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The energetics of isomerisation in Keggin-series aluminate cations†

C. André Ohlin,*[a] James R. Rustad[b] and William H. Casey[c,d]

Electronic-structure calculations show that the ε-isomer of the polyoxoaluminate ion in the Keggin structure $[AlO_4\text{-}(Al(OH)_2\text{-}(H_2O))_{12}]^{7+}$ is the thermodynamically favoured one. Direct inter-conversion between the ε- and δ-isomers *via* cap rotation has a prohibitively high energy barrier *in vacuo*, suggesting that isomeri-sation in solution either proceeds *via* a dissolution–precipitation pathway, or that solvation and/or coordination to counterions reduces the barrier significantly. The implications for the formation of the $[Al_2O_8Al_{28}(OH)_{56}(H_2O)_{26}]^{18+}$ ion are discussed.

Hydrolysis of aluminum in water results in an array of oligo-mers.[1] Most conspicuous of these are isomers of the Baker–Figgis–Keggin series having the stoichiometry $[AlO_4\text{-}(Al(OH)_2(H_2O))_{12}]^{7+}$ (ε-Al_{13}),[2,3] but very large oligomers form as well, such as the $[Al_2O_8Al_{28}(OH)_{56}(H_2O)_{26}]^{18+}$ (Al_{30}) polyoxo-aluminate cluster.[4,5] Out of the five possible Baker–Figgis type isomers of the Al_{13} cluster (see Fig. 1),[6] the ε-isomer is the easiest to synthesize under ambient conditions and has fur-thermore been detected in soils. Other isomers have been syn-thesized only relatively recently. The δ-isomer was isolated as recently as 2000 [4] and the γ-isomer was isolated just last year.[7] The α-isomer has yet to be synthesized at benchtop tempera-tures but is found in the mineral Zunyite, which is formed under hydrothermal conditions, and contains silicate bonds at a μ_3-oxygen site in one of the trimeric groups. The β-Al_{13} isomer has never been observed experimentally.

Ageing of solutions containing Al_{13} leads to formation of the larger Al_{30} cluster, which consists of two δ-Al_{13} isomers

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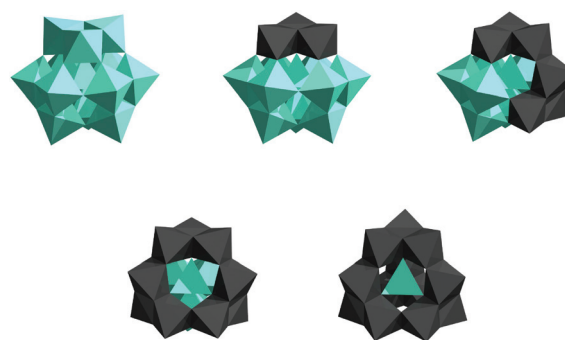[d]*Department of Geology, University of California, One Shields Avenue, Davis, CA, USA*

Fig. 1 Baker–Figgis isomers of the Keggin ion. From left to right and top to bottom: α, β, γ, δ and ε isomers. The rotated triads relative to the α isomer are indicated in grey. Note how the aluminium octahedra become increasingly edge-sharing instead of corner-sharing through the series.

joined through a flat aluminate tetramer.[4,5,8] The formation of this Al_{30} cluster is accompanied by consumption of the Al_{13} Keggin ions,[4,9] in some cases over 11 years.[10]

Taulelle suggested that there must exist a coupled equili-brium between the ε- and δ-isomers, with the latter isomer being key to formation of the Al_{30}.[11] The conclusion was based largely on ageing and ^{27}Al-NMR studies, and no energetic information was derived in their study. The idea, however, invites questions about whether the predominance of the ε-isomer is due to thermodynamic or kinetic control.

In this Communication we begin to assign energies for the various step reactions and in particular compare the relative energetics of the ε- and δ-Al_{13} isomers and their interconver-sions through a series of electronic-structure calculations, including a forced cap rotation of a structural trimeric group that defines the various isomers. Because isomerisation is an essential step in the reactions that lead to formation of the largest polyoxoaluminate cluster isolated, Al_{30}, these calcu-lations provide insight into the dynamics of aluminate clusters and aluminate minerals. We limit our discussion to either *in vacuo* calculations or implicit solvation models, which are

the most accessible levels of theory for treating such large clusters. See ESI† for full computational details.

The relative gas-phase energies ($\Delta\varepsilon$) of the different Baker–Figgis isomers were calculated using density functional theory, and span a range of 10–12 kcal mol^{-1} using the 6-31+G(d,p) basis set, and 14–17 kcal mol^{-1} at the 6-311++G(2d,2p) level depending on the exchange–correlation functional, with the different ranges being expected due to the variational principle. Regardless of the basis set or the exchange–correlation functional, the same stability trend is seen, with $\varepsilon > \delta > \alpha > \gamma$ (see Fig. 2). The effect of the exchange–correlation functional is quite small, and becomes noticeable only when comparing the energies obtained using B3PW91 and X3LYP with those of PBE0 for the ε-isomer. This theoretical result accords with experimental observations in which the ε-isomer is the major product under ambient conditions and readily synthesized, and with the δ-isomer appearing as a minor species, and the other isomers either not having been isolated or only having been isolated under more extreme conditions such as those detailed recently where the γ-isomer was synthesized in a saturated Ca(OH)$_2$:glycine mixture.[7] Clearly strong solvation and coordination interactions, or both, are needed to select isomers.

The stability trend when accounting for solvation using the polarizable continuum model (PCM) by Tomasi *et al.*[12] was also investigated using the default parameters for water in G09. The absolute difference, ε_{solv}, between the electronic energy in the absence, ε_0, and presence, ε_0^{PCM}, of the polarizable continuum is highly sensitive to the structure, and changes by several kcal mol^{-1} depending on the basis set. For example, at B3PW91/6-31+G(d,p) and B3PW91/6-311++G(2d,2p), ε_{solv} is 1249.9 and 1254.3 kcal mol^{-1}, respectively. On the other hand, the relative difference, $(\varepsilon_0^{isomer} - \varepsilon_0^{\alpha}) - (\varepsilon_0^{isomer} - \varepsilon_0^{PCM,\alpha})$, varies only by 1.2 kcal mol^{-1} or less (see Fig. 3). The consequence is that at *e.g.* B3PW91/6-31+G(d,p) the α-isomer is 8 kcal mol^{-1} more stable than the ε one, while at B3PW91/6-311++G(2d,2p) they are of similar energies. Note
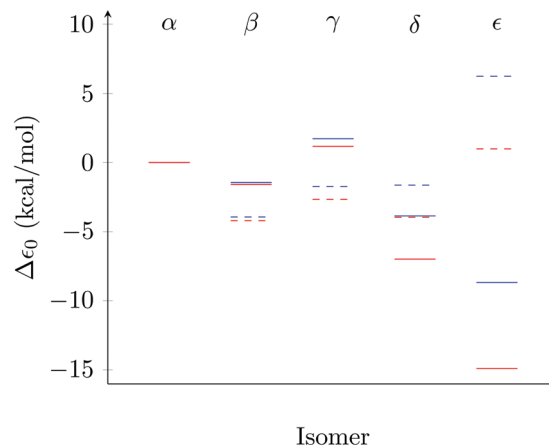
Fig. 3 Gas phase (solid) $\Delta\varepsilon$, and with implicit solvation using PCM (dashed) for B3PW91 with the 6-31+G(d,p) (blue) and 6-311++G(2d,2p) (red) basis sets. All energies are given relative to the energy of the α isomer for each method.

that in the present case this is not due to the PCM model benefiting from the larger basis set, but rather is due to the variational principle affecting the gas phase electronic energy of the molecules. An unfortunate effect of this is that while the observed qualitative gas phase stability trends are insensitive to the size of the basis set, once an implicit solvation model is applied the trend will become quite sensitive to the size of the basis set. Note also that implicit solvation models generally are highly inaccurate for ionic species, with mean errors for organic monovalent cationic species found to be 6–11 kcal mol^{-1} in one study which used PCM.[13] The errors are likely much more severe for large polyvalent ions such as Al$_{13}$. In addition, implicit solvation models do not account for specific interactions, such as hydrogen bonding, which are significant for poly-hydroxy poly-aqua ions such as Al$_{13}$. We conclude that it is thus probably not advisable to use purely implicit solvation models when evaluating the energetics of large polymeric metal-oxide ions.

Baker–Figgis–Keggin-type ions are not limited to the group 13 polyoxocations, but include heteropolyoxotungstate and -molybdate anions of the form $[XM_{12}O_{40}]^{n-}$ (M = Mo(VI), W(VI); X is a tetrahedral centre such as Al(III), Si(IV) or P(V)) as well. In the case of these highly negatively charged ions the most stable structure both experimentally and computationally is the α-isomer.[14–16] It has been suggested that this is due to the M(VI)–M(VI) repulsion between edge-sharing octahedra destabilising the structure.[17] Al(III) has both a smaller total charge and ionic radius than *e.g.* W(VI) (68 *vs.* 74 pm),[18] which would lead to a reduced repulsive destabilisation.

However, the stability order of the isomers of the reduced Keggin polyoxothiometalate $[MoO_4Mo_{12}S_{12}(OH)_{12}]^{2-}$ was found computationally to be $\varepsilon > \delta > \gamma > \beta > \alpha$.[19] It was suggested that Mo(V)–Mo(V) bond formation between edge-sharing octahedra caused the lower energies of the γ, δ and ε-isomers relative to the α and β ones. A similar effect was found computationally for the step-wise reduction of
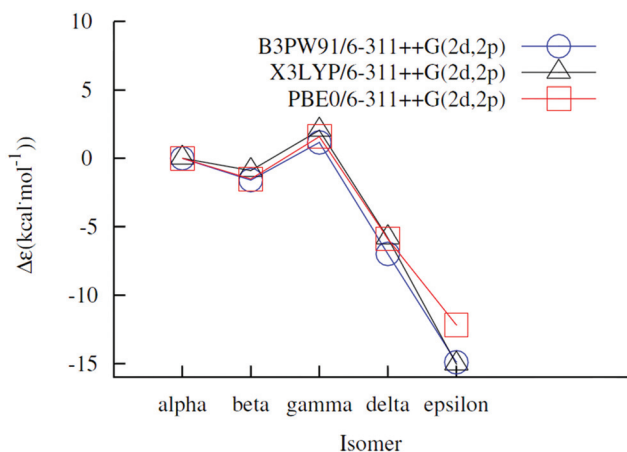

Fig. 2 Gas phase energies ($\Delta\varepsilon$) of the different isomers for different exchange–correlation functionals using the 6-311++G(2d,2p) basis set. All energies are given relative to the α-Al$_{13}$ isomer for each method.

$[PW_{12}O_{40}]^{3-}$, in which the β- and γ-isomers are becoming progressively more stable relative to the α-isomer which was attributed to the relative energies and degeneracy of the LUMO orbitals.[16] The degree of covalency in the group 6 Keggin polyoxoanions, however, is expected to be much larger than in the Al(III)-oxyhydroxide ions which have no d–p hybridization to give axial 'yl' oxygens.

An analysis of the Al–Al distances in the different isomers shows that there is a correlation, although weak, between the presence of very short distances and high energies (see Fig. 4) in the γ-, δ-, and ε-isomers. The γ-isomer, which is the least stable, has four Al–Al distances shorter than 0.291 nm, while the δ-isomer has two, and the ε-isomer has none. This suggests that simple Coulombic repulsion may partially account for the relative stabilities of the γ-, δ- and ε-isomers. It does not, however, explain the relative stabilities of the α-, β- and ε-isomers. Also note that the β-isomer has two Al–Al distances shorter than 0.291 nm, yet is marginally more stable than the α-isomer. Introducing one instance of edge-sharing thus lowers the energy enough to compensate for the Coulombic repulsion.

We have also calculated the electronic energy requirements of the direct interconversion between the ε- and δ-isomers. The nudged elastic band (NEB) approach is a chain-of-states method for finding minimum energy paths.[20] Briefly, a reaction trajectory was generated by interpolating the atomic positions between the geometries in the ε- and δ-isomers, and selecting different structures on this trajectory. These structures were then optimised to find a minimum energy pathway. This approach thus does not simply look for an isolated transition state, but finds a series of intermediate structures that make up a reaction trajectory. The NEB method yielded a trajectory with an approximate barrier of rotation of 85 kcal mol^{-1} (>355 kJ mol^{-1}), which corresponds to a rate of reaction of ca. 4×10^{-50} s^{-1} (see Fig. 5). Hence, isomerisation via simple cap rotation is not a viable pathway, at least under the
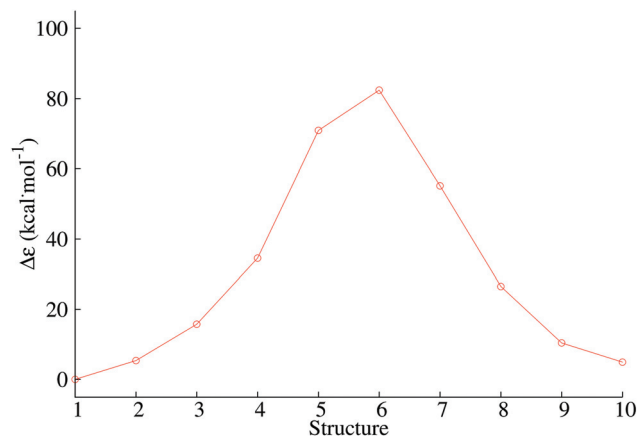

Fig. 5 NEB-derived gas-phase energy profile for the conversion of the ε-isomer to the δ one through cap rotation. Structure 1 is ε-Al$_{13}$ and structure 10 is δ-Al$_{13}$; energies are given relative to that of the ε-isomer. The energy barrier is ca. 85 kcal mol^{-1}, suggesting that this is not a major pathway under ambient conditions.

conditions of these calculations (no explicit waters, no counterions).

Ageing of solutions of ε-Al$_{13}$ leads to the formation of Al$_{30}$, which consists of two δ-Al$_{13}$ units connected by a tetra-aluminate unit.[4] In contrast, ageing of the isostructural and isoelectronic ε-$[GaO_4(Al(OH)_2 (H_2O))_{12}]^{7+}$ (GaAl$_{12}$) ion does not yield either Al$_{30}$ or Ga$_2$Al$_{28}$ clusters.[9] This is in accordance with our observation that the rotational barrier is too high for cap rotation to be a viable isomerisation pathway, and that isomerisation instead proceeds via full or partial decomposition of the Keggin ion. For GaAl$_{12}$, which is thermodynamically more stable than Al$_{13}$ as a solution of Ga(III) hydrolysis ions and n-Al$_{13}$ converts spontaneously to a solution of Al(III) hydrolysis ions and the ε-GaAl$_{12}$,[9] neither pathway is accessible in simple hydrolysis experiments, suggesting that the central Ga(III)–μ$_4$ oxo bond is strengthened to either prevent dissociation,[21] or cap rotation.

Sun et al. have argued for a sulfate-mediated pathway for the ε- to δ-Al$_{13}$ isomerisation based on strong interactions between sulfate ions and Al$_{13}$ found in crystal structures. In this model the isomerisation proceeds via direct rotation of an Al$_3$ triad and the rotating triad is capped by a sulfate ion.[22] This pathway is supported by the observation by Rowsell et al. that the crystal structure of the sodium salt of δ-Al$_{13}$ contains one sodium ion strongly coordinated to an Al$_3$ triad, and which they suggested may play a role in the ε to δ transformation.[4]

If the sole role of the sulfate and sodium ions is to lower the barrier of rotation then this may be a feasible route for the synthesis of Ga$_2$Al$_{28}$ from ε-GaAl$_{12}$. On the other hand, if the formation of the δ-isomer proceeds via dissociation of the ε-isomer, then the higher thermodynamic stability of ε-GaAl$_{12}$ relative to ε-Al$_{13}$ will prevent either Al$_{30}$ or Ga$_2$Al$_{28}$ from forming. To date no Al$_{30}$ or Ga$_2$Al$_{28}$ clusters have been observed as products from ageing of GaAl$_{12}$.
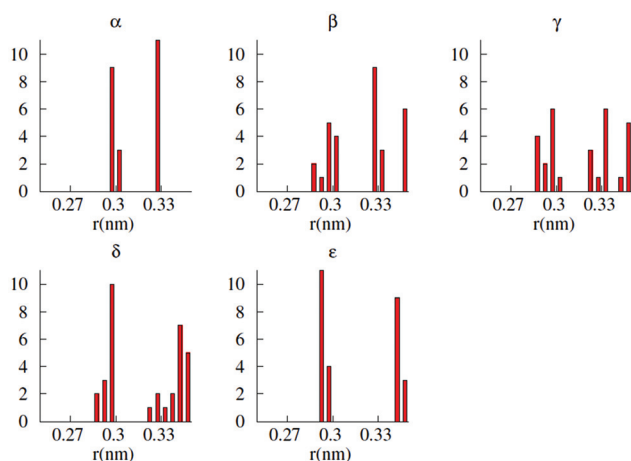

Fig. 4 Distribution of Al–Al distances shorter than or equal to 0.35 nm in the different isomers. A bin width of 5 pm was used. Structures were optimised at the B3PW91/6-311++G(2d,2p) level of theory.

Conclusions

Gas-phase computations at the density functional theory level suggest that the ε-isomer of the Al_{13} cation is the most stable one, followed by the δ-isomer. This trend is in accordance with what is found in speciation studies. Including solvation energies obtained using an implicit solvation model, in contrast, leads to the suggestion that the most stable isomer is the β one, which is the only Baker–Figgis isomer of the Al_{13} cluster never to have been experimentally isolated. This implies that the implicit solvation models can be highly misleading when used to estimate the solvation contribution to the relative energies of polyionic species.

Furthermore, direct rotation of an Al_3 cap to convert the ε-Al_{13} isomer to the δ-isomer is associated with a prohibitively high energy barrier, indicating that isomerisation must proceed *via* a different mechanism. Whether the rotation can be catalysed by sodium and sulfate ions, or whether isomerisation must proceed *via* at least partial decomposition of the Al_{13} cluster is still unresolved.

Acknowledgements

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