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Energetics of heterometal substitution in ε-Keggin $[MO_4Al_{12}(OH)_{24}(OH_2)_{12}]^{6/7/8+}$ ions

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ABSTRACT

Aluminum hydroxide ions in the ε-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 MAl_{12} ε-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 (ΔH_{soln}) at 28 °C in 5 N HCl for the selenate salts of $GaAl_{12}^{7+}$ and $AlAl_{12}^{7+}$, was measured as –869.71 ± 5.18 and –958.04 ± 2.79 kJ/mol, respectively. The enthalpies of formation from the elements, $\Delta H^{\circ}_{f,el}$, for the selenate salts of $GaAl_{12}^{7+}$ and $AlAl_{12}^{7+}$, are –23 075.02 ± 61.68 and –23 334.18 ± 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 MAl_{12} clusters (M = Si^{IV}, Fe^{III}, Be^{II}, Mg^{II}, or Zn^{II}).

Keywords: Thermodynamics, calorimetry, DFT, ε-Keggin, aluminum hydroxide, Al_{13}