 230°C for 97 h. After cooling, the addition of 0.4 g of KCl produced a white precipitate of $[AmP_5W_{30}O_{110}]^{12-}$, which was washed with ca. 1.5 ml of ice-cold H_2O in a 15-ml centrifuge cone and dried to obtain a 94% yield. The white Cm-exchanged Preyssler anion was prepared under the same conditions from the addition of a solution of $^{248}CmCl_3$ (400 μl, 3.01 mg) to a solution of $K_{12.5}Na_{1.5}[NaP_5W_{30}O_{110}]\cdot 15H_2O$ (1.2 ml, 107.8 mg). To prepare the thorium-exchanged anion, a solution of $Th(NO_3)_4\cdot 4H_2O$ (3 ml, 70.5 mg) was added to a solution of $K_{12.5}Na_{1.5}[NaP_5W_{30}O_{110}]\cdot 15H_2O$ (12 ml, 1.006 g), which was sealed in a Parr 4748 large capacity bomb and heated at 238°C for 96 h. After cooling, the addition of 4 g of KCl produced a white precipitate of $[ThP_5W_{30}O_{110}]^{11-}$, which was collected on filter paper (Whatman No. 42), washed with ca. 10 ml of ice-cold H_2O, and air-dried. The white La-exchanged Preyssler anion was prepared from a La^{3+} chloride and Preyssler anion solution as described above for Th-exchange.

2.2. Voltammetry

Cyclic voltammograms were collected as described elsewhere [11,14] by use of a BAS Inc. 100B/W electrochemical workstation, a BAS C-2 cell stand, and three BAS electrodes, including a 3-mm dia. glassy carbon stationary working electrode; a Pt wire auxiliary electrode; and a Ag/AgCl (3 M NaCl) reference electrode. All data were obtained at ambient temperature at a scan rate of 100 mV s^{-1} and, except for $[CmP_5W_{30}O_{110}]^{12-}$ with a solution concentration of ca. 20 μM, the other $[REP_5W_{30}O_{110}]^{n-}$ were examined at solution concentrations of ca. 500 μM in a supporting aqueous electrolyte of 1 M H_2SO_4 (Fisher Optima) prepared from 18 MΩ cm H_2O (Barnstead E-pure).

3. Results and discussion

Cyclic voltammetry (CV) provides a convenient analytical technique to determine whether or not Na^+ in the parent compound, $[NaP_5W_{30}O_{110}]^{14-}$, has been exchanged for a RE ion [4,14]. The CV data for the products obtained from the La^{3+} and Th^{4+} exchange reactions are shown in Fig. 1a and Fig. 1b, respectively. The cyclic voltammograms of $[LaP_5W_{30}O_{110}]^{12-}$ and $[ThP_5W_{30}O_{110}]^{11-}$ are different from that for $[NaP_5W_{30}O_{110}]^{14-}$, indicating that the exchange reaction was successful. Both voltammograms of Fig. 1a,b exhibit five closely spaced redox waves, which are due to the reduction of W^{6+} in the P–W–O framework in two-electron steps [4]. Neither La^{3+} nor Th^{4+} participate directly in the voltammetric response

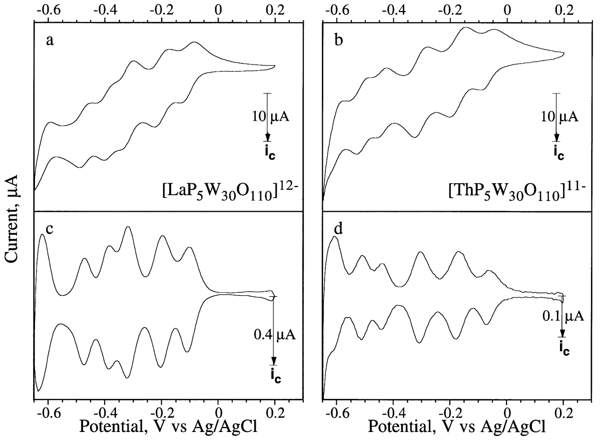

Fig. 1. Primary cyclic voltammetry data (top) and the semi-derivative results (bottom) for $[LaP_5W_{30}O_{110}]^{12-}$ (a,c) and $[ThP_5W_{30}O_{110}]^{11-}$ (b,d).

shown in Fig. 1. The CV data for $[LaP_5W_{30}O_{110}]^{12-}$ are essentially the same as those reported for the other RE^{3+}-exchanged Preyssler anions [4,10,11,14], except $[EuP_5W_{30}O_{110}]^{12-}$.

Although the primary CV data of Fig. 1a for $[LaP_5W_{30}O_{110}]^{12-}$ and Fig. 1b for $[ThP_5W_{30}O_{110}]^{11-}$ are similar, there are subtle differences between the two that become obvious through semi-differentiation of the primary data—the results of which are shown in Fig. 1c,d. Considerable improvement in the resolution of the tail-shape redox waves of Fig. 1a,b is evident in Fig. 1c, d, revealing variations in the voltammetric response. Starting at +0.2 V vs. Ag/AgCl (on the right in Fig. 1a–d) and going to −0.65 V (on the left), the five redox waves appear in different patterns for the La^{3+}- and Th^{4+}-exchanged Preyssler anions. For $[LaP_5W_{30}O_{110}]^{12-}$, the first two waves are separated from the following three waves by a deep waist band at −0.26 V, whereas for $[ThP_5W_{30}O_{110}]^{11-}$, the first three are separated from the following two by a waist band at −0.38 V.

The formal potentials ($E_{1/2}$) for each of the five reduction waves in $[LaP_5W_{30}O_{110}]^{12-}$ and $[ThP_5W_{30}O_{110}]^{11-}$ are listed in Table 1. The third reduction wave has the same $E_{1/2}$ for both $[LaP_5W_{30}O_{110}]^{12-}$ and $[ThP_5W_{30}O_{110}]^{11-}$, whereas the potentials of the first two waves (#1 and #2 in Table 1) for $[ThP_5W_{30}O_{110}]^{11-}$ are more positive than those for $[LaP_5W_{30}O_{110}]^{12-}$. For the last two waves (#4 and #5 in Table 1), the $E_{1/2}$ values for $[ThP_5W_{30}O_{110}]^{11-}$ are more negative than those for $[LaP_5W_{30}O_{110}]^{12-}$. These results indicate that although La^{3+} and Th^{4+} do not have any direct electrochemical activity, their presence affects the bulk voltammetric response of the framework. This suggests that the redox behavior of $[REP_5W_{30}O_{110}]^{n-}$ is influenced by the overall anionic charge (n), where $n=11$ for Th^{4+} and $n=12$ for La^{3+}. Precedence for this is provided by the reported CV of Keggin-type heteropolyoxometalates, which reveals an anionic charge dependence of their redox potentials [26].

The changes in the cyclic voltammograms of $[REP_5W_{30}O_{110}]^{n-}$ with different RE valence are clear enough to permit the use of CV to assist with the assignment of RE valence for cases where there might be some ambiguity, or to determine if the RE in $[REP_5W_{30}O_{110}]^{n-}$ is redox active. In this latter regard, we note that the CV data for the uranium-exchanged Preyssler anion prepared in our laboratories [10], and measured under the conditions described herein, are nearly identical to those shown for $[ThP_5W_{30}O_{110}]^{11-}$ in Fig. 1b,d. This observation is in agreement with U XANES data [17] showing that tetravalent uranium is exchanged for Na^+.

Table 1
Formal potentials ($E_{1/2}$)[a] for the five redox couples in the cyclic voltammetry of the $[REP_5W_{30}O_{110}]^{n-}$ anions in a supporting electrolyte of 1 M H_2SO_4 at ambient temperature

RE^{n+}	$E_{1/2}$ (V) vs. Ag/AgCl[b]				
	#5	#4	#3	#2	#1
La^{3+}	−0.47	−0.39	−0.32	−0.20	−0.11
Th^{4+}	−0.51	−0.44	−0.31	−0.17	−0.07
Am^{3+}	−0.48	−0.40	−0.32	−0.20	−0.11
Cm^{3+}	−0.48	−0.39	−0.31	−0.20	−0.10

[a] $(E_{pc}+E_{pa})/2$, where E_{pc} and E_{pa} are the cathodic and anodic peak potentials, respectively.

[b] The redox potential for the BAS Inc. silver/silver chloride reference electrode is +0.196 V vs. NHE at 25°C, see Ref. [27].

The primary CV data for $[AmP_5W_{30}O_{110}]^{12-}$ and $[CmP_5W_{30}O_{110}]^{12-}$ are shown in Fig. 2a and Fig. 2b, respectively. The semi-derivative results are shown directly below in Fig. 2c,d, and the formal potentials are tabulated in Table 1. All of the data of Fig. 2 are in close agreement with the corresponding data for $[LaP_5W_{30}O_{110}]^{12-}$ of Fig. 1a,c. The two- followed by three-wave pattern with a waist band at ca. −0.26 V is evident in the CV data of $[AmP_5W_{30}O_{110}]^{12-}$ and $[CmP_5W_{30}O_{110}]^{12-}$. Furthermore, the formal potentials for each of the five redox waves of $[AmP_5W_{30}O_{110}]^{12-}$ and $[CmP_5W_{30}O_{110}]^{12-}$ shown in Table 1 are the same (to within ±0.01 V) as those for $[LaP_5W_{30}O_{110}]^{12-}$. From these similarities, we conclude that: (1) trivalent Am and trivalent Cm are encapsulated within the Preyssler anion; (2) neither Am^{3+} nor Cm^{3+} are electroactive in this system; and (3) the voltammetric response seen in Fig. 2 is due to the reduction of the framework.

Because the CV of $[AmP_5W_{30}O_{110}]^{12-}$ resembles that of $[RE^{3+}P_5W_{30}O_{110}]^{12-}$, it is unlikely that Am^{3+} is reduced at any potential shown in Fig. 2a,c. Moreover, scans out to potentials of +1 V did not reveal the presence of additional redox waves. This suggests that Am^{3+} was not oxidized to Am^{4+} under the electrochemical conditions used herein. The CV data of Fig. 2a,c suggest that complexation of Am^{3+} with $[P_5W_{30}O_{110}]^{15-}$ does not shift the formal potentials of either of the Am(III)/Am(II) or Am(III)/Am(IV) redox couples to within the potential region

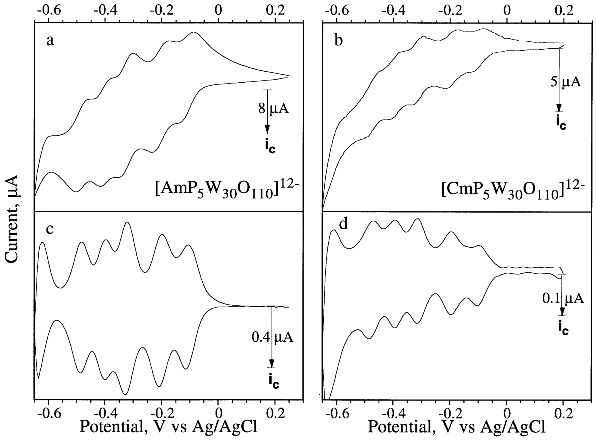

Fig. 2. Primary cyclic voltammetry data (top) and the semi-derivative results (bottom) for $[AmP_5W_{30}O_{110}]^{12-}$ (a,c) and $[CmP_5W_{30}O_{110}]^{12-}$ (b,d).

(−0.65 to +1.0 V vs. Ag/AgCl) studied herein. Although steep, the descending tail-shape voltammogram for $[CmP_5W_{30}O_{110}]^{12-}$ of Fig. 2b does not affect our interpretation of these data. The background slope is accentuated because of the minuscule concentration of $[CmP_5W_{30}O_{110}]^{12-}$ available for study.

The successful preparation of $[LaP_5W_{30}O_{110}]^{12-}$ and $[ThP_5W_{30}O_{110}]^{11-}$ reported here suggests that the prior synthetic failures [4,10] were due to kinetic problems with the exchange reaction, rather than thermodynamic (i.e. stability) problems with the exchange products. In order to prepare these two compounds as well as the first two transuranic complexes, $[AmP_5W_{30}O_{110}]^{12-}$ and $[CmP_5W_{30}O_{110}]^{12-}$, we had to resort to extreme conditions of reaction temperature (230–240°C) and time (ca. 100 h) in Teflon-lined bombs. Remarkably, the $[P_5W_{30}O_{110}]^{15-}$ framework did not break up. Nonetheless, the demanding conditions, together with the very sluggish nature of the exchange reaction, limit the technological prospects of $[P_5W_{30}O_{110}]^{15-}$ as a RE complexant in separation processes.

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