# Aluminium-27 Nuclear Magnetic Resonance Studies of Heteropolyanions containing Aluminium as Heteroatom

By **J. W. Akitt** * and **Alan Farthing**, School of Chemistry, University of Leeds, Leeds LS2 9JT

The preparation of $[AlW_{12}O_{40}]^{5-}$ and of $[AlMo_6O_{21}]^{3-}$ has been monitored by $^{27}Al$ n.m.r. spectroscopy. It is possible to distinguish between aluminium in octahedral and tetrahedral environments. The preparation of $[AlW_{12}O_{40}]^{5-}$ gives rise to four species containing aluminium of which one is the desired product, one is probably a protonated form of it, and one may be the 2 : 18 (Al : W) anion.

DURING the course of the present study on the hydrolysis of $Al^{III}$ using $^{27}Al$ n.m.r. spectroscopy [1] it became desirable to extend our knowledge of the range of chemical shifts and linewidths exhibited by the $^{27}Al$ nucleus to confirm whether it was in fact generally possible to differentiate between Al atoms when in tetrahedral or octahedral environments.[2] We decided to investigate the alumino-tungstates and -molybdates whose preparation and structure are known with reasonable certainty and contain aluminium in both types of environment. In addition, the 1:12 (Al:M) anions bear a strong structural resemblance to the ion $[AlO_4Al_{12}(OH)_{24}(OH_2)_{12}]^{7+}$ which is produced during the hydrolysis of $Al^{III}$.[3] Thus we might expect that the central Al of each 1:12 ion would have similar linewidths and chemical shifts, the latter of course being modified by the different charge density on the two ions. The results were expected also to be of interest in their own right and to add to the rapidly accumulating n.m.r. data on the polyanions.[4,5]

## EXPERIMENTAL

The $^{27}Al$ n.m.r. data were obtained as described previously.[1]

The 12-tungstoaluminate [6,7] was prepared as below and the n.m.r. spectra recorded as indicated. Nitric acid (1 mol dm$^{-3}$, 97.2 cm$^3$) was added slowly to $Na_2[WO_4]\cdot 2H_2O$ (28.06 g) dissolved in water (200 cm$^3$), the solution brought to the boil, and $Al[NO_3]_3\cdot 9H_2O$ (5.0 g) in water (250 cm$^3$) added over 20 h. The solution was concentrated, cooled, and eventually filtered. It was further cooled to 0 °C, diethyl ether (150 cm$^3$) and 6 mol dm$^{-3}$ $H_2SO_4$ (200 cm$^3$) were added, and the whole shaken vigorously then allowed to settle. The lower of the three layers containing the complex of the product was separated, washed with dry diethyl ether, run into an equal volume of water, and the ether evaporated. The $^{27}Al$ n.m.r. spectrum of the resulting aqueous solution is shown in Figure 1(*a*). The solution was then evaporated to dryness, baked at 130 °C to convert any metatungstic acid to an insoluble form, and extracted with water to give a solution whose spectrum is shown in Figure 1(*b*). Both spectra show two sharp lines in the low-field region.

Crystals containing predominantly a single component were obtained by crystallising first the potassium salt and then the caesium salt. The former gave a line at 71.7 p.p.m. in the n.m.r. spectrum. Single-crystal *X*-ray analysis showed that the crystals may be isomorphous with $K_5[BW_{12}O_{40}]\cdot 18H_2O$ [8,9] [Hexagonal, space group $P6_222$, with $a = 18.93(2)$, $c = 12.42(2)$ Å]. Chemical assay gave the approximate formula $K_{4\cdot 5}AlW_{12}O_{40}\cdot 13H_2O$. (There is a large uncertainty on the $H_2O$ figure, *ca.* 20%.) The caesium salt gave a line at 71.2 p.p.m. in the n.m.r. spectrum. Assay showed that this salt was probably $Cs_2[H_3AlW_{12}O_{40}]\cdot 9H_2O$ [8.45% Cs (calc. 8.05%); 0.55% $H_2O$ as H (calc. 0.55%)]. The *X*-ray analysis gave a rhombohedral space group $R3c$ or $R\bar{3}c$ with $a = 18.768(10)$ Å and $\alpha = 55.26(4)°$ which suggests that the product may be isomorphous with a series of related salts of which $[Zn(OH_2)_6]_2[SiW_{12}O_{40}]\cdot 15H_2O$ is typical.[8] Overall yield *ca.* 10%.

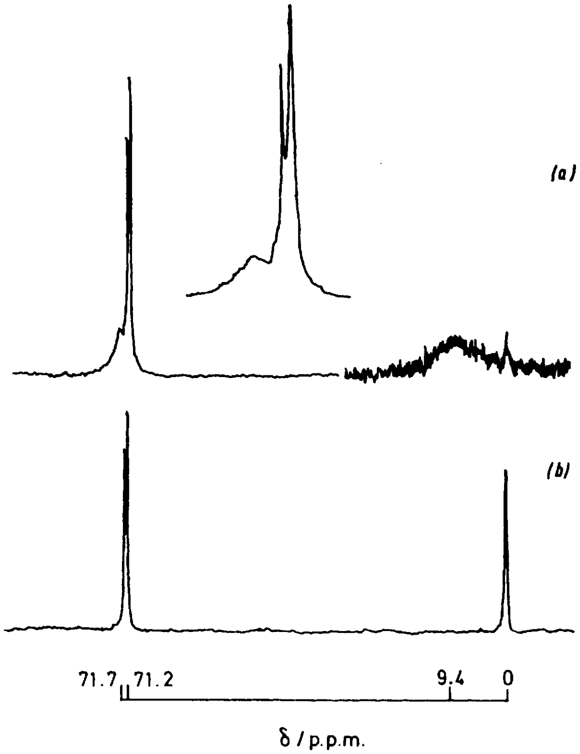

FIGURE 1 The $^{27}Al$ n.m.r. spectra of solutions obtained during the preparation of $[AlW_{12}O_{40}]^{5-}$ before (*a*) and after (*b*) baking. In (*a*) the inset spectrum is horizontally expanded four times

The 6-molybdoaluminate was prepared as the ammonium salt by appropriate modification of the method for the sodium salt.[10] The yield was nearly quantitative. *X*-Ray fluorescence analysis gave Mo/Al = 6±0.1. The $^{27}Al$ n.m.r. spectrum of its solution contained a single resonance at 15.4 p.p.m. with a linewidth of *ca.* 50 Hz.

## DISCUSSION

The $^{27}$Al n.m.r. spectra of the 12-tungstoaluminate solutions indicate that this preparation gives rise to a very complex system. Aluminium exists in at least five different environments, only one of which, giving the line at highest field, corresponds to a known species, $[Al(OH_2)_6]^{3+}$. The two sharp lines at 71.2 and 71.7 p.p.m. are the only resonances that are observed in solutions of the final products. They are situated between the $[Al(OH)_4]^-$ resonance (80 p.p.m.) and the $AlO_4$ resonance (62.5 p.p.m.) in $[AlO_4Al_{12}(OH)_{24}(OH_2)_{12}]^{7+}$ and their unusually small width (8 and 2.5 Hz respectively) points to the aluminium being in a very symmetrical environment. Thus it seems safe to assign these lines to central Al atoms in species based on $[AlW_{12}O_{40}]^{5-}$, with a tetrahedral $AlO_4$ environment. Thus the preparation appears to produce two 1:12 anions which differ slightly in some way. The assays of the two salts indicate that the potassium salt may contain some $H_3O^+$ replacing the $K^+$, while the caesium salt contains only two $Cs^+$ ions and so must include three protons. However, the existence of two $^{27}$Al resonances shows that this difference is manifested in the anion itself. It could be a structural difference although this might lead to distortion of the symmetry around the $AlO_4$ unit and thus to a broadened line. Alternatively, it could indicate protonation of the anion to give a $[H_3AlW_{12}O_{40}]^{2-}$ ion which would presumably retain its symmetry by proton exchange. Equally, a combination of these possibilities may occur: structural change, protonation of the anion, and replacement of $Cs^+$ by $H_3O^+$. Much more detailed information is required before these possibilities can be distinguished.

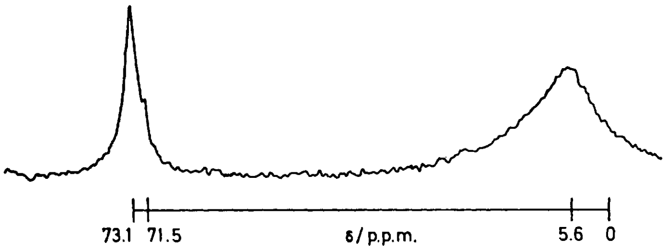

FIGURE 2 The $^{27}$Al n.m.r. spectrum of a preparation carried out at 20 °C. The chemical shifts differ slightly from those in Figure 1, although the difference is only significant in the case of the high-field line, where there is in any case no reason to assume that the by-product will be the same as in the normal preparation

This leaves two broad resonances to be assigned, one at 9.4 (width *ca.* 300) and one at 73.1 p.p.m. (width *ca.* 100 Hz). Both essentially are removed by the baking process. We find that if the preparation is repeated but the $Al[NO_3]_3 \cdot 9H_2O$ is added at 20 instead of at 100 °C then the line at 73.1 p.p.m. is predominant (Figure 2). Such solutions will not give crystals of $Cs_2[H_3AlW_{12}O_{40}]$ on addition of CsCl. The broad resonance at 73.1 p.p.m. also appears when a 12-tungstoaluminate is recrystallised. It is known for other systems that ageing a 1 : 12 heteropolyanion solution often gives rise to a 2 : 18 heteropolyanion, and it is known that these 2 : 18 anions are thermally unstable.[3] The $AlO_4$ groups in such an ion are in a very similar environment to those in the 1 : 12 species so that they would be expected to have a very similar chemical shift. The increased molecular size would lead to a three- or four-fold increase in linewidth and a further increase would be likely due to the loss of regular symmetry around the $AlO_4$ groups. Thus the observed spectra and behaviour are consistent with the presence of the anion $[(AlO_4)_2W_{18}O_{54}]^{10-}$ to give the line at 73.1 p.p.m.

The resonance at 9.4 p.p.m. is close to those of $[Al(OH_2)_6]^{3+}$ and the 6-molybdoaluminate and can be assigned to an octahedral environment. It could be a hydrolysis product of $Al^{3+}$, since the pH of the final solution is not unduly low, a species in which a tungsten atom has been replaced by Al, or even a quite different W–Al species, although these possibilities cannot be differentiated on the basis of the present data.

The spectrum of the 6-molybdoaluminate is much simpler, as indeed would be expected when a quantitative yield was obtained. The broad line at 15.4 p.p.m. can be assigned to the octahedral Al in a structure which is presumably similar to that of the $CrMo_6O_{24}$ unit.[11] The relatively small linewidth arises partly because the molecule is fairly small but also indicates that the $AlO_6$ unit cannot be much distorted.

We acknowledge support for this project from both the S.R.C. and the Mond division of Imperial Chemical Industries Ltd. through the award of a CASE award (to A. F.). We also thank Dr. W. S. McDonald for obtaining the *X*-ray data.

[0/1374 *Received, 5th September,* 1980]

## REFERENCES

[1] J. W. Akitt and A. Farthing, *J. Magn. Reson.*, 1978, **32**, 345 and previous and following papers.

[2] J. W. Akitt, *Ann. Rev. NMR Spectrosc.*, 1972, **A5**, 465.

[3] D. L. Kepert, 'Comprehensive Inorganic Chemistry,' eds. J. C. Bailar, H. J. Emeleus, R. Nyholm, and A. F. Trotman-Dickenson, Pergamon, Oxford, 1973, vol. 4, ch. 51.

[4] M. Filowitz and W. G. Klemperer, *J. Chem. Soc., Chem. Commun.*, 1976, 233.

[5] R. Acerate, C. F. Hammer, and L. C. W. Baker, *J. Am. Chem. Soc.*, 1979, **101**, 267.

[6] J. A. Mair and J. L. T. Waugh, *J. Chem. Soc.*, 1950, 2372.

[7] D. H. Brown, *J. Chem. Soc.*, 1962, 3281.

[8] O. Kraus, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, 1936, **A94**, 256; **A93**, 379.

[9] K. Erics, N. F. Yannoni, U. C. Agarwala, V. E. Simmons, and L. C. W. Baker, *Acta Crystallogr.*, 1960, **13**, 1139.

[10] L. C. W. Baker, G. Foster, W. Tan, F. Scholnick, and T. P. McCutcheon, *J. Am. Chem. Soc.*, 1955, **77**, 2136.

[11] A. Perloff, *Inorg. Chem.*, 1979, **9**, 2228.