Alumatrane, $Al(OCH_2CH_2)_3N$: A Reinvestigation of Its Oligomeric Behavior

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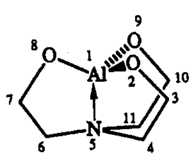
In various literature reports the behavior of the title compound **1** has been described as dimeric in the gas phase; monomeric, hexameric, and octameric in solution; and tetrameric (by X-ray crystallography) in the solid state. Herein we present mass spectral evidence for the presence of both $\mathbf{1}_2$ and $\mathbf{1}_4$ in the gas phase. ^{27}Al NMR evidence is put forth for the tetramer $\mathbf{1}_4$ as the only detectable oligomer in solution, wherein $\mathbf{1}_4$ contains one hexacoordinate and three pentacoordinate aluminums. ^1H, ^1H DQF COSY experiments confirm the presence of $\mathbf{1}_4$ in solution and VT ^{13}C NMR spectral studies reveal the occurrence of an interesting dynamic behavior of $\mathbf{1}_4$ in which the three pentacoordinate alumatranes rotate around their pseudo-3-fold axes while remaining fluxionally oxygen-bridged to the central cage containing the hexacoordinated aluminum. Solid-state ^{27}Al and ^{13}C NMR and Al_{2p}, N_{1s}, and O_{1s} XPS evidence has also been gathered that is consistent with the tetrameric structure of solid alumatrane.

Introduction

Alumatrane, depicted as the monomer **1**,[1] has been the subject of several studies,[2–5] and its oligomeric properties have been discussed in three reviews.[6–8] In benzene solution, a cryoscopic



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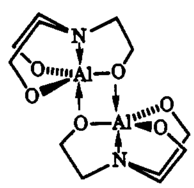


$\mathbf{1}_2$

determination of the molecular weight[2] indicated the degree of association to be octameric, while an ebullioscopic measurement[3] suggested hexameric behavior for **1**. A mass spectroscopic (EI 70 eV) study[4] clearly revealed the stability of the dimer $\mathbf{1}_2$ and ruled out the presence of higher oligomers in the gas phase. The crystal and molecular structure of $\mathbf{1}_4 \cdot 3i\text{-PrOH} \cdot 0.5C_6H_6$[5] established the tetrameric nature of **1** in the solid state.

Alumatrane has been prepared by several methods. Transesterification of aluminum alkoxide with triethanolamine can be carried out with or without a solvent[2–4] according to eq 1.

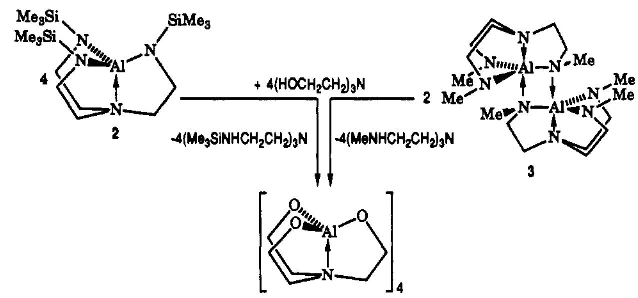
$$n\text{Al(OR)}_3 + n(\text{HOCH}_2\text{CH}_2)_3\text{N} \longrightarrow [\text{Al(OCH}_2\text{CH}_2)_3\text{N}]_n + 3n\text{ROH} \quad (1)$$

$$\text{R} = i\text{-Pr}, i\text{-Bu}$$

Triethylaluminum also reacts with triethanolamine according to eq 2 to afford alumatrane.[7,8]

$$n\text{Al(C}_2\text{H}_5)_3 + n(\text{HOCH}_2\text{CH}_2)_3\text{N} \longrightarrow [\text{Al(OCH}_2\text{CH}_2)_3\text{N}]_n + 3n\text{C}_2\text{H}_6 \quad (2)$$

Scheme I



In our reinvestigation of this compound, we employed the alcoholysis of tris(dimethylamido)aluminum with triethanolamine and also the transligation of **2**[9] and **3**[9] by triethanolamine (Scheme I); a reaction we recently reported for azagermatranes.[10] Using mild chemical ionization by NH_3 gas, we have been able to observe both $\mathbf{1}_2$ and $\mathbf{1}_4$ in the gas phase by mass spectroscopy. A paucity of reliable NMR data in the literature led us to perform a multinuclear NMR study on alumatrane which revealed the presence of the tetramer $\mathbf{1}_4$ in solution. An interesting dynamic behavior of $\mathbf{1}_4$ was observed at elevated temperatures in a ^{13}C VT NMR study. Solid-state NMR and XPS data consistent with the tetrameric solid-state structure[5] and with the tetrameric structure found in solution by our NMR studies are also presented.

Experimental Section

All reactions were carried out under argon with the strict exclusion of moisture using Schlenk or drybox techniques.[11] Solvents were dried over and distilled from Na/benzophenone under nitrogen. Deuterated solvents were dried over and distilled from CaH_2 under an argon atmosphere. The starting material $[Al(NMe_2)_3]_2$ was prepared using the published procedure,[12a] and it was characterized by ^1H, ^{13}C, and ^{27}Al NMR spectroscopy.[12b] Triethanolamine (Fisher) was vacuum-distilled at 174–175 °C at 0.03 Torr prior to use. Alumaazatranes **2** and **3** were prepared according to our procedure published elsewhere.[9]

Solution NMR spectra were recorded in sealed 5-mm NMR tubes on a Varian VXR 300 spectrometer with deuterated solvents as an internal lock. ^1H (299.94 MHz) and ^{13}C (75.429 MHz) spectra were referenced to the corresponding TMS signals. A ^1H,^1H DQF COSY NMR spectrum

(1) 2,8,9-Trioxa-5-aza-1-alumatricyclo[3.3.3.0[1,5]]undecane.

(2) Hein, F.; Albert, P. W. *Z. Anorg. Allg. Chem.* **1952**, *269*, 67.
(3) Mehrotra, R. C.; Mehrotra, R. K. *J. Indian Chem. Soc.* **1962**, *39*, 677.
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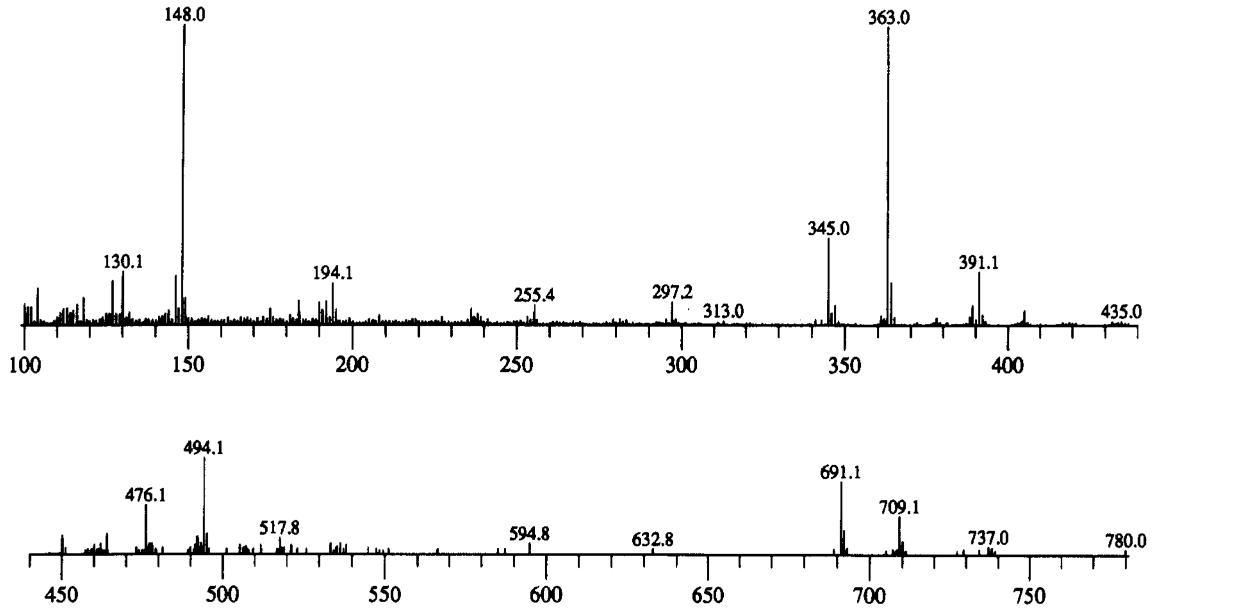


Figure 1. Negative-ion NH_3 CI mass spectrum of alumatrane. The enhancement factor of the lower trace is 5 times that of the upper trace.

was acquired with 1024 × 512 data points and was zero-filled to 1024 × 1024 data points before weighting by a sine bell function and Fourier transformation. A digital resolution of 1.1 Hz/point was obtained. ^{27}Al (78.157 MHz) spectra were referenced to the external standard 0.2 M $Al(ClO_4)_3$/0.1 M $HClO_4$ in D_2O. The chemical shifts were corrected for the difference in chemical shift between D_2O and the lock solvent used. The background signal,[13] which was found as a broad peak at ~61 ppm ($\Delta\nu_{1/2}$ = 4100 Hz at 30 °C), did not interfere with our spectra owing to its low intensity.

Solid-state NMR spectra were recorded on a Bruker MSL 300 instrument. ^{27}Al (78.205 MHz) MAS spectra were referenced to the signal from a 1 M aqueous solution of $Al(NO_3)_3$. A 90° pulse length of 4 μs and a relaxation delay of 1 s were used. A spinning rate of 3.5 kHz was employed. ^{13}C (75.470 MHz) CP MAS spectra were referenced to the methyl signal of glycine at 43.0 ppm. A standard single-contact spin-lock cross polarization sequence with a proton 90° pulse length of 5.5 μs, a contact time of 3 ms, an acquisition time of 96 ms, and a relaxation delay of 6 s were used. The sample was spun at 3.7 and 3.9 kHz. Samples were packed in a nitrogen-filled glovebox into Teflon airtight rotor inserts which were placed in zirconia rotors with Kel-F or ceramic (in case of measurement at 100 °C) rotor caps.

X-ray photoelectron spectra (XPS) were recorded on a Perkin-Elmer 5500 Multitechnique System equipped with a non-monochromated Mg source (E = 1253.6 eV) operated at 300 W. The pressure in the vacuum chamber was less than 5 × 10^{-9} Torr. The energy resolution was 0.86 eV for Ag $3d_{5/2}$ emission, with a pass energy at 11.75 eV. The electron binding energies were calibrated, and charging was referenced to the C_{1s} signal of the methylene groups of alumatrane with the value set to 286.0 eV. The powdery sample of alumatrane was loaded on the probe in a nitrogen-filled glovebox.

Mass spectra were recorded on a Finnigan 4000 low-resolution (70 eV EI, NH_3CI) and a Kratos MS-50 high-resolution instrument. The masses are reported for the most abundant isotope present. IR spectra were taken on an IBM IR-98 FTIR spectrometer (4000–400 cm^{-1}) using Nujol mulls between KBr disks or as KBr pellets. Elemental analyses were carried out by Desert Analytics.

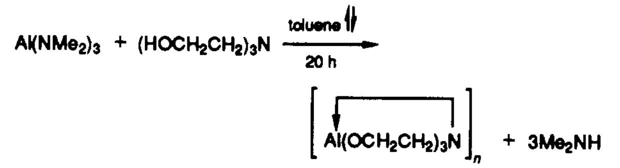
Preparation of Alumatrane. Method A. Solutions of $[Al(NMe_2)_3]_2$ (0.87 g, 5.5 mmol) in 40 mL of toluene and $(HOCH_2CH_2)_3N$ (0.84 g, 5.6 mmol) in 40 mL of toluene were added simultaneously within 20 min to 150 mL of toluene with vigorous stirring. The reaction solution was stirred at room temperature for 2 h and then heated to reflux for 20 h. After the mixture was cooled to room temperature, the solvent was removed in vacuum until ~50 mL remained and a white solid began to precipitate. The precipitation was completed by addition of 75 mL of ether. The resulting solid was filtered off, washed with 50 mL of ether, and dried in vacuum at 50 °C for 18 h, giving a 77% yield (0.73 g) of product. The product was sublimed at 280–290 °C at 5 × 10^{-3} Torr.

Method B. Triethanolamine (0.95 mL, 0.71 mmol) was added dropwise to a solution of **2** (2.75 g, 0.710 mmol) in 120 mL of toluene. After 79 h of stirring at room temperature, the solvent was removed under vacuum and 120 mL of ether was added. The slurry was stirred for 2 h and then filtered. The resulting white solid was washed with 15 mL of ether and dried under vacuum (2 × 10^{-3} Torr) at 95 °C for 10 h to give 0.77 g (64% yield) of product. ^1H NMR (toluene-d_8, −10 °C): δ 2.00–2.46 (m, 6H), 2.73 (dd, J = 1.5, 13.8 Hz, 1H), 3.12 (ddd, J = 4.2, 13.5, 13.5 Hz, 1H), 3.24 (m, 1H), 3.63–3.87 (m, 5H), 4.07 (ddd, J = 4.5, 10.2, 10.2 Hz, 1H), 4.50 (ddd, J = 2.3, 12.2, 12.2 Hz, 1H). In the ^1H NMR spectrum just described, couplings of 1.5–4.5 Hz represent $^3J_{HH(gauche)}$ values and those of 10.2–13.8 Hz denote $^2J_{HH(geminal)}$ and $^3J_{HH(trans)}$ values. ^{13}C NMR (toluene-d_8, −20 °C): δ 60.4, 58.4, 57.8, 56.4 (CH_2O groups), 54.3, 53.9, 53.2, 51.8 (CH_2N groups). ^{27}Al NMR: see Discussion and Table I. LRMS: see Discussion and Figure 1. IR (KBr pellet, 4000–400 cm^{-1}): ν 2960 s, 2913 s, 2868 s, 2817 s, 2718 w, 2689 w, 1478 vw, 1450 m, 1390 vw, 1374 w, 1364 sh, 1345 vw, 1323 w, 1266 m, 1243 vw, 1203 vw, 1161 vw, 1115 vs, 1094 vs, 1080 vs, 1045 m, 1014 vs, 920 s, 903 s, 874 s, 833 vw, 751 vw, 712 vs, 671 vs, 640 m, 617 s, 603 vs, 548 vs, 503 w, 491 vw, 449 v, 409 m. Anal. Calcd for $C_6H_{12}O_3NAl$: C, 41.62; H, 6.99; N, 8.09. Found: C, 41.99; H, 7.30; N, 8.12.

Reaction of 3 with Triethanolamine. Triethanolamine (0.01 mL, 0.08 mmol) was added to a solution of **3** (0.04 g, 0.09 mmol) in 0.5 mL of benzene-d_6. The gel-like precipitate which initially formed dissolved to give a clear solution within 40 min. ^1H and ^{13}C NMR spectra showed the presence of tetrameric $\mathbf{1}_4$ (see above), unreacted excess **3**,[9] and $(MeNHCH_2CH_2)_3N$[14] as the only species in the reaction solution.

Discussion

Syntheses. Alumatrane was prepared in good yield (77%) by the alcoholysis of $Al(NMe_2)_3$ with triethanolamine according to eq 3 in refluxing toluene. The alcoholysis of amides has proven



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to be a useful route to various metallic and metalloidal atranes.[7,15–17] Alumatrane apparently binds solvents very tightly,

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Table I. Solution and Solid-State ^{27}Al NMR Data for Alumatrane

medium	$\delta(^{27}Al)$ (ppm)	$\Delta\nu_{1/2}$ (Hz)^a	T (°C)	I^b
toluene-d_8	5.2 ± 0.1	75	30	1.0
		60	50	1.0
		45	100	1.0
	67 ± 1	2300	30	2.5
		2100	50	2.8
		1100	100	3.0
chloroform-d_1	4.9 ± 0.1	110	25	1.0
		70	50	1.0
	66 ± 1	2300	25	2.3
		1600	50	2.5
acetonitrile-d_3	5.2 ± 0.1	90	50	1.0
	66 ± 1	1100	50	2.7
solid state	3.3 ± 0.2^c	680^d	20	
		610^d	50	
		560^d	100	

^{a} A line-broadening factor of 10 Hz was applied. ^{b} Integral intensity. ^{c} The single maximum peak is accompanied by a spinning-sideband pattern of low intensity. ^{d} A line-broadening factor of 20 Hz was applied.

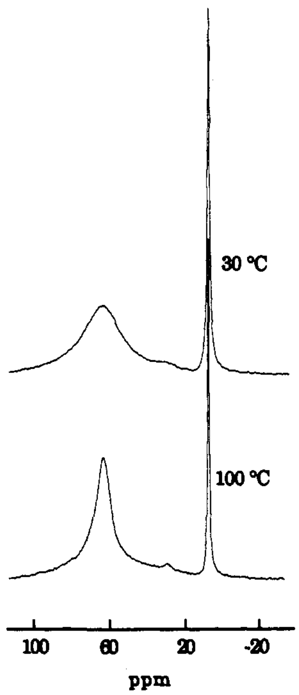

Figure 2. ^{27}Al NMR spectra of alumatrane in toluene-d_8 at 30 and 100 °C.

and long periods of drying under vacuum at elevated temperature were necessary to expel the last traces of solvent. The sample for elemental analysis was sublimed at 280–290 °C and 5 × 10^{-3} Torr, but no differences between sublimed and merely vacuum-dried material could be noted in the MS or ^{1}H NMR spectra.

An alternative method for the preparation of alumatrane is the transligation of azatranes **2**[9] and **3**[9] with triethanolamine in benzene or toluene according to Scheme I. This reaction is analogous to the transformation of azagermatranes to germatranes in the presence of triethanolamine, which was reported recently from our laboratories.[10] Although transligation is not the method of choice for the preparation of alumatrane, it is interesting to note the facility with which the central aluminum atom exchanges a tetradentate nitrogen ligand for an oxygen-containing one. This can undoubtedly be attributed to a higher Al–O bond energy compared with that of Al–N. Following the reaction of **3** with triethanolamine in benzene-d_6 by ^{1}H and ^{13}C NMR spectroscopy showed quantitative formation of alumatrane.

Mass Spectra. The electron-impact mass spectrum (70 eV) of alumatrane was identical with the published one,[4] except for

(17) Verkade, J. G. *Acc. Chem. Res.*, in press.

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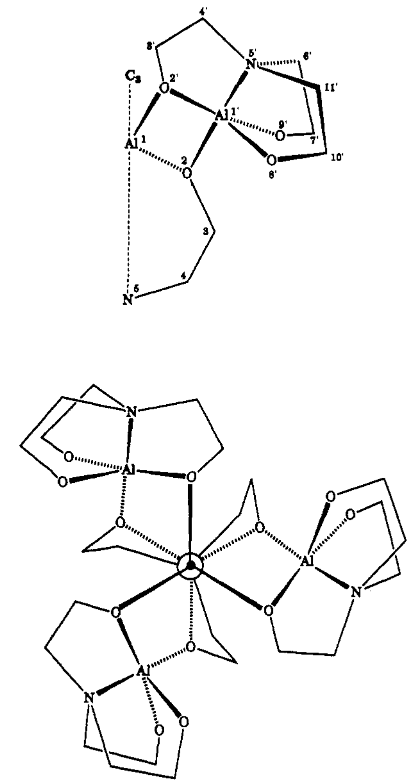
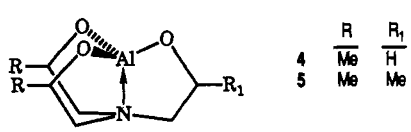


Figure 3. Side view of an equivalent one-third of tetrameric alumatrane $\mathbf{1}_4$ with the numbering scheme (a) and a view down the C_3 axis of tetramer $\mathbf{1}_4$ (b).

the presence of the peak at m/z 562. This peak brought to our attention the possible existence of a stable tetrameric ion in the gas phase. Using mild chemical ionization by ammonia gas, both dimeric $(\mathbf{1}_2\text{-H})^-$ and tetrameric $(\mathbf{1}_4\text{-H})^-$ ions were found in the negative-ion detection spectrum (Figure 1), together with cluster ions $(\mathbf{1}_2 + NH_3)^-$ and $(\mathbf{1}_4 + NH_3)^-$. The importance of NH_3 as an ionizing agent in this instance was demonstrated by the failure of our attempt to chemically ionize alumatrane by Ar gas.

Solution NMR Spectra. Two reports on the ^{27}Al NMR spectroscopy of alumatranes **1**, **4**, and **5** have appeared,[18,19]



claiming monomeric behavior for these compounds in chloroform solutions and a tetrahedral environment around the central aluminum atom. These conclusions are based on measured values of ^{27}Al chemical shifts of 122, 117, and 124 ppm for **1**, **4**, and **5**, respectively. Our results, which are in sharp contrast to those given in the previous studies,[18,19] are listed in Table I. As an example of our observations, the ^{27}Al NMR spectra of alumatrane at 30 and 100 °C in toluene-d_8 are shown in Figure 2. The main features of these spectra in all three solvents (toluene-d_8, chloroform-d_1, and acetonitrile-d_3) are a broad peak at approximately 66 ppm, a sharp signal at 5 ppm, and a small, broad resonance at 30 ppm. Although elevated temperatures reduce the quadrupolar relaxation rate of aluminum nuclei[20] ($I = {}^5/_2$), thus causing narrowing of the signals, the chemical shifts are

(18) Li, E.; Xu, G.; Wang, T.; Lu, K.; Wu, G.; Tao, J.; Feng, Y. *Huaxue Tongbao* **1985**, *6*, 22; *Chem. Abstr.* **1986**, *104*, 121849h.
(19) Wang, T.; Lu, K.; Wu, G. *Huaxue Tongbao* **1986**, *5*, 33; *Chem. Abstr.* **1987**, *105*, 202098k.
(20) Kriz, O.; Casensky; B.; Lycka, A.; Fusek, J.; Hermanek, S. *J. Magn. Reson.* **1984**, *60*, 375.

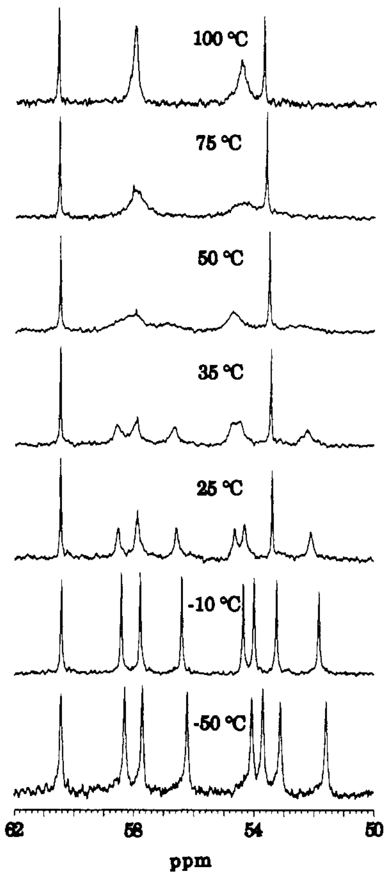


Figure 4. Variable-temperature ^{13}C NMR spectra of alumatrane in toluene-d_8.

Table II. XPS Data for Alumatrane

element[a]	binding energy (eV)[b]	peak area[c]	whm (eV)[d]
Al_{2p}	73.8	2.6	1.6
	74.6	1.0	1.7
C_{1s}	286.0	*e*	1.8
N_{1s}	400.1	3.3	1.7
	398.8	1.0	1.6
O_{1s}	531.0	1.0	1.6
	532.1	1.1	1.7

[a] Atomic composition of the sample surface: Al, 1.00; O, 3.37; N, 0.92; C, 5.75. [b] The C_{1s} peak was used as a reference. [c] Peaks were curve-fitted by a nonlinear least-squares optimization procedure and integrated by parabolic interpolation using the PHI software package. [d] Width at half-maximum. [e] The peak cannot be resolved into two components.

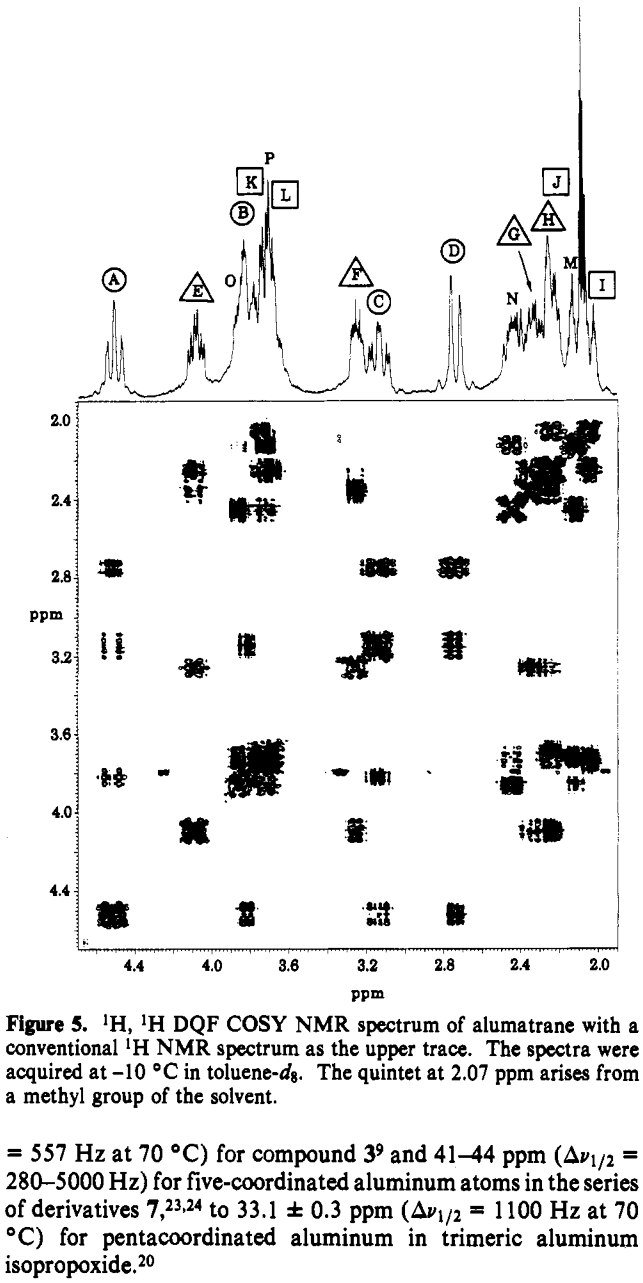
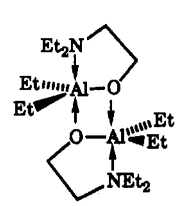


Figure 5. ^{1}H, ^{1}H DQF COSY NMR spectrum of alumatrane with a conventional ^{1}H NMR spectrum as the upper trace. The spectra were acquired at −10 °C in toluene-d_8. The quintet at 2.07 ppm arises from a methyl group of the solvent.

temperature-independent within experimental error. The integrated intensities at 100 °C for the signals at 67 and 5.2 ppm in toluene-d_8 are 3 and 1, respectively. These observations are consistent with the presence of tetramer $\mathbf{1}_4$[5] (Figure 3) in solution as a major species. The relatively sharp signal at 5.2 ppm belongs to a single hexacoordinated aluminum atom, whereas the broad signal at 67 ppm can be assigned to three equivalent pentacoordinated aluminum atoms. For comparison, the chemical shifts of hexacoordinated aluminum atoms in the series of tetrameric $[Al(OR)_3]_4$ (R = Et, *i*-Pr, *i*-Bu, *n*-Pent, *i*-Pent, *n*-Hex, c-Hex, benzyl)[20,21] range from 3 to 7.5 ppm and their line widths at the half-height range from 50 to 170 Hz at 70 °C. The assignment of the signal at 67 ppm is based on a comparison of ^{27}Al chemical shifts of the few compounds known to possess a pentacoordinated aluminum. Their shifts span a range from 112 ppm ($\Delta\nu_{1/2}$ = 7200 Hz at 27 °C) for compound **6**,[22,23] through 83 ppm ($\Delta\nu_{1/2}$ = 557 Hz at 70 °C) for compound **3**[9] and 41–44 ppm ($\Delta\nu_{1/2}$ = 280–5000 Hz) for five-coordinated aluminum atoms in the series of derivatives **7**,[23,24] to 33.1 ± 0.3 ppm ($\Delta\nu_{1/2}$ = 1100 Hz at 70 °C) for pentacoordinated aluminum in trimeric aluminum isopropoxide.[20]



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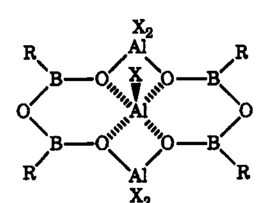

R = Me, Et, *n*-Bu, Ph
X = Cl, Br

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The small signal at 30 ppm can be tentatively assigned to a pentacoordinate aluminum atom in dimeric $\mathbf{1}_2$. The large line width of this signal even at 100 °C precluded reliable integration. Therefore no conclusions can be drawn as to a possible dynamic equilibrium between tetrameric $\mathbf{1}_4$ and dimeric $\mathbf{1}_2$ in solution. The difference in the ^{27}Al chemical shift between the pentacoordinate aluminum atoms in $\mathbf{1}_4$ and in $\mathbf{1}_2$ can be rationalized by postulating the presence of different degrees of transannulation in the two structures. A wide range of transannular bond distances

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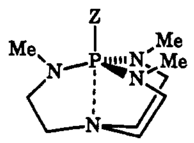
has recently been reported in a series of phosphorus analogues **8** where Z varies in electron-withdrawing power.[25]

Interestingly, compound **9** was found[26] to exhibit a ^{27}Al chemical shift of 68 ppm ($\Delta\nu_{1/2}$ = 3000 Hz) and to react with benzylamine affording a 1:1 adduct allegedly possessing pentacoordinated aluminum. However, two signals in the ^{27}Al NMR spectrum of that adduct were reported, namely, 66 ppm ($\Delta\nu_{1/2}$ = 800 Hz) and 3.9 ($\Delta\nu_{1/2}$ = 30 Hz), without explanation. These results can be rationalized by the presence of a tetramer $\mathbf{9}_4$ (66 and 3.9 ppm) analogous to $\mathbf{1}_4$ in solution.



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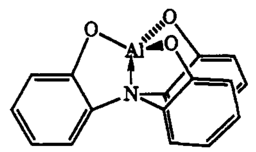

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Tetramer $\mathbf{1}_4$ was shown by X-ray means to possess C_3 symmetry in the solid state,[5] implying the presence of two enantiomers in the solid state and perhaps also in solution at low temperature. With a 3-fold axis as the only symmetry element, the tetrameric molecule of alumatrane features eight nonequivalent carbon atoms (Figure 3) which can be observed as separate peaks of approximately equal intensity in the ^{13}C NMR spectrum of $\mathbf{1}_4$ at −50 °C (Figure 4). When the temperature is raised, a complex dynamic process begins to take place. At lower temperatures (up to 50 °C), the prevailing process is assumed to be racemization via synchronous conformational flipping of the five-membered rings containing Al(1) and N(5) and the four-membered Al(1)–O(2)–Al(1′)–O(2′) rings, which averages the four signals from carbons 7′, 10′ and 6′, 11′ into two broad signals. A further temperature increase presumably accelerates the rotation of peripheral alumatrane units around the Al(1′)–N(5′) axes, ultimately averaging carbon signals 7′, 10′, 3′ and 6′, 11′, 4′ into two broad singlets at 100 °C. Signals arising from two carbons of the central alumatrane unit (i.e., 3, 4) remain as sharp singlets within the temperature range measured. This, together with the unchanged appearance of the ^{27}Al NMR spectrum from 25 to 100 °C, demonstrates that any dissociation of the tetramer into smaller units or any exchange of peripheral and central alumatrane units is undetectable in this novel fluxional process. The rotation of peripheral units can be accomplished by a temporary breakage of the Al(1)–O(2′) bond, and it is completed by a 120° flip around the Al(1′)–N(5′) axis, allowing O(8′) or O(9′) to bind to Al(1). We assume that all three peripheral units flip quickly and randomly one at a time, thus preserving, on the average, the C_3 symmetry of the tetramer. Simultaneous flipping of all three peripheral units would be expected to be inhibited on energy grounds.

The ^{1}H NMR resonances of alumatrane are broadened by the aforementioned dynamic process at higher temperatures, and they are complicated by the diastereotopicity of the methylene protons at lower temperatures (Figure 3). The ^{1}H NMR spectrum of a chloroform-d_1 solution of alumatrane at −30 °C exhibits four complicated multiplets centered at 2.86, 3.54, 3.79, and 4.05 ppm. Better separation of these signals was obtained by using toluene-d_8 as a solvent, and the spectrum is shown in Figure 5 together with the result of a ^{1}H, ^{1}H DQF COSY experiment. By the analysis of integrals of individual multiplets and the cross-peak pattern, sixteen proton signals can be identified and broken down into four groups: A, B, C, D/E, F, G, H/I, J, K, L/M, N, O, P, which belong to four inequivalent OCH_2CH_2N arms, as expected for the rigid tetramer $\mathbf{1}_4$. Further separation was not attained even at −50 °C, and only substantial broadening and overlapping of some of the signals occurred. An attempt to simplify the appearance of the ^{1}H NMR spectrum by recording it at 100 °C in toluene-d_8 was only partially successful. Signals A, C, and D (Figure 5) remained virtually unchanged, while the other signals broadened and overlapped into four broad signals at 2.41, 2.47, 3.67, and 3.86 ppm, thus precluding a complete assignment.

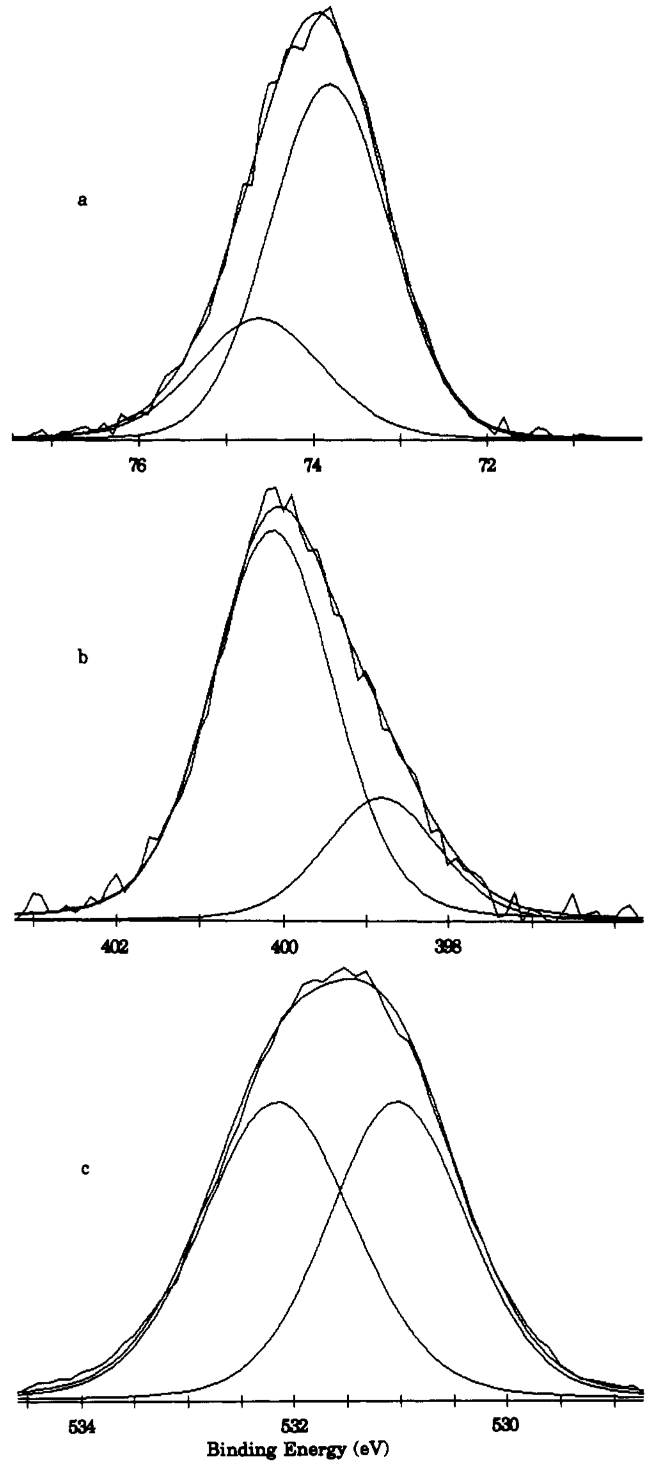

Figure 6. XPS spectra of alumatrane for Al_{2p} (a), N_{1s} (b), and O_{1s} (c) electrons.

Solid-State NMR Spectra. To relate our results from the solution NMR measurements to the known crystal and molecular structure of alumatrane,[5] we have recorded the ^{27}Al and ^{13}C solid state NMR spectra of alumatrane at 20, 50, and 100 °C. The ^{27}Al spectrum (Table I) features a relatively sharp peak at 3.3

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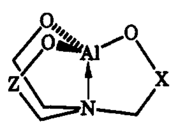
± 0.2 ppm with one maximum.[27] Its line width decreases as the temperature is raised, while the value of the chemical shift remains constant. On the basis of these observations, this peak can be reliably assigned to the hexacoordinated aluminum atom in an axially symmetrical environment in the central alumatrane unit (Figure 3). The lack of a signal for the pentacoordinate aluminum can be ascribed to a large asymmetry of the charge distribution around the five-coordinate aluminum nucleus, causing the quadrupole interaction to broaden the signal beyond the limit of detection. A ^{13}C CP MAS spectrum at 25, 50, and 100 °C shows, in each case, two broad overlapping signals at 58 and 55 ppm ($\Delta\nu_{1/2}$ = 300 and 490 Hz), which can be assigned to the CH_2N and CH_2O groups, respectively.

X-ray Photoelectron Spectra. The XPS data in Table II are consistent with the tetrameric structure of alumatrane in the solid state. The results of the nonlinear least-squares curve-fitting procedure for Al_{2p}, N_{1s}, and O_{1s} peaks are shown in Figure 6. The authors of the previously reported XPS study on alumatrane, as well as its analogues **10** and **11**, found one type



	X	Z
10	CH_2	C=O
11	C=O	C=O

of aluminum, oxygen, and nitrogen and concluded that these compounds were monomeric with tetracoordinate aluminum atoms.[28] As the atomic composition of the alumatrane sample surface shows (Table II), the Al:O:N:C ratio is close to the expected value 1:3:1:6. (It is reasonable to assume here that the surface can be considered to represent the bulk of the sample.) If contamination of the sample surface by moisture followed by subsequent hydrolysis of alumatrane had occurred during sample preparation, a dramatic increase in the oxygen content would have been expected. In our experiment, two kinds of nitrogen were identified in the ratio 1:3. Their N_{1s} binding energies of 398.8 and 400.1 eV correspond nicely to values for amine and ammonium types of nitrogen, respectively.[29] The O_{1s} peak was separated into two components of equal intensity. The high and low binding energy bands at 532.1 and 531.0 eV represent six tricoordinate and six dicoordinate oxygens in alumatrane $\mathbf{1}_4$, respectively. Because the separation between the two maxima for the Al_{2p} peaks is close to the resolution of the measurement, we tentatively assign the larger peak with the binding energy of 73.8 eV to the three pentacoordinate aluminum atoms and the smaller peak at 74.6 eV to the unique hexacoordinate aluminum. Values of binding energies of octahedrally coordinated aluminum species vary from 72.9 eV for $Al(acac)_3$, through 74.0 eV for γ-Al_2O_3, to 74.7 eV for corundum and spinel.[29] AlN with the wurtzite structure displays the value of 74.4 eV for tetrahedrally coordinated aluminum,[29] indicating little dependence of the Al_{2p} binding energy on coordination number.

Conclusions. According to our ^{27}Al, ^{1}H, and ^{13}C NMR results, alumatrane is tetrameric in solution. This contrasts earlier molecular weight measurements based on colligative properties of solutions, indicating hexameric[3] and octameric behavior,[2] and a monomeric structure based on a single broad peak observed in an ^{27}Al NMR spectrum.[18,19] The solution NMR data we obtain for $\mathbf{1}_4$ are consistent with the tetrameric structure found in the solid state,[5] with the added feature that three peripheral alumatrane units of the tetramer rotate around their 3-fold axes while remaining fluxionally oxygen-bridged to the central unit. Our CI mass spectra clearly reveal the presence of $\mathbf{1}_4$ in the gas phase, while an earlier EI study[4] ruled out gas-phase oligomers above $\mathbf{1}_2$.

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