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^{27}Al NMR spectroscopy of ethylaluminum halides

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Abstract

^{27}Al NMR data for the dimeric compounds of the $(Et_{3-n}AlX_n)_2$ type ($n = 0$–3; X = Cl, Br and I) have been determined. A characteristic U-shaped relationship between the ^{27}Al NMR chemical shift and the value of n was found, together with a correlation between available ^{27}Al nuclear quadrupole coupling constants (NQCC) and the $\delta(^{27}Al)$ NMR values for four-coordinate Al atoms. On the bases of this correlation, it is concluded that the U-shaped relationship arises principally from the changes in the ground-state charge-distribution at Al nucleus.

Introduction

Although the ethylaluminum halides $(Et_{3-n}AlX_n)_n$, ($n = 1$, 1.5, and 2; X = Cl, Br and I) have been widely used in the preparation of the Ziegler–Natta catalytic systems, ^{27}Al NMR spectroscopy has not been used for their more detailed study. Recently, the $\delta(^{27}Al)$ values for ethylaluminum chlorides, namely 140 ppm [1] and 122 ppm [2] [relative to $Al(acac)_3$] for $EtAlCl_2$ and 167 ppm for Et_2AlCl [1,2], were reported. In terms of the general relationship between the coordination number of Al atoms and the corresponding chemical shifts [1–4], the chemical shifts of the four-coordinate Al atoms in dimeric ethylaluminum halides might be expected to fall within the range 40–180 ppm.

Results

The ^{27}Al NMR data for the ethylaluminum halides $(Et_{3-n}AlX_n)_2$, ($n = 1$ and 2) are presented in Table 1. This Table also includes the ^{27}Al NMR parameters for the aluminum halides ($n = 3$), for which the previously published parameters are inconsistent [3,5], and the ^{27}Al NMR data for triethylaluminum ($n = 0$) [2,6]. Except for $\delta(^{27}Al)$ of $(AlI_3)_2$, the chemical shift values for the other compounds lie in the expected range of 40–180 ppm. It can be seen that in the series of $(Et_{3-n}AlX_n)_2$ compounds, the difference between $\delta(^{27}Al)$ for $n = 1$ and $n = 3$ increases in the order X = Cl < Br < I. A plot of $\delta(^{27}Al)$ against n for $n = 0$–3 and for a given X, has a characteristic U-shape. When account is taken of the reproducibility of the observed ^{27}Al NMR data, the chemical shift values do not change significantly over

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Table 1

^{27}Al NMR spectroscopic data for 0.4 M solution of $(Et_{3-n}AlX_n)_2$ in n-heptane at 23°C

X	$n = 0$		$n = 1$		$n = 2$		$n = 3$	
	δ [a]	$W_{1/2}$ [b]	δ	$W_{1/2}$	δ	$W_{1/2}$	δ	$W_{1/2}$
–	155 [c]	1790 [c]	–		–		–	
	154 [d]	2550 [d]						
Cl	–		170	2850	130	1350	99	< 600 [e]
Br	–		171	3050	126	1500	77	470
I	–		170	3550	95	1650	−24	460

[a] Chemical shifts $\delta(^{27}Al)$ in ppm are relative to external aqueous $[Al(OH_2)_6]^{3+}$, $\delta(^{27}Al)$ 0.0 ppm. The $\delta(^{27}Al)$ values shown in the Table are an average of 20–30 measurements. The estimated accuracy of $\delta(^{27}Al)$ is ±2 ppm. [b] Line width at half height (Hz); the estimated accuracy for $W_{1/2}$ is ±80 Hz. [c] Ref. 6. [d] Ref. 2. [e] Measured in benzene.

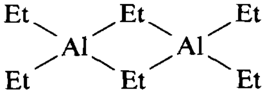
the temperature range 23–80°C, and are also independent of either the solvents used (n-heptane, toluene and xylene) or the concentration (0.1–1.5 mol · l^{-1}) of the solution. Interestingly, the identity of the bridging halogen X (Cl, Br, I) has no significant influence on the chemical shift of the ^{27}Al NMR signal of $(Et_2AlX)_2$ (Table 1). The line-widths ($W_{1/2}$) of the ^{27}Al NMR signals in the series of the compounds examined decrease with increasing n ($n = 1$–3) and at the same time a U-shaped dependence on n ($n = 0$–3) of the value of $W_{1/2}$ can be observed for a given X.

Discussion

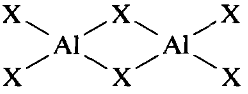
Samples of the compounds used for the measurements were prepared from triethylaluminum ($n = 0$) and the corresponding aluminum halide ($n = 3$), as depicted in Eq. 1:

$$r\text{AlEt}_3 + s\text{AlX}_3 \longrightarrow \text{Et}_{3r}\text{Al}_{r+s}\text{X}_{3s} \qquad (1)$$

Of 18 possible dimeric aluminum species that can be theoretically formed in the reaction shown in Eq. 1, we consider eight of them, namely I–VIII, to be important:



(I)



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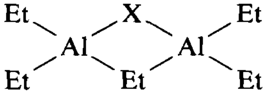

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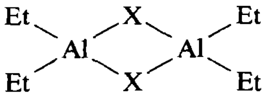

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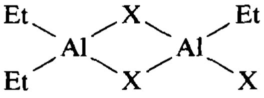

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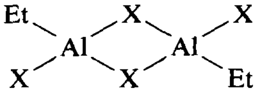

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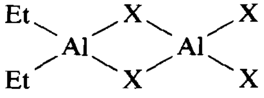

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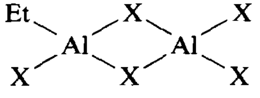
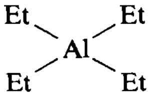
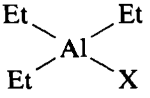


(VIII)

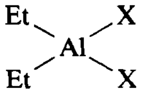
In the molecules I–VIII, the ^{27}Al nuclei exist in five different nearest-neighbour surroundings **A**–**E**:



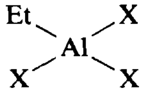
(A)



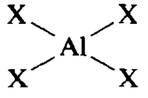
(B)



(C)



(D)



(E)

In all systems thus formed, i.e. regardless of the type of halogen, the solvent (n-heptane, xylene, toluene), the aluminum concentration (0.1–1.5 $\text{mol} \cdot \text{l}^{-1}$), and the temperature range (23–80 ° C), the following observations were made:

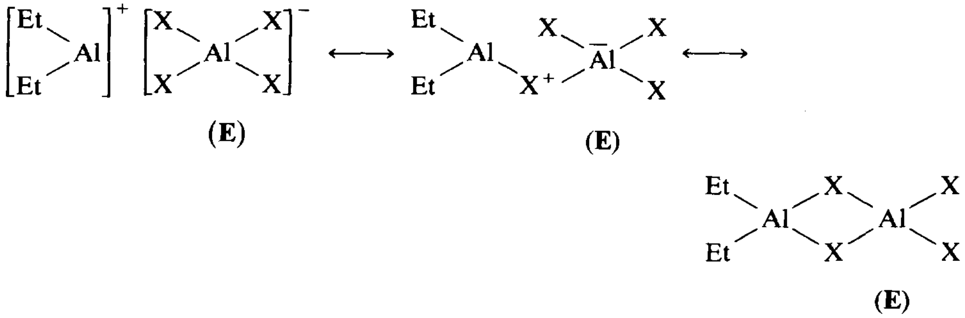
(a): For $r/s > 2$, the spectra showed a broad unsymmetrical peak consisting of two signals, one assigned to unchanged I, i.e. to environment type **A** (resonating at 155 ppm to lower field depending on the conditions [6]), and another one (at 170, 171, 170 ppm for X = Cl, Br and I, see Table 1), assigned to IV, i.e. to environment type **C**. The next ^{27}Al signal attributable to the mixed dimer III, i.e. to environment type **B**, which was previously reported for Cl and Me substituents [7], was not found under the conditions used in this work.

(b): For $r/s = 2$, the spectra exhibited only one signal (at 171, 170, 171 ppm, for X = Cl, Br and I, see Table 1), which was assigned to the compounds IV, i.e. to environment type **C**, (see above).

(c): For $2 > r/s > 0.5$, (including $r/s = 1$), the ^{27}Al NMR spectra displayed two signals assigned to environment type **C** (see above) and type **D** (at 131, 126, 95 ppm for X = Cl, Br and I, see Table 1). These are consequently assigned to compounds IV or V or, alternatively, to VI or V. The relative intensities of these resonances corresponded approximately to the starting r/s ratio.

The results (a–c) thus obtained by ^{27}Al NMR spectroscopy seem to confirm the previously reported conclusion [8], that the exchange reactions in Eq. 1 proceed non-randomly, being controlled by the enthalpic reaction term.

(d): For $r/s \cong 0.5$ the ^{27}Al NMR spectra of the samples studied (the analytically determined composition of which varied from $\text{AlEt}_{0.98}\text{Cl}_{2.02}$ to $\text{AlEt}_{1.01}\text{Cl}_{1.98}$) exhibited two signals: (i) a dominant resonance signal from environment type **D** (see above); and (ii) a relatively narrow signal from environment type **E**, (at 99, 77, −24 ppm for X = Cl, Br and I, see Table 1). The relative intensity of this narrow signal ranged from 4 to 6% for Cl and from 4 to 8% for Br and I, and was roughly independent of the concentration of samples, the temperature of measurement, and the solvent used. For stoicheiometric reasons (in the samples studied the analytically determined excess of II did not exceed 2 mol%), the ^{27}Al NMR spectra should have shown, together with a signal from environment type **E**, an equivalent signal from the environment type **C** (2–6%); (if the conclusions for cases a–c (above) hold, we can exclude the presence of unchanged I). A distinct signal from the environment type **C** was, however, not found under the conditions of the measurement; this may be because the surrounding in type **C** can be found in the compounds IV and V (above described), as well as in compound VII; in these molecules an Al atom bearing four halogen atoms might then occur in the following different arrangements:



(E) (E) (E)

The resulting ^{27}Al NMR signal of Et_2Al would then have an extremely large half-width and so be undetectable under the conditions of measurement.

Discussion of the U-shaped dependence of $\delta(^{27}Al)$ on n

The U-shaped dependence of δ on n has been described for the $H_{4-n}Al(OR)_n^-$ anions [9], and discussed in more detail for the ^{119}Sn and ^{29}Si nuclei in compounds of the R_nMY_{4-n} type, ($n = 1$–4; R = mostly alkyl, and Y stands for either a halogen or a group of distinctly different electronegativity compared to R) [10–16]. An exact explanation of this effect is not yet available. One explanation of the "sagging" dependence of the $\delta(^{13}C)$ on n in the series of $H_{4-n}CY_n$ ($n = 1$–4; Y = Cl, Br, I and OR) compounds that was based on changes in the diamagnetic contributions to the shielding of the nucleus [17] but most other authors [10–16] have sought an explanation of the U-shaped dependence in changes of the so-called "paramagnetic" contributions to the shielding [18]. Although there is a limited number of values in the present work concerning the $(Et_{3-n}AlX_n)_2$ series, Table 2 shows that there is also a "similar" U-shaped dependence of the ^{27}Al nuclear quadrupole coupling constants (NQCC) on n. Comparison of all the available ^{27}Al NQCC values for four-coordinate Al compounds [22] with the corresponding ^{27}Al NMR shifts (Table 1 and 2 together with 3) reveals a weak positive correlation ($r = 0.83$, statistically significant at 0.05 and 0.01 levels). In the light of this correlation, the shielding at the Al nucleus can be seen to depend principally on the local ground-state charge distribution [18–21]. The U-shaped dependence of δ on n can be therefore explained in simple terms by the changes in the populations of the p-AO's used by the Al atom in question for bonding, and changes in the internal angles between the bonds [22,23]. These two factors will be to some extent interdependent. Similarly the

Table 2

^{27}Al NQCC [a] (MHz) for some $(Et_{3-n}AlX_n)_2$ compounds at −196 °C

X	n			
	0	1	2	3
–	23.2	–	–	–
Cl	–	37.8	25.6	–
Br	–	38.2	–	13.9
I	–	38.0	–	–

[a] Ref. 22.

Table 3

Available ^{27}Al NQCC [a] (at −196 °C) and corresponding $\delta(^{27}\text{Al})$ [b] data for some organoaluminum compounds with four-coordinate Al atoms

Compound	NQCC (MHz)	δ [c] (ppm)
$(Me_2AlCl)_2$	36.4	180
$(Me_2AlOMe)_3$	20.9	152
$(Me_3Al)_2$	23.7	153
$(Et_2AlOEt)_2$	22.7	151
$((t\text{-}Bu)_3Al)_{1/2}$ [d]	45.4	255

[a] Ref. 22. [b] Refs. 1 and 2; 20–50% solutions in toluene-d_8 measured at 27–37 °C. [c] Chemical shifts $\delta(^{27}\text{Al})$ are relative to external standard sat. sol. $[Al(acac)_3]$ in benzene-d_6. [d] Extent of the association in the solid is unknown at −196 °C.

observed U-shaped dependence of $W_{1/2}$ on n in Table 1 arises from the dependence of $W_{1/2}$ on NQCC.

Experimental

Samples prepared by reaction 1, by heating of the mixture for 2 h, were sealed under argon in 10 mm diameter tubes, together with a capillary containing an aqueous solution of $[Al(OH_2)_6]^{3+}$, ($\delta(^{27}\text{Al}) = 0$ ppm). The ^{27}Al NMR spectra were recorded at 52.13 MHz with a Varian XL-200 spectrometer. To ensure the reproducibility of the ^{27}Al NMR data, optimum values of the alpha delay, acquisition time, number of transients, pulse width, transmitter offset and receiver gain were carefully selected to prevent distortion of the baseline. Under these conditions, the observed signals can be well represented by a Lorentzian type of curve, the parameters of which can be calculated by the non-linear least-squares method.

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