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Synthesis of a gallium-functionalized polyoxovanadate-alkoxide cluster: Toward a general route for heterometal installation

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ABSTRACT.

Incorporating transition metal ions into Lindqvist polyoxovanadate-alkoxide (POV-alkoxide) clusters has been shown to be an effective method for tuning the electronic properties of these molecular assemblies. Herein, we report the synthesis of a gallium-functionalized POV-alkoxide cluster, extending the family of heterometal-functionalized clusters to a metalloid ion. Complex $[\text{V}_5\text{O}_6(\text{OCH}_3)_{12}\text{GaCl}]$ was characterized by infrared and electronic absorption spectroscopies and cyclic voltammetry, revealing the retention of the extensive delocalization upon installation of the $3d^{10}$ ion. The new reaction conditions developed for $[\text{V}_5\text{O}_6(\text{OCH}_3)_{12}\text{GaCl}]$ were shown to successfully generate the iron analogue, $[\text{V}_5\text{O}_6(\text{OCH}_3)_{12}\text{FeCl}]$, from a ferric salt precursor. However, attempts at installing other group 13 ions, e.g. In^{III} , instead produced the cyclic hexavanadate cluster, $[\text{Bu}_4\text{N}][\text{V}_6\text{O}_6(\text{OCH}_3)_{12}\text{Cl}]$.

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