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# Isolation and characterization of the $[\text{Ga}_2\text{Al}_{18}\text{O}_8(\text{OH})_{36}(\text{H}_2\text{O})_{12}]^{8+}$ cluster: Cationic variations on the Wells-Dawson topology

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The structural chemistry of Group 13 polyoxometalates lags far behind related negatively charged transition metal species and limits the development of advanced materials. A novel heterometallic cluster  $[\text{Ga}_2\text{Al}_{18}\text{O}_8(\text{OH})_{36}(\text{H}_2\text{O})_{12}]^{8+}$  ( $\text{Ga}_2\text{Al}_{18}$ ) has been isolated using a supramolecular approach and structurally characterized using single-crystal X-ray diffraction.  $\text{Ga}_2\text{Al}_{18}$  represents the Wells-Dawson structure polycations and variations in the structural topology may be related to the initial stabilization of the Keggin isomer. DFT calculations on the related  $\epsilon$ -Keggins ( $\text{GaAl}_{12}$  and  $\text{Al}_{13}$ ),  $\text{Ga}_2\text{Al}_{18}$ , and theoretical  $\text{Al}_2\text{Al}_{18}$  clusters reveal similar features of electronic structure, suggesting additional heteroatom substitution in other isostructural clusters should be possible.

Polyoxometalate (POM) chemistry represents a diverse array of isolated clusters with a range of sizes, redox properties, photochemical and catalytic functions, and charge distributions.<sup>1</sup> Formally, POMs represent a class of inorganic compounds that are based upon isolated metal oxide clusters with the general formula  $\{\text{MO}_x\}_n$ .<sup>2</sup> A vast majority of these polyoxoanion species are composed of Group 5 and 6 transition metals, but heteropolyanions with  $\text{SiO}_4^{4-}$ ,  $\text{PO}_4^{3-}$ , or  $\text{SO}_4^{2-}$  are also common.<sup>2</sup> Thousands of POMs have been synthesized and structurally characterized, but the most common forms for heteropolyanions include Keggin  $[\text{XM}_{12}\text{O}_{40}]^{n-}$ , Wells-Dawson  $[\text{X}_2\text{M}_{18}\text{O}_{62}]^{n-}$ , and Anderson  $[\text{XM}_6\text{O}_{24}]^{n-}$  structures. The ability to isolate lacunary fragments and the variable composition of this class of compounds creates a wealth of polyoxoanions with tunable chemical and physical properties.<sup>3</sup>

Positively charged POM species are a technologically important, yet less developed class of compounds that currently displays only minimal structural diversity.<sup>4</sup> Group 13 polycations are widely utilized as clarifying agents for water treatment and more recently are being developed as precursors for advanced ceramics and thin-films.<sup>4-5</sup> Only a handful of polyoxocations have been previously reported and

these phases can be classified as either Keggin or “flat” topologies. The  $\delta$ - and  $\epsilon$ -isomers of the Keggin  $[\text{Al}_{13}\text{O}_4\text{OH}_{24}(\text{H}_2\text{O})_{12}]^{7+}$  ( $\text{Al}_{13}$ ) ion have been identified as the major species in partially hydrolysed aqueous solutions and additional condensation reactions form the related  $\text{Al}_{26}$ ,  $\text{Al}_{30}$  and  $\text{Al}_{32}$  species.<sup>4,6</sup> Metal substitution within the Keggin clusters has only been documented for the  $\epsilon$ -form  $[\text{MAl}_{12}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+/8+}$ ,  $M = \text{Ga}, \text{Ge}$  ( $\text{GaAl}_{12}$ ,  $\text{GeAl}_{12}$ ).<sup>7</sup> “Flat” Al (III) and mixed In(III)/Ga(III) clusters with similarities to the Anderson topology have also been synthesized and identified as an important species in aqueous solutions during electrochemical hydrolysis.<sup>5</sup> Deviations from these two structural topologies for polycation are rare and demonstrate the lack of knowledge for this class of POM.

Difficulties in the isolation of polycations of the Group 13 metals can be linked to low solubility and the tendency of these elements to undergo additional hydrolysis reactions and condense to form solid amorphous phases. We have recently developed a supramolecular approach to the crystallization of polycations that has led to the isolation of several Al(III) Keggin-type species.<sup>6</sup> Herein, we report the  $[\text{Ga}_2\text{Al}_{18}\text{O}_8(\text{OH})_{36}(\text{H}_2\text{O})_{12}]^{8+}$  ( $\text{Ga}_2\text{Al}_{18}$ ) cluster, which represents a novel structure motif that has not been previously reported for the polyoxometalate class of compounds.

$\text{Ga}_2\text{Al}_{18}$  was synthesized by heating a partially hydrolysed aqueous solution with a Ga/Al ratio of 1:2 at 80 °C for 24 hours in a hydrothermal vessel. The resulting solution was cooled, transferred to a glass vial, and 2,7 Naphthalene disulfonate (2,7-NDS) was added as the co-crystallization agent. After three weeks of room-temperature evaporation, crystalline material formed on the bottom of the vial and the structure was characterized using single-crystal X-ray diffraction.

Each  $\text{Ga}_2\text{Al}_{18}$  cluster contains one crystallographically unique, tetrahedrally coordinated Ga(III) cation with Ga-O bond-lengths ranging from 1.858(3) to 1.898(3) Å (Fig. 1). Nine distinct Al(III) cations are octahedrally coordinated by shared oxo, hydroxo, or terminal water groups with an average bond distance of 1.896(3) Å. Elongation of the Al3-O2 and Al2-O14

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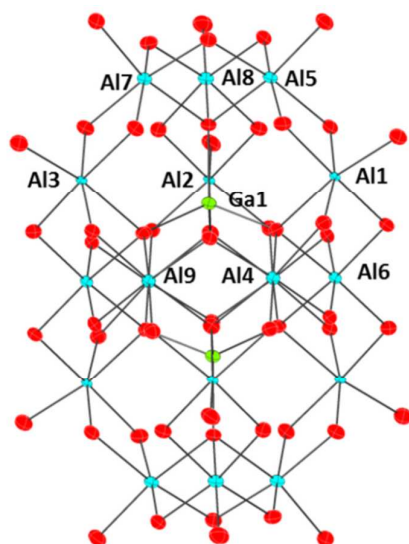
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Electronic Supplementary Information (ESI) available: Additional synthetic and characterization details, bond distance and valence Tables, CIF file, computational methods details, benchmarking, and additional computational results. See DOI: 10.1039/x0xx00000x

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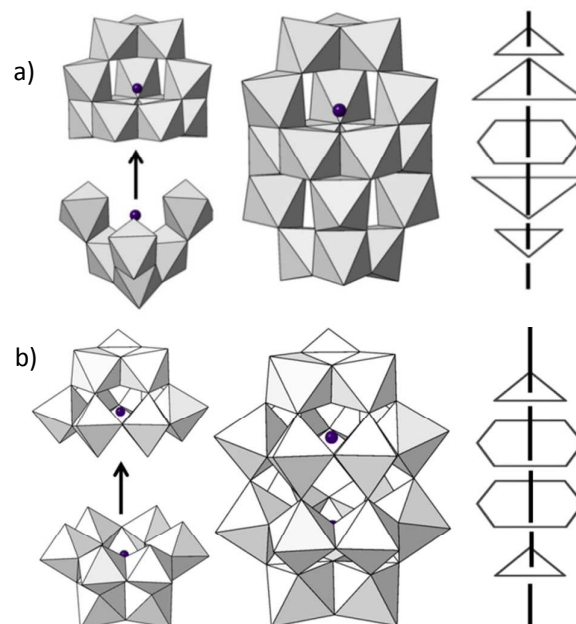
**FIGURE 1.** The  $\text{Ga}_2\text{Al}_{18}$  polycation contains two central tetrahedrally coordinated Ga(III) cations surrounded by Al(III) octahedra to form the  $[\text{Ga}_2\text{Al}_{18}\text{O}_8(\text{OH})_{36}(\text{H}_2\text{O})_{12}]^{8+}$  molecular unit. The Ga, Al, and O atoms are depicted as green, blue, and red thermal ellipsoids, respectively

bond lengths are observed at 2.087(3) and 2.060(3) Å, respectively, which are the result of a slight mismatch in the dimensions of the inner cavity and the  $\text{GaO}_4$  tetrahedron. The observed distances are similar to those reported in  $\text{GaAl}_{12}$ , although smaller distortions are observed for the Al-O bonds within the Keggin cluster.<sup>7</sup>

The  $\text{Ga}_2\text{Al}_{18}$  polycation is composed of a complete  $\epsilon$ -Keggin cluster linked to a lacunary fragment (Figure 2a). A centrally-located  $\text{GaO}_4$  tetrahedron is surrounded by octahedrally coordinated Al atoms that are arranged into four sets of  $[\text{Al}_3(\mu_2\text{-OH})_6(\text{H}_2\text{O})_3]$  trimers to form the  $\epsilon$ -Keggin cluster. Isomeric variations of the Keggin clusters are delineated by the orientation of each trimer and in the  $\epsilon$ -form these units are linked through edge sharing between the octahedrally coordinated Al(III) sites. The lacunary  $\epsilon$ -Keggin fragment consists of one  $[\text{Al}_3(\mu_2\text{-OH})_6(\text{H}_2\text{O})_3]$  trimer and three additional edge-sharing Al(III) octahedra bonded on the exterior edges, resulting in the formation of a hexameric unit. A tetrahedrally coordinated Ga(III) cation is nestled within the bowl-shaped fragment and becomes encapsulated in the  $\text{Ga}_2\text{Al}_{18}$  cluster when the individual components are joined through shared  $\mu_2$ -OH groups.

Bond valence analysis of the diffraction data indicated that the overall molecular formula of the cluster is  $[\text{Ga}_2\text{Al}_{18}\text{O}_8(\text{OH})_{36}(\text{H}_2\text{O})_{12}]^{8+}$ . Naphthalene disulfonate anions were added as a co-crystallization agent and have been utilized successfully in the past to isolate novel polynuclear clusters because of favourable interactions with the sulfonate functional groups and the additional intermolecular forces ( $\pi$ - $\pi$  and H-bonding).<sup>6</sup> Solvent molecules are also present in the interstitial regions, leading the overall formation of  $[\text{Ga}_2\text{Al}_{18}\text{O}_8(\text{OH})_{36}(\text{H}_2\text{O})_{12}](2,7\text{-NDS})_4(\text{H}_2\text{O})_{30.5}$ .

The  $\text{Ga}_2\text{Al}_{18}$  cluster contains a similar metal ratio as the commonly observed Wells-Dawson structure  $[\text{X}_2\text{M}_{18}\text{O}_{62}]^{n-}$ , but the structural topology is different from the negatively charged POM species. Wells-Dawson clusters are composed of two  $\alpha$ -



**FIGURE 2.** (a) The  $\text{Ga}_2\text{Al}_{18}$  cluster is created from the combination of complete and partial  $\epsilon$ -Keggin molecules. (b) The Wells-Dawson  $[\text{X}_2\text{M}_{18}\text{O}_{62}]^{n-}$  cluster is formed from two lacunary  $\alpha$ -Keggin molecule. The wire diagram depicts the positioning of the octahedrally coordinated metal atoms within the exterior of the cluster and highlights the topographic variations between the two clusters.

Keggin fragments (Fig 2b), which represents the opposite end of the spectrum (all shared vertices) from the  $\epsilon$ -form (all shared edges).<sup>2</sup> Isomeric forms have also previously been reported for the Wells-Dawson structure, where the  $\alpha$  and  $\beta$ -forms vary based upon a  $60^\circ$  rotation of one of the capping trimeric units.<sup>8</sup> Previous DFT calculations performed on W(VI) and Mo(VI) Wells-Dawson clusters indicate that the  $\alpha$ -isomers are slightly more stable than the corresponding  $\beta$ -forms.<sup>9</sup>

Current and previously reported crystallization studies suggest that polyanions and polycations within the heterometallic POMs will form the isomeric end-members for Keggin-type molecules and related species. For polyoxoanions, the  $\alpha$ - and  $\beta$ -forms commonly occur and theoretical studies indicate that the kinetic and thermal stability of the  $\beta$ -isomer is dependent on the identity of the heteroatom.<sup>10</sup> In the fully oxidized  $[\text{XM}_{12}\text{O}_{40}]^{n-}$  cluster, DFT calculations determined that stabilization of the  $\beta$ -isomer occurs in the order  $\text{Al(III)} > \text{Si(IV)} > \text{P(V)}$  and  $\text{Ga(III)} > \text{Ge(IV)} > \text{As(V)}$  for  $\text{M} = \text{W}$  and  $\text{Mo}$  respectively.<sup>10</sup> The thermodynamic stabilities of the pure Al(III) and related heterometallic clusters with the  $\epsilon$ -Keggin topology have been delineated experimentally<sup>11</sup> and related DFT calculations have been performed by Reusser et al. on hypothetical  $[\text{XO}_4\text{Al}_2\text{OH}_2\text{H}_2(\text{H}_2\text{O})_{12}]^{6/7/8+}$  clusters ( $\text{X} = \text{Zn(II)}$ ,  $\text{Mg(II)}$ ,  $\text{Be(II)}$ ,  $\text{Fe(III)}$ ,  $\text{Si(IV)}$ ).<sup>12</sup> Results of this study found that the valence and size of the substituting heteroatom influenced the stability of the  $\epsilon$ -Keggin in the order  $\text{Zn(II)} > \text{Mg(II)} > \text{Be(II)} > \text{Ga(III)} > \text{Fe(III)} > \text{Al(III)} > \text{Ge(IV)} > \text{Si(IV)}$ .<sup>12</sup>

To obtain an understanding of the electronic structure of the  $\text{Ga}_2\text{Al}_{18}$  cluster and its dependence on the identity of the central tetrahedral atom, periodic DFT calculations were carried out using the DMol<sup>3</sup> package developed by Delley.<sup>13</sup> The cluster was modelled in the experimentally determined

triclinic cell geometry at fixed lattice parameters, but with full optimization of the atomic coordinates to a force tolerance of 0.0020 eV/Å. An additional simplification made to the model system was to omit the 2,7-NDS and instead model sulfate in place of the sulfonate groups, as done in our previous study.<sup>6b</sup> The resulting model cell has a stoichiometry of  $[\text{Ga}_2\text{Al}_{18}\text{O}_8(\text{OH})_{36}(\text{H}_2\text{O})_{12}](\text{SO}_4)_4(\text{H}_2\text{O})_{32}$ . For comparison, we also model the cluster with Al(III) substituted for Ga(III), and refer to this analogue as  $\text{Al}_2\text{Al}_{18}$ . The resulting Ga-O bond distances overlap with the range of values in the experimental structure with individual distances, varying by up to 2.15%. In the  $\text{Al}_2\text{Al}_{18}$  structure, the tetrahedral Al-O distances range from 1.829 to 1.860 Å. Further details of both model cluster geometries are given in the supplemental information section.

The model cluster electronic structure is analysed by comparing Mulliken partial charge information and projected density of states (PDOS), which gives an atom-by-atom, state-by-state decomposition of the total charge density. The charge analysis yields values of 1.39 and 1.41 e for the tetrahedral Ga and Al, respectively. The greater extent of ionization of Al is also reflected in the partial charge values of the oxygen atoms bound to the tetrahedral cations (-0.96 e in  $\text{Ga}_2\text{Al}_{18}$  and -0.98 e in  $\text{Al}_2\text{Al}_{18}$ ). The PDOS of the two cluster models are shown in Figure 3 and demonstrates that the salient features are similar in both. Localized Ga(Al) *s* and *O p* PDOS intensity at common energy values, indicative of covalent interaction, is noted near 7.2 and 5.2 eV below the Fermi level, while broad Ga(Al) *p* and *O p* overlap is seen in the range of -1 to -5 eV. For both cations, the *d* states show similar intensity to the *p* states, indicative of hypervalency.

For comparison, the electronic structure of the  $\epsilon$ -Keggin  $\text{GaAl}_{12}$  and  $\text{Al}_{13}$  was also calculated. As reported in the supplemental information, the valence PDOS of the Keggin structures are strikingly similar both to each other and to that of  $\text{Ga}_2\text{Al}_{18}$  and  $\text{Al}_2\text{Al}_{18}$ . We interpret the similar electronic fingerprint of the two categories of cluster geometries with heteroatom substitutions to be indicative that there is no unique stabilization provided by the heteroatom in either the  $\text{GaAl}_{12}$  or  $\text{Ga}_2\text{Al}_{18}$  cluster. Therefore, substitution of the central

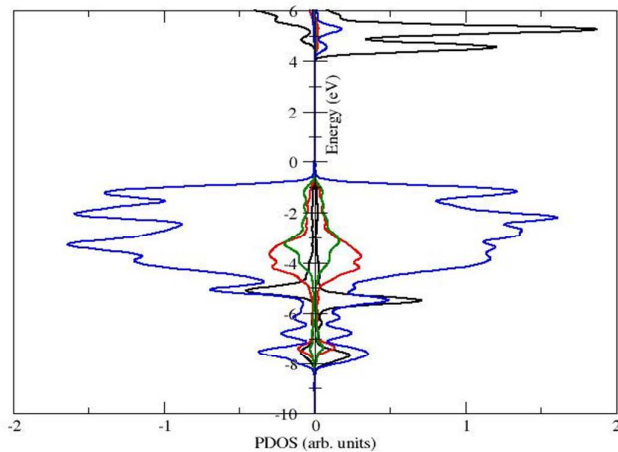


FIGURE 3. DFT calculated PDOS of  $\text{Ga}_2\text{Al}_{18}$  and the theoretical  $\text{Al}_2\text{Al}_{18}$  analogue. The PDOS of  $\text{Al}_2\text{Al}_{18}$  are plotted as negative values while those of  $\text{Ga}_2\text{Al}_{18}$  are shown as positive. The Fermi level is set to  $\gamma=0$ . In each graph the tetrahedral metal-*s*, *p*, and *d* projections are shown in black, red, and green, respectively, while the *O-p* projection is shown in blue.

tetrahedral sites should be thermodynamically amenable for the formation of the related  $\text{X}_2\text{Al}_{18}$  ( $\text{X} = \text{Ge(IV)}, \text{Al(III)}$ ) clusters. Our comparative analysis of cluster electronic structure yields results that are not aligned with other considerations of the Wells-Dawson cluster,<sup>9-10</sup> motivating additional combined experimental and theoretical investigations with a range of metal substitutions.

The propensity of the cationic and anionic POMs to form the end-members of the Keggin isomeric range suggests that different topologies will be observed in related lacunary clusters. While polyoxoanion clusters have been extensively explored, additional studies are necessary on related Group 13 polycations to delineate the energetics along the isomeric series. Understanding the relationships between the subtle structural changes and the related energetics and reactivities of these clusters can provide advances in the basic understanding of structure-function relationships and the use of Group 13 POMs in advanced applications.

## Notes and references

† Crystal data:  $\text{C}_{40}\text{H}_{154}\text{O}_{111}\text{S}_8\text{Al}_{18}\text{Ga}_2$ , Triclinic *P*-1,  $a = 10.0721(7)$  Å,  $b = 16.7628(11)$  Å,  $c = 17.7945(12)$  Å,  $\alpha = 90.852(2)^\circ$ ,  $\beta = 99.861(2)^\circ$ ,  $\gamma = 101.175(2)^\circ$ ,  $V = 2900.3(3)$  Å<sup>3</sup>,  $Z = 1$ , 64071 reflections collected, 10188 unique,  $F(000) = 1680$ ,  $S = 1.031$ . Final  $R_1$  values were 0.0462 ( $I > 2\sigma(I)$ ) and 0.0757 (all data). CCDC 1058796. SEM acknowledges financial support from the National Science Foundation (CHE-1254127) and the use of computational resources from University of Iowa High Performance Computing. We thank Fu Chen, Santhana Velupillai, and Lynn Teesch for NMR and ESI-MS support.

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