Energetics of heterometal substitution in e-Keggin [MO$_4$Al$_{12}$(OH)$_{24}$(H$_2$O)$_{12}$]$^{6/7/8+}$ ions

DANA REUSSER$^1$, WILLIAM H. CASEY$^2$ AND ALEXANDRA NAVROTSKY$^1$.

$^1$Peter A. Rock Thermochemistry Laboratory and NEAT ORU, University of California at Davis, Davis, California 95616, U.S.A. 
$^2$Department of Chemistry, Department of Geology, University of California at Davis, Davis, California 95616, U.S.A.

**ABSTRACT**

Aluminum hydroxide ions in the e-Keggin structure provide geochemical models for how structure affects reactivity, and consequently, how aqueous ions evolve to bulk precipitates. Here we report a systematic comparison of heterometal substitution into the MAI$_2$ e-Keggin structure, where M = Ga$^{III}$, Al$^{III}$, or Ge$^{IV}$. We use direct solution calorimetric techniques to compare the energetics of these substituted structures and complement these measurements with density functional theory (DFT) calculations to further examine this structure as a host to alternative heterometals. The measured enthalpy of solution ($\Delta H_{sol}$) at 28 °C in 5 N HCl for the selenide salts of GaAl$_{12}^5$ and AlAl$_{12}^7$ was measured as $-869.71 \pm 5.18$ and $-958.04 \pm 2.79$ kJ/mol, respectively. The enthalpies of formation from the elements, $\Delta H_{calc}$, for the selenide salts of GaAl$_{12}^5$ and AlAl$_{12}^7$, are $-23075.02 \pm 61.68$ and $-23334.18 \pm 60.38$ kJ/mol, respectively, supplanting previous values. We compare structural relationships to both experimental and calculated energies to identify the driving forces that control these substitutions and stability, and establish that tetrahedral M-O bond lengths are closely related to the strain and stability of the structure. We show that substitution depends on the size and valence of the heterometal through energetics, and we extend our thermodynamic and structural relationships to other not yet synthesized MAI$_2$ clusters (M = Si$^{IV}$, Fe$^{III}$, Be$^{II}$, Mg$^{II}$, or Zn$^{II}$).

**Keywords:** Thermodynamics, calorimetry, DFT, e-Keggin, aluminum hydroxide, Al$_3$O atoms (Rustad et al. 2004). This partly detached intermediate accepts addition of an isotopically distinct solvent oxygen to the undercoordinated metal before condensing back into the stable form (Rustad and Casey 2012). The extent to which these intermediates form is extraordinarily sensitive to heteroatom substitutions in the inert core of the stable molecule, well away from the sites of oxygen-isotope exchange. By suppressing or enhancing the metastable equilibrium, these single-atom substitutions exert a disproportionate influence over the kinetics of isotope-exchange reactions throughout the structure (Rustad et al. 2004). This idea has been extended to other classes of oxide clusters (Rustad and Casey 2012) and the authors argue from them that it is ensembles of metastable intermediates, and not hypothetical transition states, that control rates of both isotope-exchanges and dissociations at the solution-oxide interface.

**INTRODUCTION**

Geochemists are intensely interested in understanding the ligand and electron exchange reactions affecting minerals in soil and water. These minerals are often oxide and hydroxide phases of iron and aluminum and have dimensions of a few nanometers to micrometers. These materials are in chemical communication with the adjacent aqueous solutions and provide a key pathway for detoxifying natural waters (Furrer et al. 2002; Stewart et al. 2009). Similar oxides are important in materials science, with applications largely in catalysis. One approach to understanding mineral oxide reactions is to employ large metal hydroxide ions as experimental models and then probe near-elementary reactions via molecular spectroscopies to discover general rules describing reactivity (Casey and Rustad 2007). A good example is provided by the aluminum hydroxide ions in the e-Keggin structure (Fig. 1). These ions expose to solution some of the same aluminum-oxygen coordination chemistries that are found in soil minerals. Such ions are much better constrained for experiments than a colloidal suspension of solids where the surface structures are incompletely known. Correspondingly, experiments on the ions have identified general controls of isotope-exchange kinetics that undoubtedly affect larger oxide structures as well. For example, oxygen-isotope exchange into bridging O atoms in these large aluminum hydroxide ions proceeds via metastable structures that form by partial detachment of metal atoms from deeper structural

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* E-mail: anavrotsky@ucdavis.edu