# Fluorination of the ε-Keggin Al$_{13}$ polycation

**Lionel Allouche and Francis Taulelle**

*RMN et Chimie du Solide, Tectonique Moléculaire du Solide UMR 7140 CNRS, Université Louis Pasteur, 4, rue Blaise Pascal, 67070 Strasbourg Cedex, France. E-mail: taulelle@chimie.u-strasbg.fr*

**Fluorination of the Al$_{13}$ polycation in ε-Keggin (Kε–J) conformation, leads to partial substitution of di-$\mu_2$-OH bridges by fluorine and enhances the formation of Al$_{30}$ polycation.**

Johansson's ε-Keggin Al$_{13}$O$_4$(OH)$_{24}$(H$_2$O)$_{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 $\mu_2$-OH bridges: the inter trimers $\mu_2$-OH-iT linkers and the intra trimers $\mu_2$-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 ($\eta$-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, $\mu_2$-OH-iT being the most labile. When the di-$\mu_2$-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 $\mu_2$-OH bridges on its further transformation is investigated.

Al$_{13}$ Kε–J is obtained by hydrolysis of an AlCl$_3$.6H$_2$O (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.
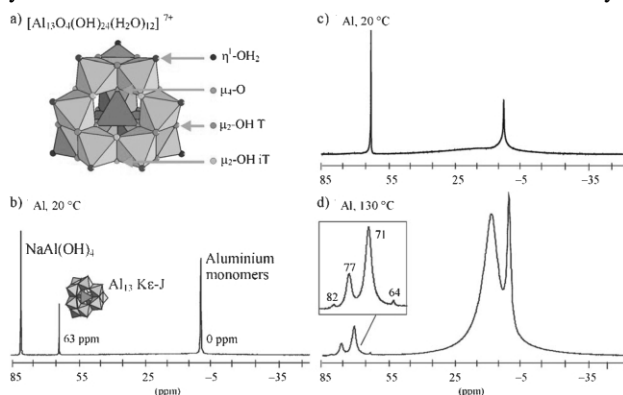
After formation of Al$_{13}$ Kε–J, the solution is cooled down to room temperature and NaF added to it. The second route uses fluorides during hydrolysis at 90 °C, with a fluoro–hydrolysis ratio $h = n_{(OH + F)}/n_{Al} = 2.46$.

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$_2$O)$_5$$^{2+}$,[7] at −157 ppm, AlF$_2$(H$_2$O)$_4$$^+$,[7] together with three lines at −148 ppm, −138 ppm and −136 ppm. The two last signals are assigned to $\mu_2$-F-T and $\mu_2$-F-iT bridges in Al$_{13}$ Kε–J. The −148 ppm signal has been reported to be the $\eta$-OH$_2$ substituted as $\eta$-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 $\eta$-H$_2$O sites, producing $\eta$-HF sites. This signal is not maintained in the solid state (see later). Therefore, it can not be assigned to $\eta$-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 $\mu_2$-OH-iT bridges than for $\mu_2$-OH-T bridges in full analogy with their $^{17}$OH$_2$ counterparts.[4] The −136 ppm signal is a doublet ($J$[$^1$H/$^{19}$F] = 27 Hz) that reduces to a singlet when $^1$H 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 $J$[$^1$H/$^{19}$F] coupling is observed in fluorination of GaAl$_{12}$. As the chemical shift of the line and its kinetics indicates a di-$\mu_2$-(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.
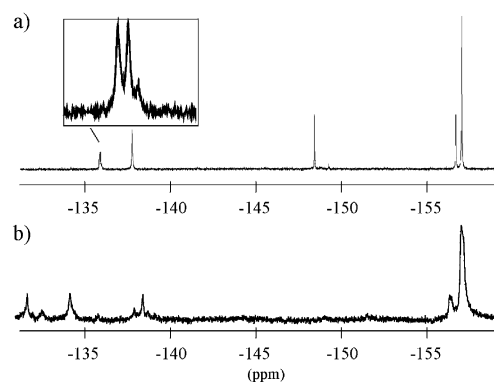


**Fig. 2** $^{19}$F NMR spectra of a) an Al$_{13}$ Kε–J aqueous solution with addition of NaF and b) after thermal treatment at 120 °C.

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-$\mu_2$-(OH,F)-iT and di-$\mu_2$-(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-$\mu_2$-(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-$\mu_2$-(OH,F) bridges is 1 : 1 in solution as well as in the crystal. Therefore, no more than one fluoride is present per di-$\mu_2$-(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 $\mu_2$-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-$\mu_2$-OH bridges followed by further conversion to $Al_{30}$ Kδ–T, fluorinated on its three types of $\mu_2$-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.

The substitution of di-$\mu_2$-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.

## Notes and references

1 G. Johansson, *Acta Chem. Scand.*, 1960, **14**, 771; J. F. Keggin, *Proc. R. Soc. London, Ser. A*, 1934, **144**, 75.

2 A. Müller, *Chem. Commun.*, 2003, **7**, 803.

3 R. C. Turner, *Can. J. Chem.*, 1976, **54**, 1910; W. Akitt and J. and M. Elders, *J. Chem. Soc., Dalton Trans.*, 1988, 1347; J. W. Akitt, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1989, **21**, 1; G. Fu, L. F. Nazar and A. D. Bain, *Chem. Mater.*, 1991, **3**, 602; J. T. Kloprogge, D. Seykens, J. W. Geus and J. B. H. Jansen, *J. Non-Cryst. Solids*, 1992, **142**, 87; D. R. Parker and P. M. Bertsch, *Environ. Sci. Technol.*, 1992, **26**, 908; J. P. Jolivet, M. Henry and J. Livage, *From solution to solid state*, John Wiley & Sons, New York, 2000; P. H. Hsu, *Clays Clay Miner.*, 1997, **45**, 286.

4 W. H. Casey, B. L. Phillips, M. Karlsson, S. Nordin, J. P. Nordin, D. J. Sullivan and S. Neugebauer-Crawford, *Geochim. Cosmochim. Acta*, 2000, **64**, 2951.

5 L. Allouche, C. Gérardin, T. Loiseau, G. Férey and F. Taulelle, *Angew. Chem., Int. Ed.*, 2000, **39**, 511; J. Rowsell and L. F. Nazar, *J. Am. Chem. Soc.*, 2000, **122**(15), 3777.

6 J. P. Nordin, D. J. Sullivan, B. L. Phillips and W. H. Casey, *Geochim. Cosmochim. Acta*, 1999, **63**, 3513.

7 A. Bodor, I. Tóth, I. Bányai, Z. Szabó and G. T. Hefter, *Inorg. Chem.*, 2000, **39**, 2530.

8 P. Yu, A. P. Lee, B. L. Phillips and W. H. Casey, *Geochim. Cosmochim. Acta*, 2003, **67**, 1065.

9 L. Allouche, C. Huguenard and F. Taulelle, *J. Phys. Chem. Solids*, 2001, **62**, 1525.

10 D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calvé, B. Alonso, J. O. Durand, B. Bujoli, Z. Gan and G. Hoatson, *Magn. Reson. Chem.*, 2002, **40**, 70.
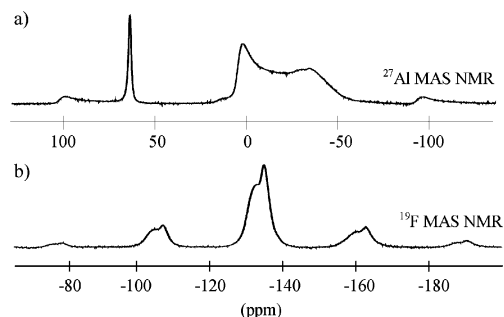
**Fig. 3** a) $^{27}Al$ and b) $^{19}F$ MAS NMR spectra of partially fluorinated $Na[Al_{13}$ Kε–J]$(SO_4)_4.xH_2O$.