Cerium Valence in Cerium-Exchanged Preyssler's Heteropolyanion through X-ray Absorption Near-Edge Structure

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The sodium ion in the heteropolytungstate known as the Preyssler anion, $[NaP_5W_{30}O_{110}]^{14-}$, was exchanged with cerium from aqueous solutions of ammonium ceric nitrate, $[NH_4]_2Ce^{IV}(NO_3)_6$, as described by Creaser et al. [*Inorg. Chem.* **1993**, *32*, 1573]. The valence of cerium in this heteropolyanion was determined through Ce L-edge XANES, X-ray absorption near-edge structure. The XANES results demonstrate that cerium is trivalent in the Ce-exchanged Preyssler heteropolyanion in the solid state and in aqueous solution (1 M H_2SO_4) at rest potential and after constant-potential, bulk electrolysis at −0.55 V vs SCE. The encapsulated sodium ion of the Preyssler anion was shown to be directly exchangeable with Ce^{III} by prolonged (48 h), high temperature (165 °C) aqueous treatments with either $Ce(NO_3)_3{\cdot}6H_2O$ or $CeCl_3{\cdot}7H_2O$ in Teflon-lined pressure vessels.

Introduction

Among the many heteropolytungstate anions,[1,2] there are two of composition $[NaSb_9W_{21}O_{86}]^{18-}$ and $[NaP_5W_{30}O_{110}]^{14-}$ (the Preyssler anion) that encapsulate lanthanide ions.[3,4] The significance and interest of these lanthanide heteropolyanions relates to their potential antiretroviral activity and applications in catalysis.[1−4] Heteropolyanions and their free acids, i.e., heteropolyacids, find use as heterogeneous solid catalysts and homogeneous solution catalysts.[5]

A previously reported, single-crystal X-ray structural study of the Preyssler anion reveals that it consists of five PW_6O_{22} units arranged in a crown to form a cylindrical cavity.[6] The Na^+ ion is asymmetrically encapsulated within this cavity. It has 5 nearest oxygen atoms at 2.66 Å and 5 distant ones at 3.16 Å. It was first reported that Na^+ was strongly bound within the cavity and not exchangeable with trivalent cations of similar radius, such as Ce^{III} and Pr^{III}.[6] Under aggressive conditions, substitution of Na^+ by Ca^{2+} and, in part, Mg^{2+}, was demonstrated.[6] Subsequent studies indicate that the encapsulated Na^+ in $[NaP_5W_{30}O_{110}]^{14-}$ can be replaced by trivalent rare earth ions (RE^{III}) to form $[REP_5W_{30}O_{110}]^{12-}$ (for $RE \equiv$ Nd, Sm−Lu).[4] Once again, no Na^+ exchange was obtained with aqueous solution treatments of Pr^{III} or Ce^{III}. However, Na^+ was exchanged in treatments with aqueous solutions of Ce^{IV}.[4] Ultimately, this preparative chemistry provides the most convincing evidence that quadrivalent cerium is encapsulated by the heteropolytungstate anion. The ability of the Preyssler anion to accept a quadrivalent ion was demonstrated by the successful exchange of Na^+ for U^{IV}.[4]

The Preyssler anion and the rare-earth-exchanged ones, $[REP_5W_{30}O_{110}]^{12-}$, are electrochemically active and form heteropoly blues. The cyclic voltammograms (CVs) of the lanthanide heteropolyanions are different from that of the parent cluster, the latter of which exhibits two reversible reduction steps of 4 electrons each and one additional multielectron step.[4,6] By comparison, the CVs of all the RE^{III}-exchanged Preyssler anions, except Eu^{III}, exhibit five reversible reduction steps of 2 electrons each between 0.0 and −0.7 V vs Ag/AgCl, which are attributable to W(VI/V) waves.[4] The CVs of the Na^+ and RE^{III} anions are sufficiently different that they have been used as an analytical test to indicate that an exchange reaction has occurred.[4] The electrochemistry of the Ce-exchanged heteropolyanion is identical to that of $[REP_5W_{30}O_{110}]^{12-}$ (for $RE \equiv$ trivalent Nd, Sm, Gd−Lu). That no Ce(IV/III) reduction wave was observed is a surprising result—because Ce^{IV} is a strong oxidant—and may indicate a remarkable stabilization of quadrivalent cerium by the heteropolytungstate anion.[4] In this regard, the stabilization of quadrivalent cerium upon coordination with unsaturated heteropolytungstate anions was reported recently.[7] Alternatively, it is possible that the Preyssler anion contains trivalent cerium. Creaser et al.[4] acknowledge this quandary—despite results from cyclic voltammetry and controlled potential electrolysis as well as from ^{31}P NMR and electronic and infrared spectroscopies, the valence of cerium in the Preyssler anion is not evident.

We have investigated the problem of the oxidation state of cerium in the Ce-exchanged Preyssler anion through use of XANES, X-ray absorption near-edge structure, which is a direct spectroscopic probe of valence. Some of the related applications of Ce L-edge XANES include studies of Ce(III)/Ce(IV) redox processes in solution systems;[8] catalysts;[9] corrosion[10] and materials sciences.[11] We also investigated the reaction of cerium(III) with the Preyssler anion. A new and direct synthesis

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of the Ce-exchanged Preyssler anion from aqueous solutions of Ce^{III} is reported.

Experimental Section

Preparations. The white, crystalline Preyssler salt, $K_{12.5}Na_{1.5}$-$[NaP_5W_{30}O_{110}]\cdot 15H_2O$, was prepared according to the method of ref 4. Its CV is identical to that reported[4,6] and is available as supplementary material (see paragraph at end of paper regarding availability of supplementary material). The yellow, cerium-exchanged salt was prepared based on ref 4 with $[NH_4]_2Ce(NO_3)_6$ as the source of quadrivalent cerium. A warm (60 °C) orange solution of $[NH_4]_2Ce(NO_3)_6$ (66 mg, 0.121 mmol, dissolved in 3 cm^3 of H_2O) was added dropwise with stirring to a warm (60°C), colorless solution of the Preyssler salt (1 g, 0.121 mmol, dissolved in 12 cm^3 of H_2O) to produce a slightly turbid, yellowish solution, which was sealed in a Parr 4748 Teflon-lined vessel and heated at 160 °C for 18 h in a Lindberg/Blue M crucible furnace. Upon cooling, 4 g of solid KCl was added to the clear yellow solution to crash out a fine, pale yellow precipitate, which was collected on Whatman filter paper (no. 42) and rinsed with ca. 10 cm^3 of ice-cold water, and dried in air. Yields of 0.67–0.77 g (61–69% based upon $[NaP_5W_{30}O_{110}]^{14-}$ and an estimated empirical formula $K_{12}[CeP_5W_{30}O_{110}]\cdot 54H_2O$) were obtained. The CV for this Ce-exchanged Preyssler anion (shown in Figure 5) is similar to that previously reported.[4] There is no evidence of the Na^+ starting material. In addition, ^{31}P NMR data were obtained in a 1 M HCl aqueous solution.[12] We estimate that ≥80% of the Na^+ was exchanged. Samples from these preparations utilizing 1 equiv of Ce^{IV} were examined by XANES.

Yields of the Ce-exchanged anion can be improved to 85–90% by increasing the reaction time and temperature and starting with a solution of Ce^{III}, as follows. A colorless warm (60 °C) solution of $Ce(NO_3)_3\cdot 6H_2O$ (53 mg, 0.121 mmol, dissolved in 3 cm^3 of H_2O) was added dropwise with stirring to a warm (60 °C) solution of the Preyssler salt (1 g, 0.121 mmol, dissolved in 12 cm^3 of H_2O). The resulting clear, colorless solution was sealed in a Parr 4748 Teflon vessel and heated at 165 °C for 48 h. Upon cooling, the clear pale yellow solution was worked up exactly as described above. The Ce^{III}-exchange reaction occurs with both 1 and 2 equiv of Ce^{III} as either $Ce(NO_3)_3\cdot 6H_2O$ or $CeCl_3\cdot 7H_2O$ for the source of trivalent cerium. The CVs of these products (shown in Figure 5) are identical to the previous report.[4]

XANES Measurements. Ce L_2- and L_1-edge XANES data were collected at ambient temperature on beam line X-19A at the National Synchrotron Light Source. The presence of broad instrumental artifacts on the Ce L_3-edge absorption threshold necessitated the collection of L_2-edge data. Cerium L_2- and L_3-edge XANES ($2p_{1/2}$ and $2p_{3/2}$ initial states, respectively) provide the same information and have the same spectral shape[11a,13] when spin–orbit coupling is small in comparison to the 5d bandwidth. X-19A was equipped with a Si⟨111⟩ double crystal monochromator. The feedback system was adjusted to provide ca. 50% of the maximum incident X-ray intensity, I_0, at every point throughout the independent Ce L_2- and L_1-edge scans. With a 0.5 mm premonochromator vertical slit, a total energy bandwidth of ca. 1.5 eV was estimated to obtain between 6000 and 6500 eV.[14] This instrumental resolution is 2.5–2.8 times smaller than the natural line widths (3.8 and 4.2 eV)[15] of the Ce L_2 and L_1 core holes, respectively. Hence, the Ce L-edge XANES shown here is somewhat broadened (6–8%) by the instrumental resolution function.

For the solid-phase reference compounds (CeO_2, $H_4Ce(SO_4)_4$, $(NH_4)_2Ce(NO_3)_6$, $CeCl_3\cdot 7H_2O$, and $CeTiO_3$), the XANES was detected by use of the electron-yield technique[16] to provide edge resonance intensities and positions that are not vitiated by sample thickness effects. The powders were pressed into the adhesive of aluminized Mylar tape, which was then attached to the back plane of an electron-yield detector (The EXAFS Co.). Helium was used as the ionization gas for the electron-yield signal, I_e, and I_0. The solid-state and solution XANES of the Ce-exchanged Preyssler heteropolytungstate prepared according to ref 4 was detected by use of an ion chamber fluorescence detector (The EXAFS Co.). The fluorescence signal, I_f, was detected with argon gas: no fluorescence filters were used. Data from 3 sequential scans were averaged to improve the signal-to-noise ratio of the I_f signal. Although the quality of the L_2 XANES is more than adequate for a conclusive analysis of the cerium oxidation state, the poor signal-to-noise of the L_2 EXAFS (extended X-ray absorption fine structure) precludes a structural analysis of the cerium coordination environment in the Preyssler anion. Fluorescence XANES was also obtained for a freshly prepared aqueous solution of 95 mM $(NH_4)_2Ce(NO_3)_6$. The solution concentration of the Ce-exchanged Preyssler anion was 7 mM in 1 M H_2SO_4.

The normalization of the XANES to a unit edge jump was performed according to conventional methods.[17] Complete displays of the normalized Ce L_2- and L_1-edge X-ray absorption fine structure are available as supplementary material. The normalized L_2 XANES were fit with the sum of Lorentz and arctangent functions convolved with a 1.3 eV Gauss instrumental broadening function, as described for L-edge resonances by Lytle.[18] Details about the solution XANES spectroelectrochemistry and cyclic voltammetry as well as additional information about the XANES measurements and data reduction are provided as supplementary material.

Results

XANES. Cerium L_2-edge XANES for two well-characterized Ce^{III} compounds, $CeTiO_3$ and $CeCl_3\cdot 7H_2O$, are shown in Figure 1a,b, respectively. The single, intense edge resonances at 6166.5 eV in the data of Figure 1 are typical of those observed in L_2-edge XANES for trivalent cerium compounds.[8–11] These spectra stand in sharp contrast to the Ce L_2-edge XANES for three well-characterized Ce^{IV} compounds, CeO_2, $H_4Ce(SO_4)_4$, and $(NH_4)_2Ce(NO_3)_6$, shown in Figure 2a-c. The double edge resonances at 6170 and 6177.5 eV of approximately equal intensities in the data of Figure 2 are typical of those observed in L_2- and L_3-edge XANES for quadrivalent cerium compounds.[8–11] The obvious differences between the Ce L_2-edge XANES of trivalent cerium, on the one hand, and quadrivalent cerium, on the other, readily serve to distinguish between these two valence states. The exact positions and intensities of the cerium L_2 edge resonances in the normalized XANES of Figures 1 and 2 are shown in Table 1. Also tabulated there are the results from the curve fitting analysis of the L_2-edge XANES.

The corresponding Ce L_1-edge XANES for each of the aforementioned reference materials is shown in Figures 3 (Ce^{III}) and 4 (Ce^{IV}). Compared to the L_2-edge XANES, there is a less

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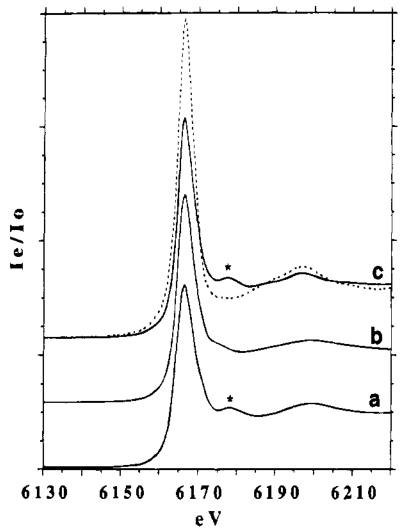

Figure 1. Cerium L_2-edge XANES for the trivalent cerium reference compounds (a) $CeTiO_3$ and (b) $CeCl_3 \cdot 7H_2O$ and (c) the cerium-exchanged Preyssler anion as the potassium salt in the solid state (solid line) and in an aqueous solution (7 mM, dashed line) of 1 M H_2SO_4 at rest potential. The vertical scale is offset for clarity.

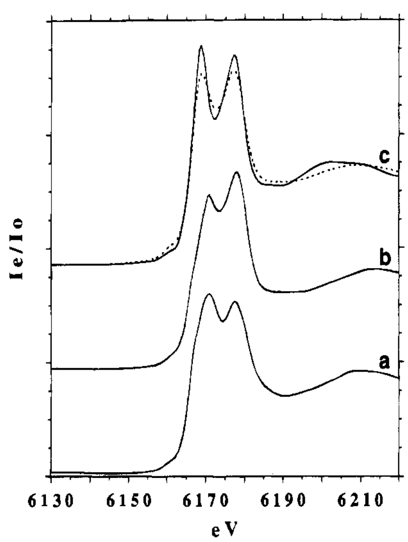

Figure 2. Cerium L_2-edge XANES for the quadrivalent cerium reference compounds (a) CeO_2, (b) $H_4Ce(SO_4)_4$, and (c) $[Ce(NO_3)_6]^{2-}$ as the ammonium salt in the solid state (solid line) and in aqueous solution (95 mM, dashed line).

dramatic modification of the L_1 edge-structure between trivalent and quadrivalent cerium compounds. Nevertheless, there is a significant shift of some 13 eV between the L_1 edge-peak energies in the XANES for Ce^{III} (ca. 6561 eV) and Ce^{IV} (ca. 6574 eV) compounds,[10] cf. Figures 3 and 4. This L_1 energy shift complements the L_2-edge XANES and provides additional evidence for the assignment of trivalent and quadrivalent oxidation states of cerium.

The L_2-edge XANES for the Ce-exchanged heteropolytungstate in the solid state and in 1 M H_2SO_4 solution at rest potential (0.3 V vs SCE) is displayed in Figure 1c. Both spectra are consistent with trivalent cerium. The normalized intensity of the single edge resonance at 6166.5 eV increases from 3.9 in the solid state to 5.7 upon dissolution; see Table 1. In addition, at ca. 11 eV above the edge resonance, the solid state L_2 XANES exhibits a small peak (marked with an asterisk in Figure 1c) that is absent in the solution XANES. This peak is identical to that observed for $CeTiO_3$ (Figure 1a) and cerium nitride, CeN. As previously demonstrated for $CeTiO_3$[11a] and CeN[11d], a comparison of the L_2- and inverted L_1-edge XANES of the Ce-exchanged Preyssler anion in the solid state suggests that the peak in question is structural.[19] Despite their differences, the L_2 XANES for the Ce-exchanged anion in the solid state and in solution is consistent with the presence of trivalent cerium.

The L_1 edge peaks in the solid state and solution XANES of the Ce-exchanged Preyssler anion (Figure 3c) occur at 6561 eV, which is confirming evidence for Ce^{III}. As with the L_2 data, the features of the L_1 XANES are similar but not exactly identical. The obvious difference between the XANES obtained in the solid state and the XANES obtained in aqueous 1 M H_2SO_4 solution is the increase of the edge peak intensity on going from solid to solution; see Figure 3c. There is also a concurrent diminution of the small post-edge peak at 6575 eV in the L_1 XANES (identified with an asterisk in Figure 3c). This L_1-edge XANES behavior is similar to that discussed above for the Ce L_2-edge XANES. The Ce L-edge solution XANES for the in situ controlled-potential electrolysis of the Ce-exchanged Preyssler anion at -0.55 V vs SCE is identical (see supplementary material) to the solution XANES obtained at rest potential. That no reduction of cerium was observed is not surprising given the presence of Ce^{III} and not Ce^{IV} in the heteropolyanion.

The Ce L_2 and L_1 XANES for $[NH_4]_2Ce(NO_3)_6$ (Figures 2c and 4c, respectively), which is the starting material for the synthesis of the Ce-exchanged Preyssler anion, are consistent with quadrivalent cerium in the solid state and in solution.[20] A comparison of the fitted L_2-edge parameters (Table 1) reveals several subtle differences between the solid state and solution XANES. It is evident that the two edge peaks become broader, less clearly resolved and less intense upon dissolution of the solid in water. Similarly, the corresponding L_1-edge XANES exhibits broader and less intense features in solution than in the solid state. These changes are attributed to a combination of hydration and hydrolysis effects, wherein the coordination of Ce^{IV} in solution is different from that in the solid. Such effects are known for dilute solutions of $[NH_4]_2Ce(NO_3)_6$,[21] and are not uncommon for transition metal complexes.[22]

Na^+ Exchange. In view of the presence of Ce^{III} in the Preyssler anion treated with aqueous solutions of Ce^{IV} at 160 °C for 12−18 h, we reinvestigated the exchange reaction with aqueous solutions of Ce^{III}. The exchange of Na^+ in the Preyssler anion with Y^{III}, Nd^{III}, Sm^{III}−Lu^{III}, and Bi^{III} is a sluggish process requiring some 12−18 h contact at elevated temperatures (145−

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Table 1. Cerium L_2-Edge Peak Intensities (INT) of the Normalized XANES Displayed in Figures 1 and 2 and the Results from the Curve-Fitting Analysis (Areas (*A*), Heights (*H*), Widths (*W*, eV), and Positions (*E*, eV)) of the Normalized XANES[a,b]

		Lorentzian				arctangent		
	INT	*A*	*H*	*W*	*E*	*H*	*W*	*E*
$Ce^{III}TiO_3$	3.23	19.5	2.52	4.9	6166.5	0.99	1.0	6163.5
$Ce^{III}Cl_3{\cdot}7H_2O$	3.70	21.5	3.04	4.5	6166.6	0.95	0.2	6163.9
$[CeP_5W_{30}O_{110}]^{12-}$ powder	3.92	22.2	3.27	4.3	6166.5	0.96	0.3	6164.1
$[CeP_5W_{30}O_{110}]^{12-}$ solution,[c] rest pot.	5.68	34.4	5.87	3.7	6166.5	0.85	2.3	6163.3
$[CeP_5W_{30}O_{110}]^{12-}$ solution,[c] −0.55 V	5.66	33.8	5.84	3.7	6166.7	0.85	2.7	6163.6
$Ce^{IV}O_2$	1.97	12.9	1.12	7.3	6170.4	0.84	0.9	6165.3
	1.89	9.4	0.96	6.3	6178.1			
$H_4Ce^{IV}(SO_4)_4$	1.92	10.9	1.05	6.6	6170.7	0.78	1.6	6165.3
	2.17	11.9	1.37	5.5	6177.9			
$[NH]_2Ce^{IV}(NO_3)_6$ powder	2.42	11.3	1.65	4.4	6168.7	0.84	1.6	6165.8
	2.31	12.7	1.54	5.3	6177.0			
$[NH]_2Ce^{IV}(NO_3)_6$ solution,[d] rest pot.	2.11	15.6	2.03	4.9	6168.5	0.86	1.1	6170.2
	2.15	12.0	1.29	5.9	6177.1			

[a] The edge resonances, due to $2p_{1/2} \rightarrow 5d$ electronic transitions, were modeled with Lorentz functions and the absorption edge jump was modeled with an arctangent function by use of the Lytle et al. algorithm (EDGFIT) and methods. [b] One Lorentz function was fit to the XANES of Ce^{III} compounds and two Lorentz functions were fit to the XANES of Ce^{IV} compounds. In both cases, a single arctangent was fit to each data set, which was convolved with a 1.3 eV Gaussian broadening function. Fitting range: 6145−6195 eV. See ref 18 and: Lytle, F. W.; Greegor, R. B.; Marques, E. C. In *Proc. 9th Int. Congr. Catal. Calgary*; Phillips, M. J., Teran, M., Eds.; The Chemical Institute of Canada: Ottawa, 1988; Vol. 5, p 54. [c] 7 mM aqueous solution in 1 M H_2SO_4. [d] Freshly prepared 95 mM aqueous solution.

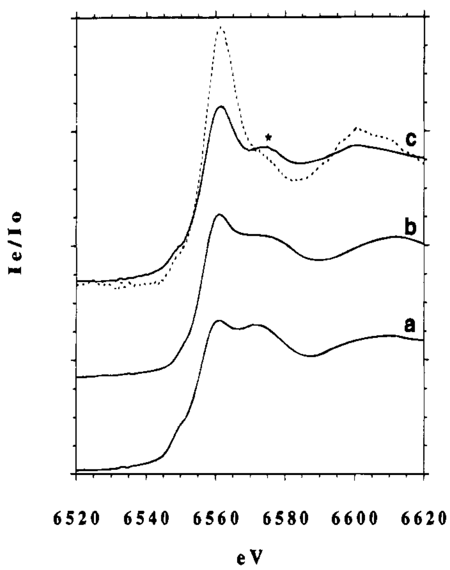

Figure 3. Cerium L_I-edge XANES for the trivalent cerium reference compounds (a) $CeTiO_3$ and (b) $CeCl_3{\cdot}7H_2O$ and (c) the cerium-exchanged Preyssler anion as the potassium salt in the solid state (solid line) and in an aqueous solution (7 mM, dashed line) of 1 M H_2SO_4 at rest potential. The vertical scale is offset for clarity.

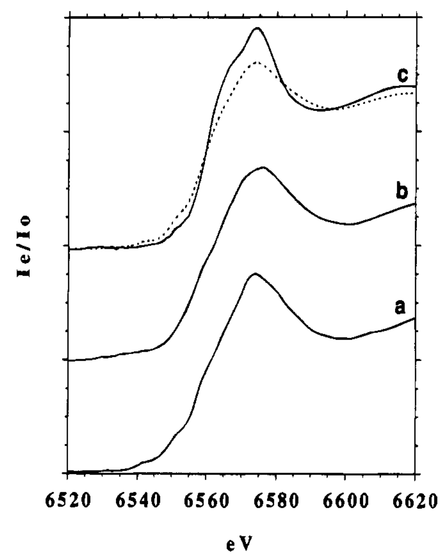

Figure 4. Cerium L_I-edge XANES for the quadrivalent cerium reference compounds (a) CeO_2, (b) $H_4Ce(SO_4)_4$, and (c) $[Ce(NO_3)_6]^{2-}$ as the ammonium salt in the solid state (solid line) and in aqueous solution (95 mM, dashed line).

180 °C) in high pressure vessels.[4] Under these conditions, neither La^{III}, Ce^{III}, or Pr^{III} can replace Na^+.[1,4] We found that Ce^{III} does replace Na^+ from aqueous solutions of either $Ce(NO_3)_3{\cdot}6H_2O$ or $CeCl_3{\cdot}7H_2O$ when the contact time is increased to 48 h at 165°C. The CVs of the cerium-exchanged Preyssler anions obtained from aqueous solutions of Ce^{III} and Ce^{IV} are identical, see Figure 5a,b, respectively. They are also identical to CVs described previously[4] for all the $[RE^{III}P_5W_{30}O_{110}]^{12-}$ anions, except Eu^{III}. Using these new conditions, we have also succeeded in the exchange of Na^+ with Pr^{III} from aqueous solutions of $Pr(NO_3)_3{\cdot}6H_2O$.[23] We have not yet been able to exchange Na^+ with La^{III}. It is possible that Ce^{III} is the largest cation (1.14 and 1.29 Å for coordination numbers VIII and XII, respectively[24]) that can be accommodated and stabilized within the heteropolyanion cavity. These observations are consistent with the hypothesis that the selectivity of $[NaP_5W_{30}O_{110}]^{14-}$ toward rare-earth ion exchange is due to a size effect—ions with large radii may be too big to fit into the central cavity.[4]

Discussion

The L_2- and L_I-edge XANES for the cerium-exchanged Preyssler anion are consistent with the presence of Ce^{III}. This is true for the solid state and solution samples at rest potential and after exhaustive constant potential electrolysis at −0.55 V vs Ag/AgCl. Although Ce^{III} can be directly exchanged for Na^+ just like the other trivalent rare earth ions (Nd, Sm-Lu), the occurrence of Ce^{III} in the heteropolyanion following exchange with aqueous $[NH_4]_2Ce^{IV}(NO_3)_6$ is unexpected. It may be rationalized in the following manner.

Ammonium ceric nitrate consists of two *oxidizable* cations, $2[NH_4]^+$, and a *reducible* anion, $[Ce(NO_3)_6]^{2-}$, containing Ce^{IV}. Quadrivalent cerium is known to be a powerful oxidant.[21,25] It

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(25) Kilbourn, B. T. *Cerium. A Guide to its Role in Chemical Technology*; Molycorp, Inc.: White Plains, NY, 1992; pp 9−19.

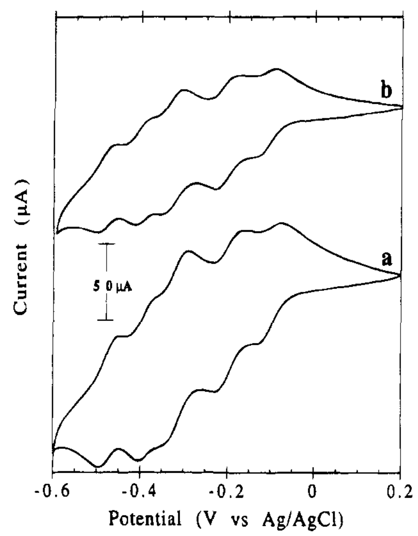

Figure 5. Cyclic voltammograms of $[CeP_5W_{30}O_{110}]^{12-}$ (in 1 M H_2SO_4 electrolyte) prepared from (a) $Ce(NO_3)_3{\cdot}6H_2O$ as described herein (anion concentration 1 mM) and (b) $[NH_4]_2Ce(NO_3)_6$ according to ref 4 (anion concentration 0.8 mM). Both CVs were recorded with BAS 100 B/W electrochemical analyzer with a glassy carbon working electrode (3.0 mm diameter), Ag/AgCl reference electrode, Pt wire auxillary electrode, and a sweep rate of −200 mV/s. The vertical scale has been offset for clarity.

is capable of oxidizing water to oxygen ($Ce^{IV} + {}^1/_2H_2O \leftrightarrow Ce^{III} + H^+ + {}^1/_4O_2$) and chloride ion to chlorine ($Ce^{IV} + Cl^- \leftrightarrow Ce^{III} + {}^1/_2Cl_2$).[26a] By analogy, quadrivalent cerium may be capable of oxidizing ammonium ion to nitrogen ($Ce^{IV} + {}^1/_3[NH_4]^+ \leftrightarrow Ce^{III} + {}^4/_3H^+ + {}^1/_6N_2$).[26b] To ascertain the reducibility of Ce^{IV}, we conducted control experiments consisting of aerobic, high temperature (165 °C) treatments of dilute (20 mM) aqueous solutions of ammonium ceric nitrate. The experimental conditions employed here were identical to those used for the exchange reaction, except that the Preyssler anion was omitted. A freshly prepared pale orange solution of $[NH_4]_2Ce(NO_3)_6$ was heated for 18 h in a Teflon-lined bomb to produce a colorless solution (typical of the aqueous Ce^{III} ion)[8a,21] and an insoluble, white, gel-like precipitate of unknown composition. A qualitative chemical analysis[27] revealed the presence of Ce^{III}. So, either with or without the Preyssler anion, Ce^{IV} is reduced under the experimental conditions employed here through the oxidation of either H_2O or $[NH_4]^+$.

Whereas this explanation accounts for the presence of Ce^{III} in the heteropolyanion, further explanation is required to understand why the exchange reaction is more facile for Ce^{IV} than Ce^{III}. Aqueous solutions of ammonium ceric nitrate are strongly acidic due to hydration and hydrolysis reactions. The aerobic, high temperature exchange of Na^+ for Ce^{III} from reactions with $[NH_4]_2Ce^{IV}(NO_3)_6$ may be pH dependent. The acidic nature of the ammonium ceric nitrate solution might catalyze the exchange. In support of this suggestion, we have found that the exchange of U^{IV} for Na^+ is pH dependent.[28] We have only been able to exchange U^{IV} (as UCl_4) for Na^+ in dilute acid, 0.05 M HCl; treatments with neutral solutions and 1 M HCl solutions produced no exchange. This may explain why solutions of Ce^{III} (which are neither acidic nor oxidizing) require somewhat more vigorous treatments than solutions of Ce^{IV} to effect the exchange with Na^+ in the Preyssler anion.

Assuming that cerium replaces Na^+ in the cylindrical cavity of the heteropolyanion framework, the changes observed in the XANES upon dissolution of the Ce-exchanged Preyssler salt in 1 M H_2SO_4 are somewhat surprising. The differences between the solid state and solution XANES (Figures 1c and 3c) are ascribed to a molecular relaxation or distortion of the heteropolyanion framework induced by hydration and protonation in 1 M H_2SO_4. A similar explanation was advanced to explain the XANES alterations of an iron porphyrin upon adsorption and exposure to electrolytes.[29] Upon dissolution, a slight relaxation of the heteropolytungstate framework could be sufficient to lead to the movement and relocation of Ce^{III} within the cylindrical vacancy. However, we cannot exclude the possibility that the Ce^{III} site is accessible to solvent water and ions despite the fact that the ends of the cylindrical cavity are restricted by five terminal oxygen atoms of the WO_6 groups.[30] Nor can we exclude the possibility that at least some of the Ce^{III} ions are outside of the cavity. Because of the dilute concentration of cerium in this heteropolyanion (ca. 1.6 wt % Ce), the Ce L-edge intensity differences between the solid state and solution XANES (see Figures 1c and 3c) are not caused, in whole, by thickness artifacts.[16] Rather, the intense edge resonance of the solution XANES may be indicative of a number of effects, such as a localized structural reorganization about Ce^{III}, bonding, hybridization, orbital mixing, etc. It is clear from this discussion that the elucidation of the Ce^{III} coordination environment in the solid state and in electrolyte solutions is a matter of some importance.

Regardless of the exchange mechanism and the cerium location, the presence of Ce^{III} in the Preyssler anion explains the electrochemical data, which are identical to the other (trivalent) rare earth exchanged Preyssler anions (except Eu^{III}) and do not show a Ce(III/IV) redox peak even at strongly cathodic potentials. Finally, the light yellow color of the Ce-exchanged Preyssler anion is not inconsistent with the presence of Ce^{III}. The trivalent cerium tungstate and cerium molybdate of composition, $(Ce^{III})_2(WO_4)_3$ and $(Ce^{III})_2(MoO_4)_3$, are yellow.[31]

Conclusions

The cerium-exchanged Preyssler anion examined herein through XANES was prepared according to the original report[4] with 1 equiv of Ce^{IV} to 1 equiv of the parent Na^+ anion. The L-edge XANES results for this Ce-exchanged Preyssler heteropolyanion are clear and unequivocal. Cerium is trivalent in the pale yellow solid salt and in aqueous solution (1 M H_2SO_4) at rest potential and after exhaustive bulk electrolysis. In view of the presence of Ce^{III} in the Preyssler anion treated with $[NH_4]_2Ce^{IV}(NO_3)_6$ in aqueous solution at 160 °C for 12−18 h, the exchange reaction with Ce^{III} was reinvestigated. Under even more extreme conditions of temperature (165 °C) and time (48 h), the direct exchange of Na^+ for Ce^{III} does occur in aqueous solutions of either $Ce(NO_3)_3{\cdot}6H_2O$ or $CeCl_3{\cdot}7H_2O$. Despite the differences between the solid state and solution XANES of the Ce-exchanged Preyssler anion, the Ce L-edge results are not inconsistent with the location of Ce^{III} within the heteropoly-

(26) (a) Baes, C. F., Jr.; Mesmer, R. E. *The Hydrolysis of Cations*; John Wiley: New York, 1976; pp 138−146. (b) In the absence of Ce^{IV}, the oxidation of ammonium ion can occur as follows: $2[NH_4]^+ \rightarrow N_2 + 8H^+ + 6e^-$; see: Pourbaix, M. *Atlas of Electrochemical Equilibria in Aqueous Solutions*; Pergamon: Oxford, U.K., 1966; p 496.

(27) Ammoniacal silver nitrate test, see: Feigl, F. *Qualitative Analysis by Spot Tests. Inorganic and Organic Applications*, 3rd ed.; Elsevier: New York, 1946; pp 160−161.

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tungstate anion framework. Additional evidence from EXAFS and single crystal X-ray diffraction is required to elucidate the exact coordination of Ce^{III}.

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Supplementary Material Available: Detailed descriptions (text and Figures I–VI) of the XANES data collection and reduction, spectroelectrochemical XANES for $[CeP_5W_{30}O_{110}]^{12-}$, electrochemistry of $[NaP_5W_{30}O_{110}]^{14-}$ and $[CeP_5W_{30}O_{110}]^{12-}$, complete X-ray absorption fine structure data for all Ce^{III} and Ce^{IV} model compounds and the Ce-exchanged Preyssler anion, and first differential XANES for $CeCl_3{\cdot}7H_2O$ as well as the join of the inverted L_1 edge XANES with the L_2 edge XANES for $CeTiO_3$ and $[CeP_5W_{30}O_{110}]^{12-}$ (15 pages). Ordering information is given on any current masthead page.