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Fluorination of the ε-Keggin Al_{13} polycation

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Fluorination of the Al_{13} polycation in ε-Keggin (Kε–J) conformation, leads to partial substitution of di-μ_2-OH bridges by fluorine and enhances the formation of Al_{30} polycation.

Johansson's ε-Keggin $Al_{13}O_4(OH)_{24}(H_2O)_{12}{}^{7+}$ polycation (Al_{13} Kε–J)[1] remains, since 1960, a keystone in aluminium polycation chemistry. Polycation chemistry develops at a slower pace than polyanion chemistry in terms of increasing the object size, due to the subtler control of M–OH–M bonds compared to the M–O–M bonds of polyanions.[2] Al_{13} Kε–J formation and its subsequent transformations are still unclear.[3]

Al_{13} Kε–J^{7+} (Fig. 1a) is composed of a four-fold coordinated central aluminium, surrounded by four trimers. Al_{13} Kε–J^{7+} contains two inequivalent μ_2-OH bridges: the inter trimers μ_2-OH-iT linkers and the intra trimers μ_2-OH-T linkers. Casey *et al.* measured by ^{17}O NMR the exchange rates of enriched water $^{17}OH_2$ with the different O or OH sites of Al_{13} Kε–J.[4] The solvating water molecules (η-OH_2) are the most labile sites, the oxo-bridges are extremely slow to exchange and the two types of hydroxo-bridges give two different rates of substitution, μ_2-OH-iT being the most labile. When the di-μ_2-OH-iT bridge opens it unlocks the isomerization by trimer rotation of Al_{13} Kε–J into its δ-Keggin forms (Al_{13} Kδ–N and in Al_{30} Kδ–T).[5]

Fluorination of Al_{13} Kε–J may affect oxo and hydroxo groups and therefore modify the isomerization equilibrium of Al_{13}. Fluorides are also known as dissolution agents for bayerite [β-$Al(OH)_3(s)$] and boehmite [γ-AlOOH].[6] The fluorination of Al_{13} Kε–J is studied here by ^{19}F and ^{27}Al NMR and the fluorinated sites assigned. The influence of fluorination of Al_{13} Kε–J μ_2-OH bridges on its further transformation is investigated.

Al_{13} Kε–J is obtained by hydrolysis of an $AlCl_3.6H_2O$ (10 ml, 5 mmol) aqueous solution, by addition of NaOH (1 M, 12.3 ml) at a hydrolysis ratio $h = n_{OH}/n_{Al} = 2.46$, at 90 °C, with strong stirring. The ^{27}Al NMR spectrum exhibits (Fig. 1b) a peak at 63 ppm, the tetrahedral site of Al_{13} Kε–J, and a peak at 0 ppm, the monomer.† All the aluminium present in the sample is observed by ^{27}Al NMR. Fluorination has been achieved in two ways. After formation of Al_{13} Kε–J, the solution is cooled down to room temperature and NaF added to it. The second route uses fluorides during hydrolysis at 90 °C, with a fluoro–hydrolysis ratio $h = n_{(OH + F)}/n_{Al} = 2.46$.

Upon addition of NaF at room temperature, no new peaks appear in the ^{27}Al NMR spectrum, implying no change in the Keggin structure (Fig. 1c). The ^{19}F NMR spectrum (Fig. 2a) exhibits five lines at −157.3 ppm, $AlF(H_2O)_5{}^{2+}$,[7] at −157 ppm, $AlF_2(H_2O)_4{}^{+}$,[7] together with three lines at −148 ppm, −138 ppm and −136 ppm. The two last signals are assigned to μ_2-F-T and μ_2-F-iT bridges in Al_{13} Kε–J. The −148 ppm signal has been reported to be the η-OH_2 substituted as η-F.[8] Actually this signal is the signature of HF. The chemical shift of HF is a function of the pH and varies from about −120 to −160 ppm. Its chemical shift at −148 ppm is consistent with the pH = 4 of these syntheses. HF might substitute η-H_2O sites, producing η-HF sites. This signal is not maintained in the solid state (see later). Therefore, it can not be assigned to η-F that will not disappear from solution to the solid state. After introduction of NaF in water, the build-up of the −138 ppm peak is slower than the −136 ppm one, but both do not seem to vary much after about 15 minutes, a much faster rate for Al_{13} than the $GaAl_{12}$ case.[8] The ^{19}F rate of exchange in $GaAl_{12}$ has been also demonstrated to be slower for μ_2-OH-iT bridges than for μ_2-OH-T bridges in full analogy with their $^{17}OH_2$ counterparts.[4] The −136 ppm signal is a doublet ($J[^1H/^{19}F] = 27$ Hz) that reduces to a singlet when ^1H decoupling is applied during ^{19}F acquisition. The −136 ppm peak is flanked by a smaller line that is not always present depending on the synthesis batch. It does not belong therefore to the same species as the one carrying the doublet. No $J[^1H/^{19}F]$ coupling is observed in fluorination of $GaAl_{12}$. As the chemical shift of the line and its kinetics indicates a di-μ_2-(OH,F)-iT site, the coupling must originate from a tricenter O–H–F interaction in the bridge. Such a tricenter interaction is only permitted if the local geometry, O–F distance and the Al–O–H angle, matches a gain in energy. The experimental answer is that it does for Al_{13} Kε–J, and not for $GaAl_{12}$. A quantum calculation should help to gain more insights about this new fact.

NaF (1 M, 120 μl) has been added to a solution of Al_{13} Kε–J (0.03 M, 2 ml) in a molar ratio $[F^-] : [Al_{13}$ Kε–$J^{7+}]$ of 2 : 1 and

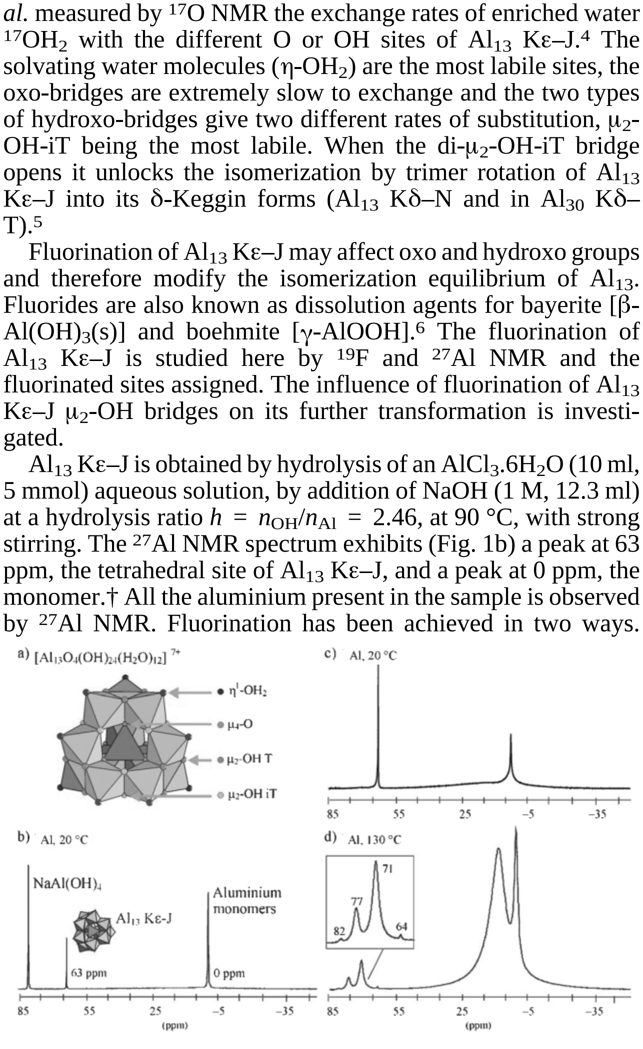

Fig. 1 a) Polyhedral representation of Al_{13} Kε–J^{7+}. b) ^{27}Al NMR spectra of an Al_{13} Kε–J aq. solution, c) with addition of NaF at 20 °C, d) at 130 °C.

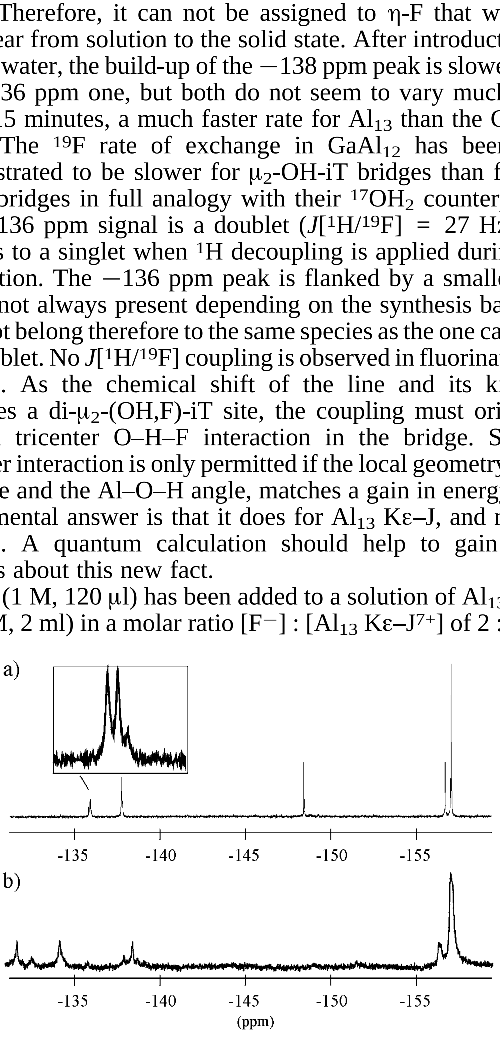

Fig. 2 ^{19}F NMR spectra of a) an Al_{13} Kε–J aqueous solution with addition of NaF and b) after thermal treatment at 120 °C.

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further crystallised by addition of Na_2SO_4 (0.5 M, 10 ml). An XRD structure determination on a single crystal confirms that the compound is fully isostructural to $Na[Al_{13}O_4(OH)_{24}(H_2O)_{12}]$ $(SO_4)_4.xH_2O$.[1] The ^{27}Al MAS NMR of a collection of many small crystals, exhibits a very similar pattern (Fig. 3a) to the spectrum of pure Na[Al_{13} Kε–J] $(SO_4)_4.xH_2O$.[9] However, compared to the original spectrum[9] a loss of the several sharp discontinuities is noticeable. The ^{19}F MAS NMR spectrum of the crystals (Fig. 3b) presents two signals at −132 ppm and −134 ppm, and no other signal, especially no signal close to −148 ppm. Only two fluoride types remain in the fluorinated Keggin, the di-μ_2-(OH,F)-iT and di-μ_2-(OH,F)-T at respectively −136 ppm and −138 ppm. The translation in chemical shifts between solution and crystal stems from the dielectric susceptibility differences between water and the solid. It is noticeable that the di-μ_2-(OH,F)-iT bridge presents an internal O–H–F tricenter interaction revealed by the *J* coupling of 27 Hz. The ratio of inter to intra di-μ_2-(OH,F) bridges is 1 : 1 in solution as well as in the crystal. Therefore, no more than one fluoride is present per di-μ_2-(OH,F) bridge.

When NaF (60 mg, 1.4 mmol) is directly added to NaOH during hydrolysis of the aluminium solution, the solution stays clear. The ^{27}Al spectrum at room temperature exhibits a broad peak at 70 ppm, a very small amount of 63 ppm tetrahedral site of the Al_{13} Kε–J and of the 0 ppm signal of the monomers. At 130 °C, to get a better resolution, the ^{27}Al spectrum is composed by four signals in the AlO_4 chemical shift range, and two in the AlO_6 range. The four AlO_4 sites resonate at 64 ppm, 71 ppm, 77 ppm and 82 ppm (Fig. 1d). Al_{13} Kε–J at 64 ppm and Al_{30} Kδ–T at 71 ppm were unambiguously assigned by NMR and XRD experiments.[9] The two AlO_6 signals at 0 and 10 ppm were assigned respectively to Al monomers and AlO_6 in Keggin shells. As suggested in the literature,[3] the line at 77 ppm could correspond to a different Keggin aluminium polycation as well as the 82 ppm signal, which has, to our knowledge, not yet been observed (pH = 4). Surprisingly, the amount of the 71 ppm site (Al_{30} Kδ–T) and of the monomers at 0 is uncommonly high for a fresh synthesis at $h = 2.46$ and a very low concentration of Al_{13} Kε–J. The addition of fluorides has strongly modified the equilibrium between Al monomers, Al_{13} Kε–J and Al_{30} Kδ–T, in favour of the latter species. Small chemical shift and line width differences are observed for the ^{27}Al NMR signals compared to their usual chemical shifts without fluorine, suggesting slight modifications in the environment of ^{27}Al nuclei. The ^{19}F spectra (not shown) exhibit many sharp peaks, in groups, around −132, −136 and −138 ppm.

In order to compare both “cold” and “hot” fluorination a solution of “cold” fluorination has been progressively heated at 90 °C, 120 °C and let cool down to room temperature. The ^{19}F spectra exhibit lines present in the spectrum of the “hot” fluorination (Fig. 2b), with a loss in resolution, leading to the same groups. Two sets of lines are present in the high frequency range. The first set of lines has chemical shifts at −132.4, −134.6 and −138.3 ppm in a 1 : 1 : 1 ratio. The second set has lines at −136.0 and −138.6 ppm in a 1 : 1 ratio. The second set is identical to the lines observed when F substitute OH of Al_{13} Kε–J. It is noticeable that no line at −148 ppm is present there. The line positions of the mono and difluoro monomers vary dramatically with temperature. When back to room temperature, the first set of three lines is the dominant feature, apart from the monomers (Fig. 2b). The two sharp lines of Al_{13} Kε–J are very small. This is in full agreement with the ^{27}Al spectrum at 130 °C (Fig. 1d). As the dominant signal in ^{27}Al NMR is the 71 ppm of Al_{30} Kδ–T, the three lines of the first set are related to the three types of μ_2-OH in this δ Keggin configuration: inside the trimer, edge sharing and vertex sharing types. Fluorination of Al_{13} Kε–J proceeds therefore through fluorination of di-μ_2-OH bridges followed by further conversion to Al_{30} Kδ–T, fluorinated on its three types of μ_2-OH bridges. Fluoride addition during synthesis at 90 °C produces the same result as a “cold” fluorination followed by further heating at the same temperature, transforming Al_{13} Kε–J into Al_{30} Kδ–T and other Keggin isomers that are not yet all fully identified and assigned.

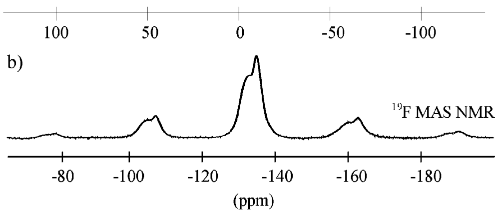

Fig. 3 a) ^{27}Al and b) ^{19}F MAS NMR spectra of partially fluorinated Na[Al_{13} Kε–J]$(SO_4)_4.xH_2O$.

The substitution of di-μ_2-OH bridges by fluorides in Al_{13} Kε–J^{7+} opens a new field of investigation. The addition of fluorides to the Keggin aluminium polycation favours the formation of Al_{30} Kδ–T and other new Keggin isomers. Fluorine may play a role in polycation chemistry comparable to its role in zeolitic materials. The fluorine route may unlock the way for polycations to reach the size of the largest polyanions.

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Notes and references

† *NMR*: ^{27}Al, ^{27}Al MAS and ^{19}F MAS NMR spectra were recorded on a Bruker DSX500 spectrometer, with respectively 130 MHz and 470 MHz resonating frequency. For liquid state experiments, a Bruker NMR probe BBO 10 mm and “hydrothermal” NMR tubes were especially designed to be aluminium free. The ^{27}Al NMR spectra were referenced to $Al(NO_3)_3.9H_2O$ (1 M), at pH = 2 (0 ppm). NaF (−221 ppm *versus* $CFCl_3$) was taken as the ^{19}F MAS NMR secondary reference. ^{27}Al NMR parameters were: repetition delay 500 ms, frequency window 20 kHz, number of scans 2048. ^{27}Al MAS NMR parameters were: repetition delay 1 s, frequency window 125 kHz, number of scans 1024 and spinning rate 14 kHz. The ^{19}F MAS NMR parameters were: repetition delay 15 s, frequency window 90 kHz, number of scans 64 and spinning rate 14 kHz. The liquid state ^{19}F NMR experiment was run on a Bruker ARX400 spectrometer, with 376 MHz resonating frequency. The ^{19}F NMR parameters were: repetition delay 10 s, frequency window 30 kHz and number of scans 64. The spectral analyses were performed with Bruker WIN-NMR and WINFIT[10] software.

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