Aluminium-27 Nuclear Magnetic Resonance: Octahedral and Tetrahedral Solvates of the Aluminium Cation

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Summary The existence of octahedral solvates of the Al^{3+} cation with trimethyl phosphate, dimethyl methylphosphonate, and dimethyl phosphite and a tetrahedral solvate of hexamethylphosphoramide, is shown by their ^{27}Al n.m.r. spectra in nitromethane.

The aluminium perchlorates $Al(TMP)_6{}^{3+},3ClO_4{}^-$ (**1**), $Al(DMMP)_6{}^{3+},3ClO_4{}^-$ (**2**), and $Al(DMP)_6{}^{3+},3ClO_4{}^-$ (**3**) [TMP = $PO(OMe)_3$; DMMP = $MePO(OMe)_2$; DMHP = $HPO(OMe)_2$] can be prepared in the solid state[1] by standard methods, and their high resolution n.m.r. spectra can be measured in nitromethane as inert solvent. The ^1H n.m.r. spectrum of (**1**) has been obtained under these conditions,[2] but it does not yield such detailed information as may be obtained from ^{31}P[3,4] or ^{27}Al[5] spectroscopy.

The ^{27}Al n.m.r. spectra of compounds (**1**)—(**3**) were accordingly examined in nitromethane solution. A sharp heptet is obtained at 22·63 MHz and 0° C, using a Bruker HX-90 spectrometer operating at variable field, and equipped with a Nicolet 1080 Fourier Transform unit. The number of lines, and their relative intensities (1:6:15:20:15:6:1), demand an octahedral arrangement of six equivalent ligands around the aluminium cation, with a coupling constant between phosphorus and the solvated metal nucleus, $P{=}O \cdots Al^{3+}$ of 19·5, 15·0, and 13·4 Hz respectively for (**1**), (**2**), and (**3**). The cubic symmetry of these solvates ensures exceptionally sharp lines. Upon addition of small quantities of water mixed octahedral solvates, $S_i \equiv AlX_i(H_2O)^{3+}_{6-i}$, are produced, as shown by the appearance of broad signals superimposed upon the previous multiplet. Up to two extra signals are obtained in this way, from S_5 and S_4. The other solvates: S_0 [*i.e.* $Al(H_2O)^{3+}_6$], S_1, S_2, and S_3 have already been described under quite different conditions,[5] from a mixture of water, organophosphorus solvent, and aluminium perchlorate. The chemical shifts, δ, obtained from the two methods (see Table) show an important point: the additivity of δ when substituting a water molecule by an organic ligand, which does not depend upon the solvent (*ca.* 3·5 p.p.m. per substitution). These results also show that the phosphoryl oxygen is a better electron-donor to the aluminium cation than the water oxygen, since all shifts are upfield relative to S_0.

Table. ^{27}Al chemical shifts for Al^{3+} solvates, $S_i \equiv AlX_i(H_2O)^{3+}_{6-i}$ [p.p.m., upfield from $Al(H_2O)_6{}^{3+}$].

X	S_0	S_1	S_2	S_3	S_4	S_5	S_6
TMP	0	3·7[a]	6·7[a]	10·0[a]	14·0	17·5	20·5
DMMP	0	3·5	6·8	10·1	14·8	17·5	20·2
DMHP	0	3·3	6·6	9·1	14·0	15·9	17·7

[a] From ref. 5.

Similar experiments with $Al(HMPA)^{3+}_4, 3ClO_4{}^-$ (**4**) (HMPA = hexamethylphosphoramide) yield very different results. A sharp quintet is obtained at −32 °C, with intensities in the ratio 1:4:6:4:1. This is clear evidence for a tetrahedral arrangement of four HMPA ligands around Al^{3+}, as already found with the Be^{2+} cation.[4] In support of this structure, ^{2}J (^{31}P–^{27}Al) increases considerably (30 *vs.* 19·5 Hz for TMP); this is in agreement with the classical dependency upon the proportion of *s* character in the aluminium atomic orbitals, *i.e.*, 1/6 for d^2sp^3 in (**1**) and 1/4 for sp^3 in (**4**). Further, the chemical shift is downfield (−34·11 p.p.m.) relative to $Al(H_2O)_6^{3+}$, as may be expected for the lower total number of ligands. The addition of water is not accompanied by the appearance of other signals. Rather the multiplet broadens and shifts upfield; it completely disappears for a ratio of $H_2O:Al^{3+}$ of *ca.* 10:1. However, one broad signal is obtained for an aqueous solution of HMPA and $Al(ClO_4)_3$, at 4 p.p.m. upfield from $Al(H_2O)_6^{3+}$, corresponding to solvation numbers of *ca.* 0·5 and 5·5 for HMPA and H_2O, *i.e.*, to an octahedral mixed solvate S_1. This clearly shows the possibility of octahedral co-ordination for water-rich solvates, and of a tetrahedral solvate: $S_4 \equiv Al(HMPA)_4^{3+}$ in anhydrous $MeNO_2$. Mixed tetrahedral solvates seem to be precluded, and addition of water probably results in the production of octahedral mixed solvates, rapidly exchanging their ligands with S_4 (tet.).

Financial support from the Direction des Recherches et Moyens d'Essais and from the Centre National de la Recherche Scientifique is gratefully acknowledged.

(*Received*, 20*th November* 1973; *Com.* 1617.)

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