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Correlated Electrons in the Eu-Exchanged Preyssler Anion $[EuP_5W_{30}O_{110}]^{n-}$

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The development of effective methodologies for including highly correlated electron interactions in theoretical descriptions of chemical bonding is proving a difficult challenge.[1] Correlated electrons can strongly influence both static and dynamic electronic responses as well as the conductivity and magnetic properties of materials.[2] From an experimental perspective, these behaviors often occur close to an f-electron valence instability, and recent experiments suggest that chemical disorder may play a fundamental role in some correlated electron behavior.[3] Correlation effects have been most extensively studied in intermetallic compounds and perovskite-related oxides. Evidence is presented herein that electroactive heteropolyanions, exemplified by $[EuP_5W_{30}O_{110}]^{n-}$, held under reducing potentials, exhibit behavior consistent with the presence of strongly correlated electrons. Specifically, the electrochemical response of $[EuP_5W_{30}O_{110}]^{n-}$ in solution deviates significantly from Nerstian statistics, which we interpret in terms of Eu f-state/framework-electron interactions. The finite size of the Preyssler anion and the unprecedented tunability of the electrochemical driving force for the electron coupling point toward a new avenue for investigating longstanding questions about correlated electron behavior.

The Preyssler anion, $[NaP_5W_{30}O_{110}]^{14-}$, an electroactive self-assembled cluster, is stable in acidic solution. At rest potential, the cluster is fully oxidized, and the W−O states are empty. Under an applied potential, this anion in solution will accept reversibly up to 10 electrons, in a multistep process, before the potential becomes reducing enough to reduce H_2O.[4] Upon reduction, the heteropolyanion becomes dark blue, indicating that the added electrons are delocalized on the W−O framework.[5] Na^+, which sits in the central cavity formed by the P−W−O donut-shaped framework, can be exchanged for a variety of ions, including those in the rare-earth (R) series. The redox behavior of the W−O framework changes qualitatively with the charge on the exchanged ion and is exemplified for the trivalent central ion by the cyclic voltammogram (CV) of an La-exchanged cluster[6] (see the Supporting Information). All of the R^{3+}-exchanged Preyssler anions exhibit a similar CV except $[EuP_5W_{30}O_{110}]^{12-}$. The chemistry of Eu suggests that this observed difference may originate with the accessibility and stability of Eu^{2+}. XANES data show that Eu is trivalent in the fully oxidized Preyssler anion at rest potential, whereas it is divalent under an applied, reducing potential of −0.55 V. These results demonstrate that the introduction of delocalized d-electrons into the W−O framework causes the Fermi level to cross the localized Eu^{3+} f-state energy, thereby resulting in the reduction of Eu^{3+}. The applied potential at which the localized f-states and the W−O states coexist near the Fermi level creates a circumstance that is known to result in strong electron correlations and nonintegral valence.[1] We report on details of the charge distribution and Eu valence of the exchanged Preyssler anion as a function of applied potential.

In situ L_3-edge X-ray absorption data were obtained from a single-site $[EuP_5W_{30}O_{110}]^{12-}$ ion in aqueous solution at ambient temperature[7] on the BESSRC CAT's bending magnet beamline at the Advanced Photon Source. Details are available in the Supporting Information. All spectra were analyzed as described elsewhere.[8]

Representative Eu spectra, obtained after the stepwise bulk electrolysis of $[EuP_5W_{30}O_{110}]^{n-}$ at each potential, are shown in Figure 1. The data demonstrate the progression of the Eu valence from trivalent to divalent with increasingly reducing applied potential. The simultaneous presence of Eu^{3+} and Eu^{2+} in solution is expected from thermodynamic considerations. For thermodynamically reversible reactions, the ions in solution are considered a canonical ensemble in which the forward and reverse redox reactions are occurring at a rate that is changing with the applied potential. The ratio of the oxidized to reduced form can be expressed as:[9]

$$r(E) = [O]/[R] = \exp\{n(E - E^{0\prime})F/RT\}$$

where [O] and [R] are the concentrations of the oxidized and reduced species and $E^{0\prime}$ is the formal potential, which corresponds to the potential at which the forward and reverse reactions occur at a similar rate. R is the gas constant, n is the number of electrons transferred in the reaction, and F is Faraday's constant. The Eu XANES data shown in Figure 1 can be used to obtain $r(E)$[8] by reexpressing eq. 1 in the Nernst formalism, $E = E^{0\prime} + (RT/nF)\ln([O]/[R])$ so that the dependence of $r(E)$ on the applied potential can be seen. The reduced XANES data, replotted by using the Nernst format in Figure 2, are not linear, in contrast to the behavior expected for an idealized electrochemical couple. Although there are two linear regions, there is a marked cusp over an applied potential of −0.15 to −0.09 V. The Eu^{3+}/Eu^{2+} ratio remains fixed at about 2:1 over this applied potential range. Verification that charge is transferred to the Preyssler anion over this potential range is obtained by independently counting the total Coulombs transferred to the $[EuP_5W_{30}O_{110}]^{n-}$ anion. The total Coulombs transferred are compared with the Eu^{3+}/Eu^{2+} ratio at the same applied potentials as the inset in Figure 2. There is a change in slope for the total charge transferred to the cluster at about −0.17 V, but it is outside of the potential range for which the Eu^{3+}/Eu^{2+} ratio is constant. Thus, the Nernst plot demonstrates that the redox behavior of Eu in $[EuP_5W_{30}O_{110}]^{n-}$ is inconsistent with that expected for a simple redox couple.

Nonlinear Nernstian behavior has been previously reported, where it has been attributed to multiple-step electron-transfer reactions,[10] spectral-overlap interference with the determination of $r(E)$,[11] or cooperation between multiple redox sites in biological molecules.[12] The sigmoidal form of our data is only exhibited in the latter two experiments. The spectral overlap situation does not pertain here because there is no spectroscopic interference, from W or other X-ray absorption edges, over the scanned energy. Similar

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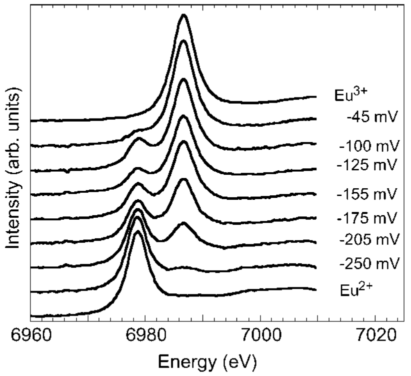

Figure 1. The Eu L_3-edge XANES spectra obtained from a single solution of $[EuP_5W_{30}O_{110}]^{n-}$ after bulk electrolysis at the specified applied potentials. The two peaks at 6979 and 6987 eV are characteristic of Eu(II) and Eu(III), respectively. All quoted potentials are vs Ag/AgCl, which has a redox potential of +0.196 V vs NHE at 25 °C.

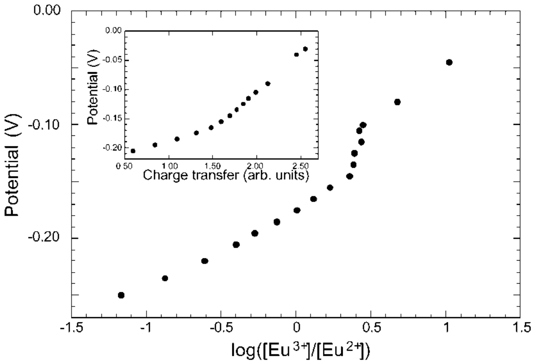

Figure 2. A Nernst plot of the data shown in Figure 1. Inset: The total charge transferred to the $[EuP_5W_{30}O_{110}]^{n-}$ ion, obtained by coulometry, is plotted over the same potential range. It can be seen from a comparison of the Nernst plot with the inset that although the Eu^{3+}/Eu^{2+} ratio is not changing over the applied-potential range of −0.09 to −0.15 V, the Preyssler anion is accepting electrons with no significant change in slope.

Nernst data to that shown in Figure 2 have been reported for cytochrome *c* oxidase[12] for which it has been suggested that intersite interactions between the redox active Fe and Cu are responsible for the nonlinearity, but the interactions are of an unspecified nature.

We too suggest that the form of our plotted data in Figure 2 arises from the interaction of the two different redox active species in our Preyssler anion, Eu, and the W−O band states. Explicitly, we suggest that this interaction involves the hybridization of the localized f_{Eu} states with the d_{W-O} band states:

$$\Psi_{IV} = \alpha\phi_f + \beta\phi_d$$

where α and β are the mixing coefficients for the f and d states, respectively. This hybridization occurs over an applied potential range for which the unhybridized states would be almost energetically degenerate. The range of constant $r(E)$ observed in our data is understood in terms of the addition of charge to a f−W−O band, and not simply the Eu single-ion states that receive the charge outside the constant r range. The f−W−O hybrid band is only partly composed of Eu f-states and therefore electrons added to this band state will have less influence on the observed final-state valence as determined by XANES.[13] As previously observed for other non-Nernstian plots,[11] the two outer regions of the plot in Figure 2 have slopes significantly different from $n = 1$, indicating weak interactions between the localized f_{Eu} states and the d_{W-O} band states that persist outside the highly correlated region. Independent support for f−W−O hybridization comes from the analysis of magnetic susceptibility data obtained from solids precipitated from solution at rest potential, fully reducing potential, and at −120 mV (see Supporting Information). The susceptiblity obtained from the intermediate sample cannot be adequately represented by any linear combination of the data from the two valence-pure samples. It has a lower than expected temperature-dependent contribution to the measured susceptibility and also a much higher temperature-independent contribution. These results are consistent with previous work on intermediate-valent materials.[14]

The results presented here on the electrochemical response of the Eu Preyssler anion at intermediate reducing potentials are consistent with those expected for correlated electrons and a nonintegral valent material. Nonintegral valence has been previously observed in Eu-containing solids, primarily intermetallics and alloys.[13] The finite size of the Preyssler cluster, together with the presence of only one rare-earth ion per cluster, reduces the complexity of this system over previously studied materials. The addition of electrons electrochemically permits the experimental distinction between the effects that arise due to changing electron count and those that arise because of chemical disorder.[3] In situ XANES spectroelectrochemistry provides an unprecedented tunability of the Fermi level relative to localized f states without the necessity of introducing other complicating factors. There are a wide variety of electroactive heteropolyanions,[15] some of which encrypt or encapsulate f ions, that offer a new avenue for investigating intermediate valence and other correlated electron properties.

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Supporting Information Available: Structure, cyclic voltamograms, experimental procedures, and magnetic susceptibilities (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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