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Octahedral and Tetrahedral Solvates of the Aluminum Cation. A Study of the Exchange of Free and Bound Organophosphorus Ligands by Nuclear Magnetic Resonance Spectroscopy

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Abstract: The existence of octahedral solvates of the Al^{3+} cation with trialkylphosphates, phosphonates, dialkyl hydrogen phosphites, and a tetrahedral solvate of hexamethylphosphorotriamide (HMPA) is shown by their ^{27}Al and ^{31}P NMR spectra in nitromethane. The kinetics of the exchange of free (A^*) and bound (A) ligand molecules, $AlA_6{}^{3+}$ or $AlA_4{}^{3+} + A^* \rightarrow AlA_5A^{*3+}$ or $AlA_3A^{*3+} + A$, have been investigated. Sharply contrasting conclusions are reached for hexa- and tetracoordinated aluminum(III). The rate laws are respectively zero and first order in free ligand for octahedral and tetrahedral solvates. These data are consistent with a dissociative and an associative substitution mechanism, respectively. This mechanistic change is accompanied by a strong decrease of the activation enthalpies and entropies. Typical values are $k_{25°} = 5.1$ sec^{-1} and 4.8×10^3 M^{-1} sec^{-1}, $\Delta H^‡ = 19.8$ and 7.7. kcal mol^{-1}, $\Delta S^‡ = 6.9$ and -10.2 eu for Al(dimethylmethylphosphonate)$_6{}^{3+}$ and Al(HMPA)$_4{}^{3+}$, respectively. Aqueous solutions of these solvates were also examined by ^{27}Al NMR; separate resonances are observed for the whole range of the various species: $AlA_i(H_2O)_{6-i}{}^{3+}$, $i = 0$–6.

A point of interest in the study of dissolved ions and their effect on the structure of the surrounding medium is the constitution of the first solvation shell. In this respect, NMR spectroscopy has proved to be an invaluable tool since, in electrolyte solutions, the presence of ions modifies the charge distribution in molecules of the solvent coordination sphere and therefore the shielding of their nuclei. The most direct method uses systems in which the exchange of solvent molecules between the various species is sufficiently slow that separate resonances are observed for the free and bound solvent, S_f and S_b, respectively.[1] However, the scope of this method is sharply restricted to a few ion-solvent systems on account of the NMR time scale, and few cations can be studied in this manner. Al^{3+} solvation shells have been extensively studied in the past in a variety of organic solvents by proton NMR.[2-7] Some extension of the possible cation-solvent systems can be hoped for on account of the larger chemical shifts of other nuclei in the solution. In 1969 and 1971, we proposed using ^{31}P[8] and ^{13}C[9] spectroscopy of organophosphorus solvents, all containing the phosphoryl P=O solvating link: trimethyl- (TMPA) and triethylphosphates (TEPA); dimethylmethyl- (DMMP) and diethylethylphosphonates (DEEP); dimethyl hydrogen phosphite (DMHP); hexamethylphosphorotriamide (HMPA).

The present paper is chiefly devoted to the study of the NMR properties of the aluminum cation itself in the same series solvents. Aluminum-27 is an attractive nucleus on account of its high sensitivity and of a 100% isotopic abundance. However, its spin number, $I = 5/2$, results in a nuclear quadrupolar moment strongly interacting with electric field gradients which originate in an asymmetrical arrangement of the ligands around the Al^{3+} cation. Therefore cubic symmetrical complexes such as $Al(H_2O)_6{}^{3+}$ are necessary for observation of sharp lines. Any deviation from pure cubic symmetry brings forth a characteristic line broadening, as it was shown[10] for the ion pair $Al(H_2O)_5(HSO_4{}^-)^{2+}$.

Our previous studies[11-14] only used aqueous solutions of the Al^{3+} cation in an organophosphorus cosolvent A, resulting in the presence of several unsymmetrical solvates: $S_i \equiv AlA_i(H_2O)_{6-i}{}^{3+}$, $i = 0$–6. More simple systems are therefore, desirable for an initial study. We then planned to study the aluminum cation coordinated to identical organophosphorus ligands; octahedral $AlA_6{}^{3+}$, $3ClO_4{}^-$ and tetrahedral $Al(HMPA)_4{}^{3+}$, $3ClO_4{}^-$ solvates were then prepared in the solid state[15] and dissolved in nitromethane, an inert solvent.[16] Such a medium also allowed an easier kinetic study by permitting addition of variable amounts of the free ligand. A significant comparison of substitution reactions of octahedral and tetrahedral complexes of the same cation is then possible. In a second step, aqueous solutions of these

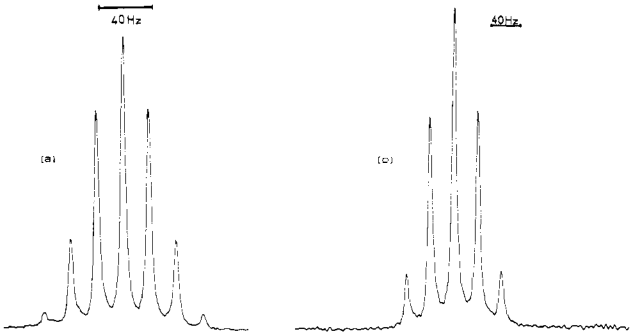

Figure 1. ^{27}Al spectra of a nitromethane solution of $Al(TMPA)_6{}^{3+}$, $3ClO_4{}^-$ at 25° (a) and $Al(HMPA)_4{}^{3+}$, $3ClO_4{}^-$ at −30° (b).

Table I. ^{27}Al Chemical Shifts for Al^{3+} Solvates $S_i \equiv AlA_i(H_2O)_{6-i}{}^{3+}$, in ppm Upfield from $Al(H_2O)_6{}^{3+}$

A	S_0	S_1	S_2	S_3	S_4	S_5	S_6
TMPA	0	3.7[a]	6.7[a]	10.0[a]	14.0[b]	17.5[b]	20.5[b]
TEPA	0	3.6	7.0	11.0	14.7	17.5[c]	21.9
DMMP	0	3.5[b]	6.8[b]	10.1[b]	14.8[b]	17.5[b]	20.2[b]
DEEP	0	3.75	7.5	11.0	14.8[d]	17.5[d]	20.2[d]
DMHP	0	3.3[b]	6.6[b]	9.1[b]	14.0[b]	15.9[b]	17.7[b]

[a] From ref 13. [b] From ref 20. [c] Lines too broad for an accurate measurement. [d] Aqueous solutions only (solvate S_6 could not be obtained in the solid state).

solvates were again examined by ^{27}Al NMR. Good evidence was thus obtained for the existence of mixed solvates, S_i, allowing a quantitative estimation in some instances.

Experimental Section

Materials. The organic solvents were obtained from Aldrich Chemicals and were checked for purity before use. Nitromethane was distilled and stored over molecular sieves. The solid solvates were prepared from hydrated aluminum perchlorate, $Al(ClO_4)_3 \cdot 8H_2O$ (Alfa Inorganics), as described by Karayannis et al.[15] All of these compounds gave satisfactory elemental analyses (C, H, O, P, Cl, Al).

Aluminum-27 Spectroscopy. The ^{27}Al spectra were obtained from a Bruker HX-90 apparatus at 22.63 MHz, using a standard ^{13}C probe and by decreasing the magnetic field from 2.114 to 2.04 T. No field-frequency lock could be used under these conditions. The NMR spectra were therefore carried out as fast as possible, either in a single scan in the continuous wave mode for concentrated solutions or by fast accumulation for the more dilute ones (ca. 0.1 *M*), using a Fourier transform unit (128 0.2-sec scans of 4K/8K points over a frequency range of 5 kHz). Chemical shifts and line intensities were taken from computer readouts. Increasing positive values of chemical shifts are toward higher field. Chemical shifts are expressed in parts per million from the resonance of $Al(H_2O)_6{}^{3+}$. This reference was obtained from a solution of $Al(ClO_4)_3$ in H_2O contained in a 5 mm o.d. tube immersed in a 10 mm o.d. NMR tube filled with the solution being studied.

Phosphorus and Proton NMR. ^1H and ^{31}P spectra were obtained from a Jeol C60-HL spectrometer operating at 60 or 24.288 MHz, respectively, with proton decoupling in the latter case. ^{31}P Fourier transform spectroscopy was also performed with the aforementioned Bruker HX-90 apparatus at 36.43 MHz.

Line-Shape Measurements. A great number of exchanges between various nuclear sites are examined in this paper: ^1H exchange between two sites; ^{27}Al exchange within a heptet and a quintet; ^{31}P exchange within a hexet. The corresponding line shapes are computed according to a matrix formulation due to Anderson,[17] Kubo,[18] and Sack.[19] All calculations were performed with the program TRECH.

The Aluminum Solvates in Nitromethane. The solid solvates $AlA_6{}^{3+}$, $3ClO_4{}^-$, where A = TMPA (**1**), TEPA (**2**), DMMP (**3**), or DMHP (**4**), were examined by ^{27}Al NMR spectroscopy in anhydrous nitromethane at 0°.[20] A sharp heptet (Figure 1a) is obtained for all samples, with line intensities in the ratio 1:6:15:20:15:6:1. Such a spectrum is accounted for by an octahedral arrangement of six equivalent ligands around the aluminum cation, with a coupling constant between phosphorus and the solvated metal nucleus, $P{=}O\cdots Al^{3+}$, of 19.5, 19.0, 15.0, and 13.4 Hz, respectively, for **1**, **2**, **3**, and **4**. This shows that the aluminum coordination number, $n_A = 6$ in the solid state, is kept in solution and that nitromethane is actually an inert solvent. The value of n_A was checked by direct integration of the total line intensities, which is then compared to the intensity of the signal of the $Al(H_2O)_6{}^{3+}$ external reference. The chemical shifts of these solvates (S_6 in Table I) are all located upfield relative to $Al(H_2O)_6{}^{3+}$ (or S_0), and their value amounts to about 20 ppm. These results show that the phosphoryl oxygen is a better electron donor to the aluminum cation than the water oxygen. This is in fair agreement with Gutmann's donor numbers[21] for these two groups of solvents: ND_{SbCl_5} = 18 and 23 for H_2O and TMPA, respectively. These results are confirmed by ^{31}P NMR. Six lines (Figure 2) are observed for all the solvates, each line corresponding to the six magnetic states of the ^{27}Al nucleus with the same probability. An additional line is obtained for the free solvent if there is any. The cubic symmetry of these solvates ensures exceptionaly sharp spectral lines.

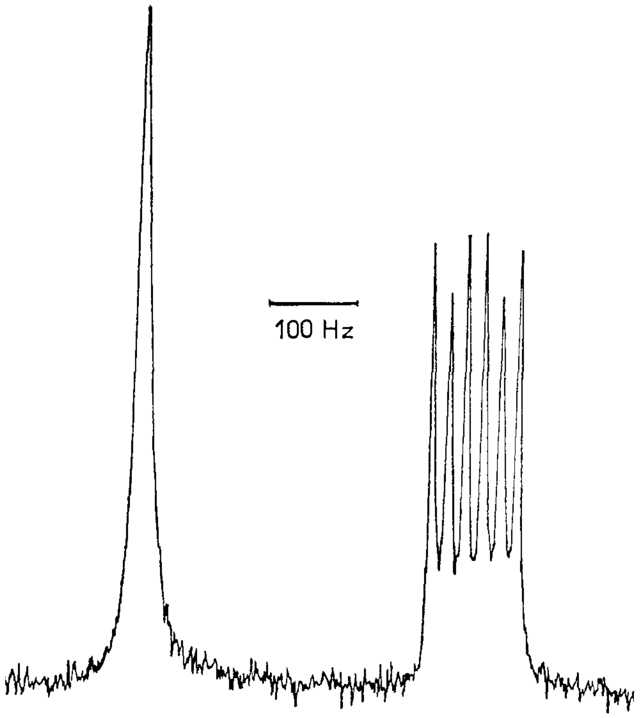

Figure 2. ^{31}P spectrum of a solution of $Al(TMPA)_6{}^{3+}$, $3ClO_4{}^-$ and of free TMPA in nitromethane at 25°.

Similar experiments with $Al(HMPA)_4{}^{3+}$, $3ClO_4{}^-$ (**5**) result in a sharp quintet by ^{27}Al NMR at −30° (Figure 1b) and a hexet by ^{31}P NMR. The number of ^{27}Al lines and their relative intensities, in the ratio 1:4:6:4:1, are clear evidence for a tetrahedral arrangement of four HMPA ligands around Al^{3+}, as already found with the Be^{2+} cation.[12] In support of this structure, $^2J_{^{31}P-^{27}Al}$ increases considerably (30 vs. 19.5 Hz for TMPA); this is in agreement with the classical dependency of J upon the proportion of s character in the aluminum atomic orbitals, i.e., $\frac{1}{6}$ for d^2sp^3 in **1** and $\frac{1}{4}$ in **5**. The chemical shift is downfield (−34.11 ppm) relative to $Al(H_2O)_6{}^{3+}$ in spite of a very high donor number of HMPA: ND_{SbCl_5} = 30. This actually results from a decreased number of ligands: four instead of six. Some evidence for this point is provided by the following experiment. A solution of **4** is added with free HMPA. The ^{27}Al spectrum consists of three groups of lines: a quintet at low field for $Al(HMPA)_4{}^{3+}$, a heptet at high field for $Al(DMHP)_6{}^{3+}$ overlapping with a broad band upfield for the mixed octahedral solvates $Al(DMHP)_5(HMPA)^{3+}$ presumably. Such experiments may be used to classify solvents according to their electron-donating properties.

Aqueous Solutions. Solutions of aluminum perchlorate in aqueous organophosphorus solvents have already been characterized by ^1H,[11] ^{31}P,[9,11] and ^{13}C NMR.[9,14] In all cases, two signals, only s_b and s_f, were observed for bound and bulk solvent, S_b and S_f, re-

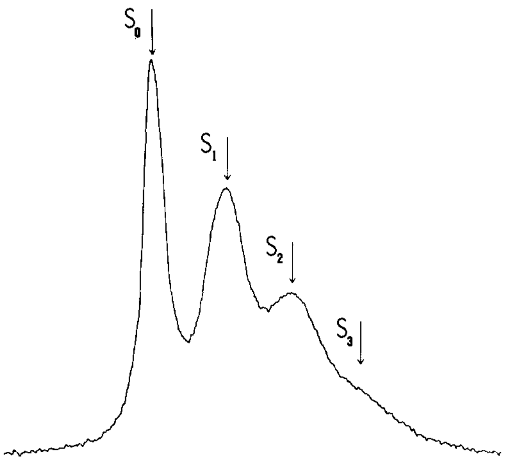

Figure 3. ^{27}Al spectrum of an aqueous solution of $Al(ClO_4)_3$ in TMPA at 65° ($\lambda = 8$; $\mu = 0.5$; $n_A = 1.03$; $S_0{:}S_1{:}S_2{:}S_3 = 31{:}39{:}26{:}4$).

spectively. The bound signal s_b actually results from a weighted mean of a series of resonances, s_0, s_1, s_2 . . ., for the various mixed solvates S_i: $AlA_i(H_2O)_{6-i}{}^{3+}$, $i = 0$–6. These species stand in equilibrium according to the reaction

$$S_i + H_2O \overset{K_i}{\rightleftharpoons} S_{i-1} + A, \; i = 1\text{–}6 \qquad (1)$$

Evidences for this point are: first, a mean organic solvation number n_A,[11,12] continuously increasing over a large range, from 0 to 5.5 for TMPA or DMMP, when the molar ratios, λ = [total H_2O]:[total A] and μ = [salt]:[total A], is varied; and second, a chemical shift which is continuously variable under the same conditions. A total mean solvation number of 6 ($n_A + n_{H_2O}$) was found in all cases, even with HMPA (cf. below), showing a hexacoordination in the Al^{3+} first solvation shell and a complete dissociation of the aluminum perchlorate (no contact ion pairs).

Aluminum NMR spectroscopy can go a step further. The ^{27}Al spectra consist of several overlapping broad lines (Figure 3) at room temperature. Warming the sample first sharpens lines by decreasing the viscosity, and, therefore, the quadrupolar correlation time of ^{27}Al, then broadens them again as chemical exchange takes place.[13] An optimum temperature of 40° was attained where these two effects were at a minimum. Up to four different signals have been detected, depending on the molar concentrations. Line positions, and relative areas, a_0, a_1, a_2, a_3, were computed with the help of a program written for this purpose, assuming lorentzian line shapes and using least-squares procedures. The signals s_0, s_1, s_2, s_3, from low to high fields, have been assigned to the different solvates: S_0, S_1, S_2, S_3, in the sequence of their appearance when concentration conditions are varied so as to increase progressively the organic solvation number. Good evidence for this point was obtained with DMMP or DEEP (Figure 4), where lines s_1 and s_2 are sharper, and therefore resolved into a doublet and a broad triplet, respectively, as a result of one or two ^{27}Al–^{31}P couplings in S_1 and S_2, respectively. One triplet only is observed for S_2, showing either the presence of one stereoisomer for S_2 (presumably the trans one) or an identical chemical shift for both cis and trans isomers. This point is consistent with an almost constant frequency interval between two consecutive signals (Table I). This is clear evidence that consecutive signals, s_i, should be assigned to the corresponding solvates, S_i, where S_i possibly represents a mixture of stereoisomers. This means also that the ^{27}Al chemical shifts are principally determined by the number of organic ligands, and that the effect, when substituting a water molecule by an organic ligand, is almost additive. Such a behavior contrasts with that observed for the nuclei of the ligands, presumably perturbed in the same way by the presence of the Al^{3+} cation, whatever be the nature of their neighbors.

The unique ^{31}P signal of bound DMMP should consist of a hexet, as for the pure solvate S_6 in nitromethane and for the same reasons. Such a multiplet is not observed, on account of a nuclear site exchange resulting from the ligand chemical exchange and the ^{27}Al quadrupolar relaxation. Keeping the free solvent concentration [S_f] as low as possible so as to cancel the chemical exchange, a progressive broadening of the ^{31}P bound signal, s_b, without any frequency shift is observed for increasing temperatures. Line shapes obtained for DMMP (Figure 5) strongly suggest the existence of an unresolved multiplet as a result of a decreased relaxation rate, $1/T_{1Q}$. Theoretical simulation of the ^{31}P spectrum was performed according to Abragam[22] for trial values of the two unknown parameters: $^2J_{^{31}P\text{-}^{27}Al}$ and $1/T_{1Q}$. At 40°, the best fit between experimental and theoretical ^{31}P lines of DMMP took place when: $J = 15 \pm 2$ Hz and $1/T_{1Q} = 60 \pm 5$ sec^{-1}. The value of J actually agrees with those previously obtained for S_6 (15.0 ± 0.1 Hz) and S_1 and S_2 (Figure 4; 15 ± 1 Hz). The ^{27}Al relaxation rate is also consistent with the line width of the corresponding ^{27}Al spectrum (Figure 4): 20 Hz $\simeq 1/(\pi T_{1Q})$. Similar ^{31}P line broadenings are observed for all organophosphorus solvents, preventing any accurate kinetic study of the chemical exchange between S_b and S_f by ^{31}P NMR.

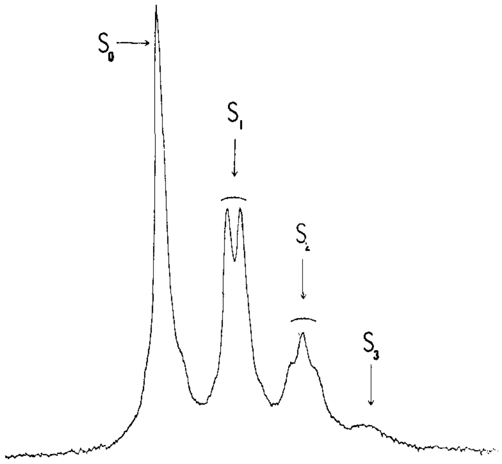

Figure 4. ^{27}Al spectrum of an aqueous solution of $Al(ClO_4)_3$ in DMMP at 50° ($\lambda = 15$; $\mu = 0.9$; $n_A = 0.88$; $S_0{:}S_1{:}S_2{:}S_3 = 41{:}35{:}18{:}6$).

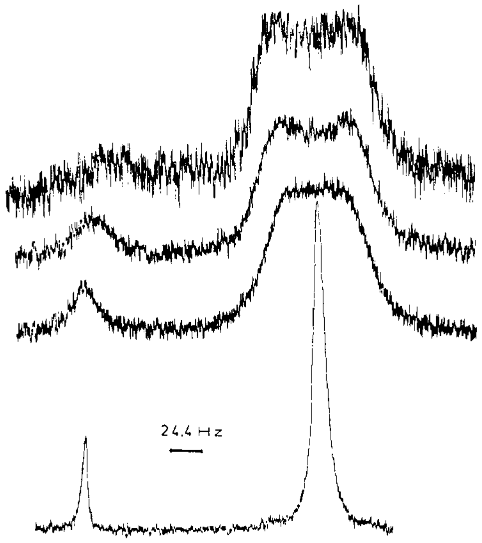

Figure 5. ^{31}P spectra of an aqueous solution of $Al(ClO_4)_3$ in DMMP ($\lambda = 14$; $\mu = 1.1$; $n_A = 0.70$) at 77, 54, 30, and −30° (from top to bottom).

Aqueous Nitromethane Solutions. In aqueous solutions, only solvates S_0, S_1, S_2, and S_3 have been detected by ^{27}Al NMR. Solvates S_4–S_6 should demand a very small content of water in the mixture to be predominant according to reaction 1. However their solubility in such media becomes too poor to satisfy the sensitivity requirements of the NMR method. These solvates, however, may be obtained under quite different conditions, using the nitromethane solutions described above and adding to them small quantities of water (the exceptional behavior of $Al(HMPA)_4{}^{3+}$ is examined further on). Mixed octahedral solvates, S_i, are then produced, as shown by the appearance of broad signals superimposed upon the S_6 multiplet (Figure 6). A table of chemical shifts is set out for the whole series of solvates in some instances (Table I). The values obtained from this second method are in good agreement with the

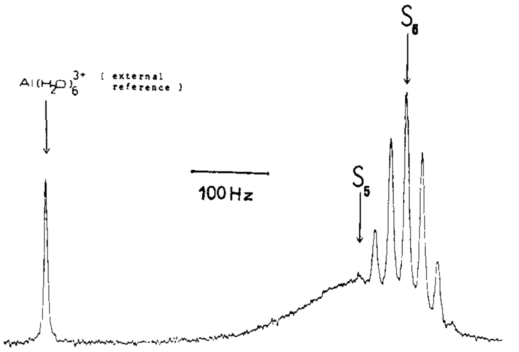

Figure 6. ^{27}Al spectrum of an aqueous solution of $Al(TMPA)_6^{3+}$, $3ClO_4^-$ in nitromethane at 25°.

previous ones. The frequency interval between two consecutive solvates is kept also constant, thus giving direct evidence for an assumption made a priori for fast-exchanging alkaline cations.[23] These results also definitely confirm the better electron-donating properties of these solvents, as compared to that of water.

This is actually a first-order approach for evaluating substituent constants which can be summed to yield a calculated value for the desired property, namely the ^{27}Al chemical shift δ_i of the solvates S_i, using the relationship

$$\delta_i \text{ (from } S_0) = \frac{i}{6}\delta_6 \qquad (2)$$

A second-order approach, already used successfully in rationalizing the chemical shifts of a variety of nuclei, ^{11}B,[24] ^{13}C,[24] ^{27}Al,[25] ^{73}Ge,[26] and ^{93}Nb,[27] is the pairwise additivity model introduced by Vladimiroff and Malinowski[28].

$$\delta_i = \Sigma C_{jk}\eta_{jk} \qquad (3)$$

C_{jk} is the number of possible interactions, η_{jk}, between the ligands, namely H_2O and TMPA if $S_i \equiv Al(TMPA)_i(H_2O)_{6-i}^{3+}$. In this case, two ligands only are considered, and three pairwise interaction parameters are needed: $\eta_{H_2O\text{-}H_2O} = 0$ (if chemical shifts are expressed from S_0); $\eta_{TMPA\text{-}TMPA} = (1/6)\delta_6 = 1.71$; $\eta_{TMPA\text{-}H_2O} = (1/4)\delta_1 = 0.925$. Chemical shifts of solvates S_1–S_5 computed according to eq 2 or 3 are reported in Table II. No significant improvement is noticed for the second-order approach. The only point of interest is to confirm that it is impossible to distinguish between isomers of a given solvate S_i on the NMR time scale.

Similar experiments with HMPA yield very different results. 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 ppm 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. Mixed tetrahedral solvates seem to be precluded if we remember the experiment described above of mutual substitution of HMPA and TMPA; mixed octahedral solvates were observed at about 4 ppm, and only one quintet at −34 ppm for $Al(HMPA)_4^{3+}$. A pentacoordinated mixed species can also be ruled out, since its signal should appear at about −15 ppm on account of the nearly perfect additivity of ligand effects on ^{27}Al chemical shifts. The addition of water to nitromethane solutions probably results in the production of octahedral mixed solvates, rapidly exchanging their ligands with tetrahedral $Al(HMPA)_4^{3+}$, and the large frequency shift between the two exchanging sites, ca. 850 Hz, explains the apparent absence of any signal at coalescence.

Thus, one may conclude that the tetrahedral structure around Al^{3+} cation is closely linked to the presence of four identical HMPA ligands. This smaller coordination number may result both from the better electron properties of the HMPA molecule and from its higher steric requirement.

Results

Solvation Numbers in Aqueous Solutions. Mean solvation numbers n_A and n_{H_2O} have been given previously for aqueous solutions of $Al(ClO_4)_3$ in the organosphosphorus cosolvents presently studied, by means of ^1H, ^{31}P, and ^{13}C NMR.[11-14] Aluminum-27 NMR yields the concentrations of the mixed species themselves from the areas a_i of their respective signals s_i. Solubility and sensitivity requirements severely restrict the range of measurable n_A values: from 0.3-0.5 to 1.2-1.7 with DMMP, DEEP, TMPA, and TEPA. No measurement has been performed with aqueous nitromethane solutions, on account of line broadness.

Table II. Experimental and Calculated Values of Chemical Shifts of Solvates $S_i \equiv Al(TMPA)_i(H_2O)_{6-i}^{3+}$

	Exptl	Eq 2	Eq 3
S_0	0	0	0
S_1	3.7	3.4	3.7
S_2	6.7	6.8	7.3 (cis) 7.4 (trans)
S_3	10.0	10.3	10.7 (cis) 10.8 (trans)
S_4	14.0	13.7	14.1 (cis) 14.2 (trans)
S_5	17.5	17.1	17.4
S_6	20.5	20.5	20.5

Table III. Aqueous Solutions of $Al(ClO_4)_3$ in DMMP; Equilibrium Data (for notations, see the text)

μ/λ	n_A	y_A	Y_A	K_1	K_2/K_1	K_3/K_2
0.3/12	0.50	0.083	0.076	0.157	1.70	
0.5/15	0.51	0.085	0.057	0.115	1.63	
0.7/20	0.54	0.090	0.037	0.066	1.84	
0.3/10	0.63	0.105	0.088	0.144	1.71	
1.1/20	0.72	0.120	0.014	0.021	1.49	2.9
0.7/15	0.85	0.141	0.034	0.044	1.61	1.7
0.5/12	0.88	0.146	0.056	0.068	1.71	1.7
0.9/15	0.88	0.146	0.020	0.023	1.71	1.7
0.3/8	0.89	0.148	0.102	0.129	1.68	1.75
0.7/12	0.93	0.155	0.040	0.045	1.70	1.6
0.9/12	1.09	0.182	0.003	0.024	1.57	1.6
0.7/10	1.23	0,204	0.020	0.015	1.92	1.6
0.5/10	1.25	0.208	0.047	0.035	1.92	1.6
0.5/8	1.26	0.210	0.062	0.046	1.92	1.7

Table IV. Aqueous Solutions of $Al(ClO_4)_3$ in TMPA; Equilibrium Data

μ/λ	n_A	y_A	Y_A	K_1	K_2/K_1	K_3/K_2
0.6/10	0.85	0.142	0.066	0.63	2.33	
0.3/6	1.01	0.168	0.134	0.12	1.90	
0.5/8	1.03	0.171	0.181	0.07	1.89	
0.3/5	1.28	0.213	0.147	1.00	2.19	2.4
0.6/8	1.46	0.243	0.023	0.01	2.42	2.0

The validity of these measurements was checked in some ways. First, the mean solvation numbers, computed according to

$$n_A = \frac{a_1 + 2a_2 + 3a_3}{a_0 + a_1 + a_2 + a_3}$$

(for solutions containing species S_0 to S_3 only) agree to ±10% with the ones mentioned above for TMPA and TEPA, and to ±5% for DMMP and DEEP where ^{27}Al lines are sharper. Second, the molar fractions a_i^* of the Al^{3+} cation in species $S_i = a_i^* = a_i/(a_1 + a_2 + a_3)$ were plotted as a function of n_A (cf. Figure 7 for DMMP and TMPA); smooth curves could be drawn without exaggerated scattering of experimental points. Supplementary data are displayed in Tables III and IV, namely the corresponding λ and μ values, and the molar fractions y_A and Y_A of the organic component in bound and free solvent: $y_A = n_A/6$ and $Y_A = (1 - \mu n_A)/(1 + \lambda - 6\mu)$.

From these tables, we observed that the composition of bulk and bound solvent may differ widely. The mean solvation number increases when the total water content, λ, decreases, as expected, but n_A also increases when the salt

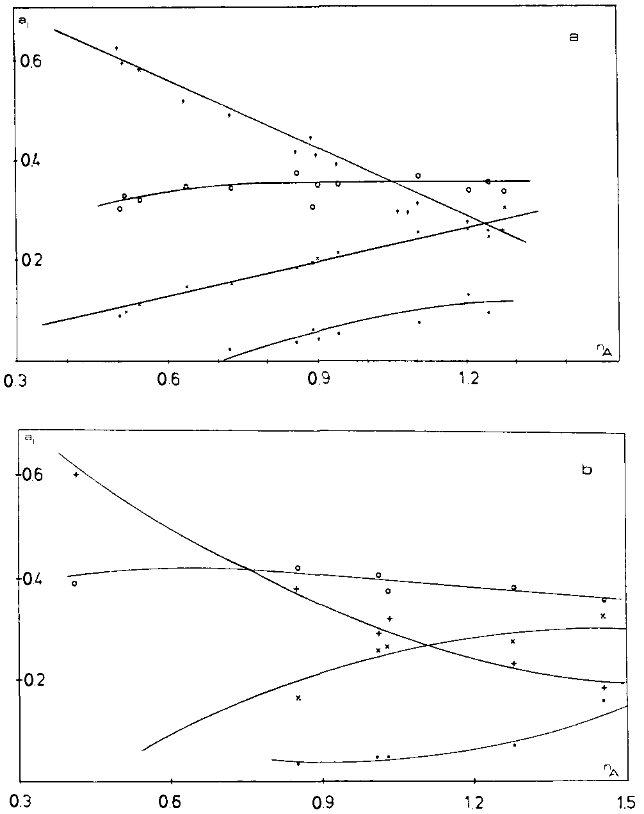

Figure 7. The molar fractions of mixed solvates S_i as a function of the mean organic solvation number n_A for a solution of $Al(ClO_4)_3$ in aqueous DMMP (a) and TMPA (b): S_0 (+); S_1 (O); S_2 (×), and S_3 (·).

concentration μ is made larger, while the bulk solvent is deprived of its organophosphorus component. This rather unexpected trend may only be accounted for by a preferential solvation of the perchlorate anion by water molecules, which makes them less available for cation solvation.

The equilibrium constants, K_i, of reaction 1, such as

$$K_1 = \frac{a_0^*}{a_1^*}\frac{Y_A}{1 - Y_A}\frac{\gamma_0\gamma_A}{\gamma_1\gamma_{H_2O}} \tag{4}$$

may be tentatively computed assuming the γ activity coefficients equal to unity and taking ideal values a_0^* and a_1^* along the smoothed curves of Figure 7. The K_1 values reported in Tables III and IV actually spread out over an order of magnitude. More rewarding conclusions are drawn when considering the ratios K_{i+1}/K_i, for example

$$K_2/K_1 = \frac{a_1^{*2}}{a_0^*a_2^*}\frac{\gamma_1^2}{\gamma_0\gamma_2} \tag{5}$$

Nearly constant values are then obtained when activity coefficients are neglected: $K_2/K_1 = 1.72 \pm 0.11$ for DMMP (average over 14 points), 1.91 ± 0.10 for DEEP (11 points), 2.41 ± 0.70 for TEPA (14 points), and 2.15 ± 0.20 for TMPA (5 points); $K_3/K_2 = 1.79 \pm 0.23$ for DMMP (10 points) and 2.2 ± 0.2 for TMPA (2 points). The invariability of these ratios means both that the activity coefficients of the solvates S_0 to S_3 are equal and that those of the free solvent molecules are responsible for the scattered values of the equilibrium constants themselves. The first conclusion seems reasonable as electrostatic interactions of the aluminum cation may be presumed to be predominant and to contribute the same amount in the various solvates. As for the activity coefficients of the free solvent compounds, the computed amplitude of their variations, from ca. 10 to 1, is not consistent with the much smaller one presumably expected for the pure mixture (without salt) with the same composition Y_A. We may therefore conclude that the presence of ions deeply perturbs the so called free solvent. Its composition Y_A probably represents only a weighted mean over successive solvation spheres around the Al^{3+} cation. An unknown value, Y_A^*, relating to the second solvation sphere should accordingly be substituted for Y_A in eq 4 to obtain constant K_1 values.

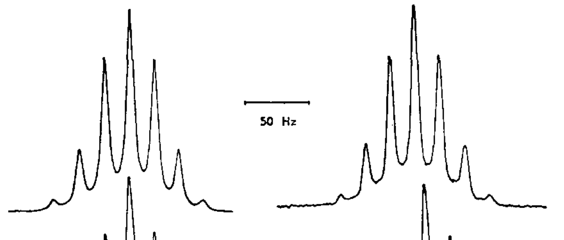

Figure 8. ^{27}Al spectra of a solution of $Al(TMPA)_6{}^{3+}, 3ClO_4{}^-$ in nitromethane. Experimental and theoretical curves (right and left) at 36.5, 43.5, 50, and 54° (from top to bottom): k = 1.5, 4.5, 8.8, and 14.5 sec^{-1}, respectively.

Finally, we notice that these ratios are quite close to their statistical values, $K_2/K_1 = 2.40$ and $K_3/K_2 = 1.87$, and that they do not agree with the values previously derived from ^1H NMR.[12] The latter discrepancy arises from the approximations used in deriving K_1 values; according to Bjerrum's method, half-integer values $(i + \frac{1}{2})$ of the mean solvation number n_A were then assumed to result from an equimolecular mixture of species S_i and S_{i+1}, while Figure 7 clearly shows the coexistence of three species at least in such solutions.

Kinetic Measurements. The coalescence of NMR spectra on increasing temperature yields the rate constant k_e for the exchange of one ligand molecule between bulk and bound solvent sites

$$S_b \xrightarrow{k_e} S_f$$

Measurements are carried out both by ^{27}Al (Figure 8) and ^1H NMR in anhydrous nitromethane, with variable concentrations of salt C_s and of free added ligand C_f. The first method yields the total number of ligands exchanged around the Al^{3+} cation per second, while the second one is related to the fate of an individual ligand molecule. The magnetization transfer rate constant in octahedral complexes is accordingly six times as high for ^{27}Al as for ^1H nuclei, $6k_e$ and k_e, respectively. Although the first number is

Table V. Kinetic Parameters for Ligand Exchange of $Al(TMPA)_6^{3+}$ in CH_3NO_2 by ^{27}Al NMR

Concentrations C_S and C_f (*M*)	k, sec^{-1} 298.2 K	309.7 K	313.2 K	316.7 K	323.2 K	327.2 K	330.2 K	$\Delta H^{\ddagger}_{25°}$, kcal mol^{-1}	$\Delta S^{\ddagger}_{25°}$, eu
0.2 and 0.64	0.36^a	1.5	2.5	4.5	8.8	14.5	18.3	24.2 ± 1	20.5 ± 3
0.2 and 2.8	0.40^a	1.5	3.3	5.5	9.0	15.0	18.0	22.7 ± 2	16 ± 6
							Mean	23.5 ± 1.5	18.2 ± 5

^{a}Extrapolated value.

Table VI. Kinetic Parameters for Ligand Exchange of $Al(DMMP)_6^{3+}$ in CH_3NO_2 by ^1H NMR

Concentrations C_S and C_f (*M*)	k, sec^{-1} 298.2 K	306.2 K	312.2 K	316.2 K	326.2 K	$\Delta H^{\ddagger}_{25°}$, kcal mol^{-1}	$\Delta S^{\ddagger}_{25°}$, eu
0.19 and 1.18	5.0	9.1	22.7	32.3	83.3	19.4 ± 1.2	9.6 ± 4.1
0.19 and 0.93	5.1	8.3	25.0	34.5	100	20.8 ± 1.9	14.1 ± 6.3
0.095 and 0.93	5.1	8.9	23.0	32.3	83.3	19.4 ± 1.4	9.4 ± 4.5
0.095 and 1.18	5.1	8.7	20.4	32.3	100	20.5 ± 1.6	13.0 ± 5
0.19 and 1.70	5.1	8.5	22.2	30.3	91	19.9 ± 1.6	11.1 ± 5
					Mean	20.0 ± 1.5	11.4 ± 5

Table VII. Kinetic Parameters for Ligand Exchange of $Al(DMMP)_6^{3+}$ in CH_3NO_2 by ^{27}Al NMR

Concentrations C_S and C_f (*M*)	k, sec^{-1} 283.2 K	293.2 K	298.2 K	301.2 K	303.2 K	306.2 K	$\Delta H^{\ddagger}_{25°}$, kcal mol^{-1}	$\Delta S^{\ddagger}_{25°}$, eu
0.15 and 0.45	1.0	2.8	5.3	7.0	8.7	10.3	17.5 ± 0.6	3.2 ± 1.8
0.15 and 0.73	0.9	2.5	4.8	7.0	8.2	10.2	18.2 ± 0.7	5.5 ± 2.0
						Mean	17.9 ± 0.6	4.4 ± 1.9

Table VIII. Kinetic Parameters for Ligand Exchange of $Al(DMHP)_6^{3+}$ in CH_3NO_2 by ^1H NMR

Concentrations C_S and C_f (*M*)	k, sec^{-1} 298.2 K	301.2 K	306.2 K	312.2 K	314.2 K	318.2 K	$\Delta H^{\ddagger}_{25°}$, kcal mol^{-1}	$\Delta S^{\ddagger}_{25°}$, eu
0.43 and 2.65	1.4^a	1.5	3.4	5.9		10.0	20.0 ± 2	9.3 ± 7.5
0.43 and 3.98			3.7					
0.43 and 5.18			3.7					
0.43 and 1.89	1.3^a	1.5	3.0	4.8	5.83^b	9.1	20.0 ± 1.4	5.3 ± 5.0
0.84 and 3.7	1.3^a	1.6	3.2	5.0		10.0	19.2 ± 1.5	6.1 ± 5.5
						Mean	19.8 ± 1.6	6.9 ± 6.0

^{a} Extrapolated value. ^{b} From ^{27}Al NMR for the sake of comparison.

more closely linked to the conventional chemical rate constant, all our results are expressed using k_e values. In this way, our kinetic parameters can be compared directly with existing proton NMR data.

^{27}Al measurements for TMPA solvates are reported in Table V. The NMR site exchange rate k_e is found independent from C_f, and is accordingly equal to the chemical rate constant k for a dissociative[30] SN1[31,32] mechanism with a pentacoordinated intermediate:

$$Al(TMPA)_6^{3+} \xrightarrow{6k} Al(TMPA)_5^{3+} + TMPA$$

$$Al(TMPA)_5^{3+} + TMPA^*{}_{(free)} \xrightarrow{fast} Al(TMPA)_5(TMPA^*)^{3+}$$

The proton NMR spectra had already been studied by Frankel,[16] and thus were not reproduced. His values, $k_{25°} = 0.36$ sec^{-1}, $\Delta H^{\ddagger} = 20.8$ kcal mol,$^{-1}$, and $\Delta S^{\ddagger} = 8.3$ eu, are in good agreement with ours.

Similar conclusions were drawn for DMMP and DMHP solvates. Rate constants of DMMP solvates are reported in Tables VI and VII from ^{27}Al and ^1H NMR; a satisfactory agreement is again found between both series of measurements. DMHP solvates could only be studied using the methoxylic proton lines; the coalescence of the ^{27}Al spectra was in effect obscured by an additional line broadening over the explored temperature range, presumably on account of ^{27}Al quadrupolar relaxation (Table VIII).

Quite different results are obtained with HMPA. Low temperatures are needed to bring the ^{27}Al site exchange to the NMR time scale. Exchange rates increase sharply as soon as a small amount of free HMPA is added to the nitromethane solutions. On the same grounds, the proton exchange is too fast to give rise to a separate signal for the free solvent even at the lowest possible temperature ($\simeq -30°$) and no kinetic measurement was possible using this spectroscopy. The NMR transfer rate k_e is actually proportional to the free HMPA content (Table IX).

$$k_e = k[\mathrm{HMPA}]$$

This is strong evidence for an SN2 associative substitution mechanism:

$$Al(HMPA)_4^{3+} + HMPA^* \text{ (free)} \xrightarrow{4k} Al(HMPA)_3(HMPA^*)^{3+} + HMPA$$

The whole set of kinetic parameters is summarized in Table X, together with results of literature related to substitution of solvent molecules around the Al^{3+} cation, and with a few data in aqueous mixtures.

Conclusion

Our data form a significant comparison between octahedral and tetrahedral coordination around the same cation under strictly similar conditions. In each case, the kinetic order of the ligand exchange reaction is determined, and accordingly brings a firm support to the presumed mechanism, *dissociative and associative*, respectively, both of

Table IX. Kinetic Parameters for Ligand Exchange of $Al(HMPA)_4^{3+}$ in CH_3NO_2 by ^{27}Al NMR

Concentrations C_s and C_f (M)	k, M^{-1} sec^{-1}						$\Delta H^{\ddagger}_{25°}$, kcal mol^{-1}	$\Delta S^{\ddagger}_{25°}$, eu
	248.2 K	253.2 K	261.2 K	267.2 K	273.2 K	278.2 K		
0.0708 and 0.0442	283	441	735					
0.0728 and 0.0178	267	407	702	913	1264	1756	7.7 ±-0.5	−10.2 ± 1.5

Table X. Kinetic Parameters for Ligand Substitution in Aluminum Solvates

Ligand	$k_{25°}$ (sec^{-1}, or M^{-1} sec^{-1})	$\Delta H^{\ddagger}_{25°}$, kcal mol^{-1}	$\Delta S^{\ddagger}_{25°}$, eu
TMPA[a]	0.38	23.5	18.2
DMMP[a]	5.1	19.0	7.9
DMHP[a]	1.33	19.8	6.9
HMPA[a]	4.8×10^3	7.7	−10.2
H_2O[b]	0.16	27	28
DMSO[b]	0.6	20	3.7
DMF[b]	0.15	17.7	4.7
DMMP−H_2O[c]	0.30	20.5	17.8
HMPA−H_2O[d]	0.23	21	16.1

[a] This work; average over ^1H and ^{27}Al NMR data. [b] Value for the pure solvent; ref 29, 2, and 3 for H_2O, DMSO, and DMF, respectively. [c] This work; $\lambda = 20$; $\mu = 1$; $n_A = 0.50$ (S_0, 60%; S_1, 30%; S_2, 10%). [d] This work; $\lambda = 23$; $\mu = 0.9$; $n_A = 0.58$.

which lead to a pentacoordinated transition state. The associative mechanism is accompanied by a strong rate increase, arising from a dramatic fall of the activation energy, by ca. 12 kcal mol^{-1}. The entropy decrease is also spectacular: −18 eu from DMMP to HMPA. No systematic study has been made for aqueous mixtures; the activation parameters reported in Table X for octahedral mixed solvates in aqueous DMMP or HMPA as well as the similarity of the rate constant value strongly suggest a dissociative mechanism.

Some data are available in the literature for substitution rates of H_2O, DMSO, and DMF ligands using the pure solvent. No kinetic order is therefore available for such reactions. However, the high activation parameters are again indicative of a dissociative mechanism.

On the whole, all substitution rates on octahedral solvates are very similar, and very slow, as it was first observed by Eigen.[33] These solvation-desolvation processes may accordingly be the rate-determining step for many reactions of the aluminum cation in solution. HMPA solvates are quite different, and using pure HMPA would increase the ligand exchange rate by five orders of magnitude. Such solvents may be expected to change many aspects of solution chemistry and electrochemistry of this element.

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