Structure of dichloroaluminium acetylacetonate in the solid state and in methylene chloride solution

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Abstract

The structure of dichloroaluminium acetylacetonate in a CH_2Cl_2 solution and in the crystalline state has been determined. On the basis of variable-temperature ^1H, ^{13}C and ^{27}Al NMR as well as of IR studies it has been found that the monomer $Cl_2Alacac$ occurs in equilibrium with a trimeric complex. The equilibrium depends on temperature and the dichloroaluminium acetylacetonate concentration in the solution. For a higher concentration and a lower temperature the trimeric complex is predominant. An X-ray structure determination revealed that in the solid state dichloroaluminium acetylacetonate occurs exclusively as the trimeric complex and its molecular structure comprises the $[Al_2Cl_2(acac)_3]^+$ cation and the $[AlCl_4]^-$ anion. The cation consists of two five-coordinated Al atoms interconnected by a double bridge of two oxygen atoms of two acac ligands. The third acac ligand is symmetrically bonded to one of the aluminium atoms. The two chlorine atoms bonded to each aluminium atom lie on the same side with respect to the plane of the $Al(O_2)Al$ bridges. Crystals of the trimer are monoclinic with space group $C2/c$ and cell constants $a = 18.81(1)$, $b = 11.30(2)$, $c = 27.70(1)$ Å, $\beta = 106.53(4)°$ and $Z = 8$. The structure was refined to a final $R = 0.067$ with 1925 observed reflections.

Introduction

In the previous papers the reactions of dialkyl- and dichloroaluminium acetylacetonates with Lewis bases were studied [1]. It was found that $R_2Alacac$ undergoes disproportionation with bases yielding a trialkylaluminium complex and aluminium triacetylacetonate (eqn. (1))

$$3R_2Alacac + 2B \longrightarrow 2R_3Al \cdot B + (acac)_3Al \quad (1)$$

The reaction of $Cl_2Alacac$ with Lewis bases proceeds differently. It results in the formation of a stable ionic complex (eqn. (2))

$$2Cl_2Alacac + 2B \longrightarrow [(acac)_2Al \cdot 2B]^+ \cdot [AlCl_4]^- \quad (2)$$

The different course of reactions (1) and (2) is explained by the low stability of the $[R_4Al]^-$ anion in comparison to that of the $[AlCl_4]^-$ anion, and the high stability of the $[(acac)_2Al \cdot 2B]^+$ cation, in which aluminium is six-coordinated.

Kroll *et al.* [2] obtained $Cl_2Alacac$ from the reaction of aluminium triacetlyacetonate with aluminium trichloride and methylaluminium dichloride with acetylacetone and found that it is a monomer in benzene solution. Dowbor [3] obtained $Cl_2Alacac$ from the reaction of $MeAlCl_2$ with acacH. She found the molecular weight of dichloroaluminium acetylacetonate increased with time. Our initial spectral studies and molecular weight measurements indicated that $Cl_2Alacac$ has a more complex structure than shown from the above works.

The purpose of this work was to study the structure of dichloroaluminium acetylacetonate in a methylene chloride solution and in the solid state.

Experimental

All experiments were carried out under dry nitrogen. Methylene chloride was dried over molecular

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sieves (type 4A), refluxed over Al_2O_3 (basic) and distilled before use Toluene was purified by distillation over a complex of potassium with benzophenone Aluminium chloride and aluminium triacetylacetone were high grade products and used without further purification Acetylacetone (2,4-pentanedione) was dried over molecular sieves and distilled before use Methylaluminium dichloride was prepared by the reaction of sesquimethylaluminium chloride and aluminium chloride, the sodium acetylacetonate was prepared by the reaction of sodium metal with acetylacetone in 96% alcohol

Preparation of dichloraluminium acetylacetonate

From the reaction of CH_3AlCl_2 with acacH

A total of 1 078 g (9 54 mmol) of CH_3AlCl_2 and 10 cm^3 CH_2Cl_2 were introduced into a Schlenk vessel and then 0 954 g (9 54 mmol) of acacH in 10 cm^3 of CH_2Cl_2 was dropped in at −78 °C under vigorous stirring The reaction proceeds already at that temperature, which is indicated by gas evolution After dropping in acacH and a gradual rise of the temperature to room temperature, the solvent was distilled off The product was then isolated by distillation, b p 103 °C/Torr, yield 88% *Anal* Found Al, 13 65 Calc for $C_5H_7Cl_2AlO_2$ Al, 13 70% Dichloroaluminium acetylacetonate is an oily liquid upon distillation, very slowly undergoing crystallization at room temperature However, this compound undergoes crystallization immediately when the receiver is placed in a bath at *c* 70 °C

From the reaction of $AlCl_3$ with $Al(acac)_3$

A total of 11 83 g (88 6 mmol) of $AlCl_3$ and 14 35 g (44 3 mmol) of $Al(acac)_3$ were introduced into a Schlenk vessel Then 30 cm^3 of CH_2Cl_2 was added at 0 °C and the reaction temperature was raised to room temperature while stirring The reaction was carried out for 1 h Further procedure was as above The yield of the distilled product is usually above 85% An identical result was obtained when carrying out the reaction in toluene

From the reaction of $AlCl_3$ with acacNa

The synthesis was carried out as described above, for 12 h A total of 4 13 g (30 9 mmol) of $AlCl_3$, 3 77 (30 9 mmol) of acacNa and 20 cm^3 of toluene as a solvent were used The yield of distilled product was *c* 45%

Crystals of dichloroaluminium acetylacetonate were grown by slow evaporation of a CH_2Cl_2 solution Because of the known instability of the compound in open air the crystal used for X-ray diffraction measurements was placed in a thin-walled quartz capillary tube under nitrogen Some silicon grease was used for fixing the position of the crystal in the capillary

Structure solution and refinement

A single-crystal CAD-Y (Enraf-Nonius) diffractometer and the ω–2ϑ scan were used for X-ray experiments

Numerical data on detailed X-ray data collection and refinement procedures are summarized in Table 1 It should be noted that rather significant deterioration of the crystal occurred during the experiment — this was manifested by as much as 50% decay of net intensity of control reflections The internal consistency index calculated after routine corrections (including correction for decay) was equal $R_{int} = 11\ 4\%$ The structure was solved by direct methods, using the SHELXS program [4a] Only two Al, two Cl and two O atoms were found on the best *E*-maps Several subsequent Fourier and difference Fourier syntheses have revealed all non-hydrogen atoms of the Al compound A few cycles of refinement with isotropic temperature factors employed of the thus obtained model yielded the conventional *R* factor value equal to 0 26 [4b] Empirical absorption correction (DIFABS [5]) and subsequent refinement with Al and Cl atoms refined with anisotropic temperature factors led to $R = 0\ 093$ ($R_w = 3\ 8/\sigma^2(F) = 0\ 075$) At this stage of the refinement residual maxima on difference Fourier maps were found at positions where possibly solvent CH_2Cl_2 molecules could be located Non-hydrogen atoms of CH_2Cl_2 were added in the final cycles of refinement and their site occupation factor (abbreviation s o f) refined, as one variable, to s o f = 0 16 Hydrogen atoms of the Al compound were not refined although were included in structure factor calculations with isotropic temperature factors assumed arbitrarily as equal to 1 3 times the temperature factor of a respective carbon atom

Spectroscopic measurements

NMR spectra were recorded on Bruker WM 400 (^{27}Al), Bruker WM 250 (^{27}Al, ^{13}C), Varian XL 100 (^{13}C) and Tesla 100 MHz (^1H) spectrometers. IR spectra were recorded on a Perkin-Elmer 225 spectrometer in nujol mulls (polyethylene film) and in CH_2Cl_2 solution (0 1 mm thick cell made of KBr plates)

Results

Dichloroaluminium acetylacetonate was obtained according to eqns (3)–(5)

$$CH_3AlCl_2 + acacH \longrightarrow Cl_2Alacac + CH_4 \tag{3}$$

TABLE 1 Data collection and structure analysis parameters

Molecular formula	$Al_3Cl_6O_6C_{15}H_{21}$[a]
Crystal size (mm)	0.15×0.2×0.5
Space group	*C*2/*c*
Unit cell	
a (Å)	18.81(1)
b (Å)	11.30(2)
c (Å)	27.70(1)
β (°)	106.53(4)
V (Å^3)	5644.4(8.7)
Z	8
Density (calc.) (g cm^3)	1.391[a]
Absorption coefficient (cm^{-1})	68.54[a]
Radiation	graphite monochromatized Cu Kα
Temperature (K)	295
No. reflections	
measured	1925
unique in structure analysis ($I > 2\sigma(I)$)	612
Final *R* values	
unweighted *R*	0.088
weighted R_w[b]	0.067
Residual extrema in final difference map (e/Å^3)	+0.43/−0.40

[a] Note: solvent molecules not included. [b] Weight = 3.1351/($\sigma^2(F)$ + 0.00001 $F \cdot F^*$)

$$2AlCl_3 + (acac)_3Al \longrightarrow 3Cl_2Alacac \qquad (4)$$

$$AlCl_3 + acacNa \longrightarrow Cl_2Alacac + NaCl \qquad (5)$$

The methods of synthesis (3) and (4) have been described earlier [2, 3]. Dichloroaluminium acetylacetonate was isolated from the post-reaction mixture by vacuum distillation as a white, crystalline solid or colourless oily liquid.

The structural analysis of dichloroaluminium acetylacetonate in the crystalline state revealed that this compound occurs as a trimeric complex and has an ionic character $[Al_2Cl_2(acac)_3]^+[AlCl_4]^-$. The cation $[Al_2Cl_2(acac)_3]^+$ consists of two five-coordinated aluminium atoms. One acetylacetonate ligand chelates one of the Al atoms and is not involved in bridging. The other two acetylacetonate ligands chelate the second Al atom and share one oxygen atom each forming oxygen bridges between two Al atoms. The two chlorine atoms are bonded to one Al atom each.

On the basis of variable-temperature ^1H, ^{13}C and ^{27}Al NMR as well as of IR studies we found that in a CH_2Cl_2 solution the trimeric complex of dichloroaluminium acetylacetonate occurs in equilibrium with the monomer $Cl_2Alacac$.

$$3Cl_2Alacac \rightleftharpoons [Al_2Cl_2(acac)_3]^+[AlCl_4]^- \qquad (6)$$

The equilibrium (6) depends on temperature and the concentration of dichloroaluminium acetylacetonate in the CH_2Cl_2 solution.

X-ray structure determination

The final atomic coordinates of the non-hydrogen atoms, some bond lengths and angles with their e.s.d.s for the trimeric complex are listed in Tables 2 and 3.

The molecular structure of the trimeric complex consists of the $[Al_2Cl_2(acac)_3]^+$ cation and the $[AlCl_4]^-$ anion. The cation has the two Al atoms interconnected by a double bridge of the two oxygen atoms numbered as O(1) and O(2) (Fig. 1). Chlorine atoms Cl(1) and Cl(2), the first bonded to Al(1) and the other to Al(2), lie on the same side with respect to the Al(1)–O(1)–Al(2)–O(2) molecular plane. Both Al(1) and Al(2) have similar, five-fold coordination of the tetragonal pyramid type. In each of the two pyramids oxygen atoms form the bases and a chlorine atom is located in the apical position. As may be deduced from the data listed in Table 4, the two O_4Cl pyramids around Al(1) and Al(2) are very much alike, the Al atoms deviating about 0.5 Å from the planes formed by the respective four oxygens. The Al–Cl axes of the pyramids form angles of 22 or 23° with the 'central' plane of the cation, i.e. with that formed by Al(1), Al(2), O(1) and O(2). Bonds Al(1)–Cl(1) and Al(2)–Cl(2) coincide with lines normal to the molecular planes formed by O(1), O(2), O(5) and O(6), and O(1), O(2), O(3) and O(4), respectively. The angle between the two lines is 46°. The $[Al_2Cl_2acac)_3]^+$ cation is asymmetric, although its general form has approximate symmetry

TABLE 2 Fractional coordinates (×10^4) for the non-hydrogen atoms for $[Cl_2Al_2(acac)_3][AlCl_4]$

Atom	*x/a*	*y/b*	*z/c*
Al(1)	8249(7)	3829(14)	4024(5)
Al(2)	6599(7)	3755(15)	3614(5)
Al(3)	7269(9)	- 1974(15)	3650(6)
Cl(1)	8676(6)	2261(10)	4407(4)
Cl(2)	6124(6)	2133(11)	3736(4)
Cl(3)	7417(7)	- 3733(12)	3391(4)
Cl(4)	6658(11)	- 2040(13)	4165(6)
Cl(5)	8305(9)	- 1211(15)	3978(5)
Cl(6)	6727(9)	- 0923(14)	3032(5)
O(1)	7478(12)	3344(20)	3490(10)
O(2)	7323(12)	4084(18)	4181(9)
O(3)	5947(15)	4848(23)	3773(11)
O(4)	6132(15)	4213(25)	2950(12)
O(5)	8783(15)	4111(25)	3605(9)
O(6)	8647(18)	5037(28)	4427(11)
C(11)	5970(27)	5081(39)	4227(21)
C(12)	6574(27)	4888(35)	4646(16)
C(13)	7192(29)	4460(35)	4640(18)
C(14)	5323(23)	5779(36)	4258(14)
C(15)	7803(20)	4232(32)	5094(12)
C(21)	6297(33)	3643(53)	2595(20)
C(22)	6852(31)	2850(43)	2631(19)
C(23)	7423(23)	2727(34)	3035(16)
C(24)	5682(24)	3889(39)	2072(15)
C(25)	8060(23)	1902(29)	3099(14)
C(31)	9268(30)	4896(46)	3630(19)
C(32)	9536(30)	5630(42)	4063(18)
C(33)	9097(37)	5696(51)	4404(23)
C(34)	9694(22)	4830(34)	3220(15)
C(35)	9405(25)	6627(34)	4800(15)

TABLE 3 Selected bond lengths and angles for $[Cl_2Al_2(acac)_3][AlCl_4]$

Bond lengths (Å)			
Al(1)–Cl(1)	2 104(18)	O(3)–C(11)	1 273(67)
Al(1)–O(1)	1 836(25)	O(4)–C(21)	1 285(71)
Al(1)–O(2)	1 933(29)	O(5)–C(31)	1 260(61)
Al(1)–O(5)	1 767(34)	O(6)–C(33)	1 143(75)
Al(1)–O(6)	1 787(33)	C(11)–C(12)	1 391(61)
Al(2)–Cl(2)	2 108(21)	C(11)–C(14)	1 473(68)
Al(2)–O(1)	1 841(29)	C(12)–C(13)	1 264(74)
Al(2)–O(2)	1 801(24)	C(13)–C(15)	1 465(53)
Al(2)–O(3)	1 879(33)	C(21)–C(22)	1 358(82)
Al(2)–O(4)	1 872(33)	C(21)–C(24)	1 600(62)
Al(3)–Cl(3)	2 158(22)	C(22)–C(23)	1 320(60)
Al(3)–Cl(4)	2 072(28)	C(23)–C(25)	1 488(57)
Al(3)–Cl(5)	2 088(22)	C(31)–C(32)	1 427(68)
Al(3)–Cl(6)	2 095(21)	C(31)–C(34)	1 567(77)
O(1)–C(23)	1 418(51)	C(32)–C(33)	1 423(96)
O(2)–C(13)	1 427(59)	C(33)–C(35)	1 511(69)
Bond angles (°)			
O(1)–Al(1)–O(2)	70 7(11)	Al(1)–O(5)–C(31)	129 0(29)
O(1)–Al(2)–O(2)	73 6(12)	Al(1)–O(6)–C(33)	130 4(39)
O(1)–Al(2)–O(4)	94 7(14)	Al(2)–O(1)–C(23)	116 6(23)
O(2)–Al(2)–O(3)	92 4(13)	Al(2)–O(2)–C(13)	124 0(27)
O(5)–Al(1)–O(6)	93 3(15)	Al(2)–O(3)–C(11)	121 8(30)
Cl(1)–Al(1)–O(6)	107 2(12)	Al(2)–O(4)–C(21)	117 7(34)
Cl(1)–Al(1)–O(5)	106 0(12)	O(2)–C(13)–C(12)	121 2(42)
Cl(1)–Al(1)–O(2)	104 6(10)	O(3)–C(11)–C(12)	125 6(47)
Cl(1)–Al(1)–O(1)	104 8(11)	C(11)–C(12)–C(13)	125 8(45)
Cl(2)–Al(2)–O(4)	107 2(12)	O(1)–C(23)–C(22)	122 5(40)
Cl(2)–Al(2)–O(3)	101 5(12)	O(4)–C(21)–C(22)	128 5(49)
Cl(2)–Al(2)–O(2)	106 8(11)	C(21)–C(22)–C(23)	123 7(49)
Cl(2)–Al(2)–O(1)	104 8(11)	O(5)–C(31)–C(32)	122 2(47)
Al(1)–O(1)–Al(2)	108 7(14)	O(6)–C(33)–C(32)	125 6(54)
Al(1)–O(2)–Al(2)	106 2(13)	C(31)–C(32)–C(33)	117 1(49)

The Al–O bond distances in the molecule are within the 1 77–1 93 Å range, the averaged value being 1 84 Å and not much different from the Al–O bond length found by Hon and Pfluger [6] in aluminium triacetylacetonate (1 892(6) Å) Our results have, by modern standards, very high e s d s This is certainly due to critically low data/parameters ratio in structure refinement (and no reasonable improvement of the model was attained when trying to refine the structure using all, i e including 'unobserved' data) For this reason discussion of geometry of the $[Al_2Cl_2(acac)_3]^+$ cation reported here is rather limited However the obtained Al–O bond distances indicate non-equivalency of the AlOAl bridges The bridge involving the O(1) atom is quite symmetric and the bonds to Al(1) and Al(2) are almost equal (1 836(25) and 1 841(29) Å) (difference = 0 005, σ_{diff} = 0 038), mostly a bridging atom gives two different O–M distances and the shorter one is to the M atom which is chelated by the ligand to which the bridge atom belongs [7] The second bridge is asymmetric (difference = 0 133, σ_{diff} = 0 037), similar inequalities in the Al–O bond lengths were described for the oligomeric metal acetylacetonates [7] This bridging unit possesses the longest Al–O bond (Al(1)–O(2), 1 933(29) Å) Thus, there is an indi-

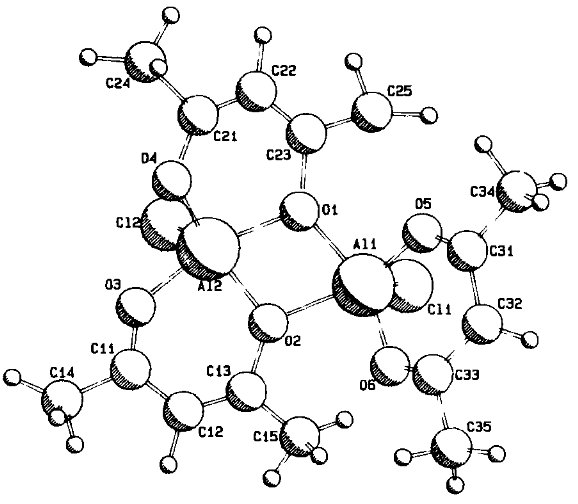

Fig 1 PLUTO drawing and atom numbering scheme for $[Al_2Cl_2(acac)_3]^+$ cation

TABLE 4 Deviation (Å) of atoms from least-squares plane for $[Al_2Cl_2(acac)_3]^+$

Atom[a]	Deviation (Å)	Atom[a]	Deviation (Å)	Atom[a]	Deviation (Å)
Plane 1		Plane 4		Plane 7	
Al(1)*	0.033	C(31)*	0.076	C(11)*	−0.069
Al(2)*	0.039	C(32)*	−0.072	C(12)*	−0.050
O(1)*	−0.076	C(33)*	0.069	C(13)*	0.012
O(2)*	−0.059	O(5)*	−0.009	C(14)*	0.105
O(3)	0.879	O(6)*	−0.004	C(15)*	−0.021
O(4)	1.116	C(34)	0.017	O(2)*	0.026
O(5)	0.879	C(35)	0.067	O(3)*	−0.036
O(6)	0.957				
Cl(1)	−1.919				
Cl(2)	−1.885				
Plane 2		Plane 5		Plane 8	
C(11)*	−0.008	O(1)*	−0.051	C(21)*	0.018
C(12)*	−0.006	O(2)*	0.045	C(22)*	−0.075
C(13)*	0.016	O(3)*	−0.063	C(23)*	−0.003
O(2)*	−0.003	O(4)*	0.069	C(24)*	0.139
O(3)*	0.004	Al(2)	−0.480	C(25)*	−0.062
C(14)	0.212			O(1)*	0.059
C(15)	−0.034			O(4)*	−0.093
Plane 3		Plane 6		Plane 9	
C(21)*	0.107	O(1)*	0.005	C(31)*	0.066
C(22)*	−0.027	O(2)*	−0.004	C(32)*	−0.099
C(23)*	−0.021	O(5)*	−0.005	C(33)*	0.046
O(1)*	0.008	O(6)*	0.006	C(34)*	0.003
O(4)*	−0.018	Al(1)	−0.494	C(35)*	0.024
C(24)	0.307			O(5)*	−0.001
C(25)	−0.129			O(6)*	−0.011

[a] Atoms used to define the l.s. plane are designated by asterisks.

cation how the bridge system can be cleaved, since the longest bond is probably the most reactive and breaking it is the first step of intra- and intermolecular rearrangement reactions in solution.

From Fig. 1 it seems clear that there are two significantly different acac moieties in the $[Al_2Cl_2(acac)_3]^+$ cation. One acac ligand chelates the Al(1) atom and is not involved in bridging. The other two chelate the Al(2) atom and share on oxygen atom each, O(1) and O(2), with Al(1). For the reason mentioned above it is hard to discuss the non-equivalency of the three acac moieties in terms of possible differences in bond lengths and angles. It seems interesting however, to note that the differences between the C–O as well as the C–C distances are significant (in spite of individual e.s.d.s (Table 3)). They indicate non-equivalency of related atoms and bond polarization in bridging acac ligands (this is in accordance with the ^{13}C NMR data, see later). For example, the average distances within the two bridging ligands for C–O(bridging) and C–O(non-bridging) are 1.423 and 1.274 Å, respectively (difference = 0.149, $\sigma_{diff} = 0.088$). Besides, as may be seen from the data listed in Table 4, the carbon atoms of the methyl groups C(14) and C(24) deviate rather significantly from the molecular planes formed by their respective chelate ring acac atoms. This may also suggest significant differences in bonding between the symmetrical and asymmetrical acac rings.

The tetrachloroaluminium anions show no indication of order in the manner they dispose themselves around the cation complexes. The interionic contacts to $[Al_2Cl_2(acac)_3]^+$ range upwards from 3.37 Å for (Al(1) Cl(3) and 3.40 Å for Al(2) Cl(3)). However, the Al(3)–Cl(3) distance (2.158(22) Å) within the tetrachloroaluminium moiety is the longest one, the other Al–Cl distances within the anion range from 2.072–2.095 Å (Table 3).

Molecular packing, as shown in Fig. 2, demonstrates also the positions of the solvent molecules. These seem to be loosely held in the crystal structure. The refined s.o.f. value (16%) and deterioration of the crystal during X-ray experiments seem to be in favor of this suggestion.

^1H NMR spectra

The variable-temperature ^1H NMR spectra of dichloroaluminium acetylacetonate in a methylene

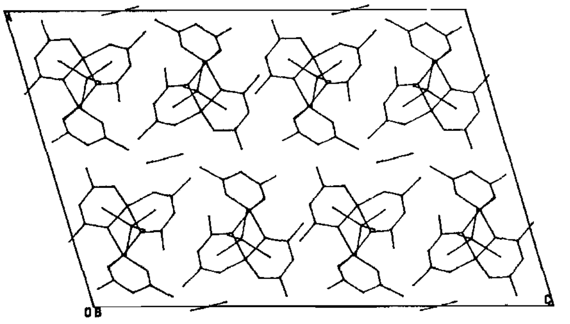

Fig 2 Projections of the crystal structure of $[Al_2Cl_2(acac)_3][AlCl_4]$ with CH_2Cl_2 molecules

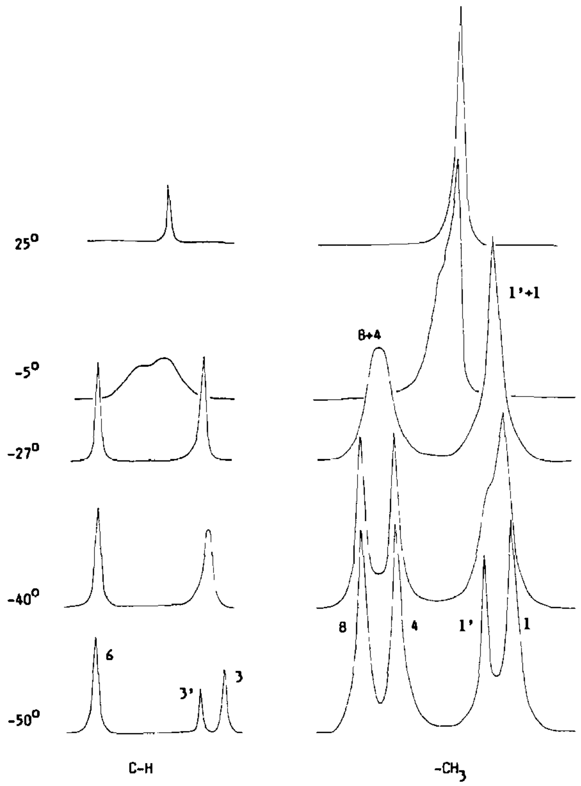

Fig 3 The variable-temperature ^1H NMR (100 MHz) spectra of dichloroaluminium acetylacetonate in CD_2Cl_2 solution (conc 15%)

chloride solution are presented in Fig 3 and the values of chemical shifts are collected in Table 5 The signals are assigned to the proton sites defined in Fig 4

At −50 °C in the ^1H NMR spectrum four and three signals occur for the CH_3 and CH protons, respectively The signals (1') and (3') of the 6 1 integration, are attributed to protons of two equivalent CH_3 groups and the CH group in the $Cl_2Alacac$ monomer (Fig 4(a)) Signals (1), (4) and (8) of the 1 1 1 integration are attributed to CH_3 protons in the $[Al_2Cl_2(acac)_3][AlCl_4]$ trimeric complex (Fig 4(b)) Signals (3) and (6) of the 1 2 integration correspond to the CH protons in the trimeric form It appeared from the relative ratio of CH_3 and CH signals and from the observed lineshape changes in the spectra with increase of temperature (Fig 3) that signal (1) corresponds to protons of two methyl groups in a symmetrical bidentate ligand, and signals (4) and (8) to non-equivalent methyl groups of the asymmetrical ligands Signal (4), at higher field, was assigned to the methyl groups bonded to carbons of the enol groups (see ^{13}C NMR study) and signal (8) corresponds to the methyl groups bonded to carbonyl carbons The CH_3 signals of the trimeric complex are slightly broader than that of the monomer even at −90 °C This indicates that pairs of methyl groups responsible for the signals in the trimer have a very similar environment

An increase of temperature from −50 to 25 °C causes a gradual broadening and then overlapping of the signals (Fig 3) The observed temperature dependence probably results from two exchange processes intramolecular rearrangements in the trimeric complex and intermolecular exchange reactions between the trimeric complex and the monomer

The relative ratio of signals of both forms of dichloroaluminium acetylacetonate depends on the concentration in solution The signals of the monomer clearly dominate for a low concentration at −50 °C With an increase in concentration, their intensity decreases considerably For example, for the concentrations of 5 4 and 20 4% the relative intensity ratio of CH_3 signals of the monomer and trimeric complex are 4 5 1 and 0 4 1, respectively An increase in concentration causes a shift of the equilibrium described by eqn (6) towards the right The position of equilibrium of reaction (6) depends also on temperature The amount of the monomer decreases and that of the trimeric complex increases with decreasing temperature This is indicated by the change of the relative signal intensities with a change of temperature For a solution of 8 4% concentration at −10 °C the ratio of intensity of the CH_3 signals (4+8) to (1+1'), is 1 2 8, at −27 °C 1 2 1, while at −40 °C the ratio of intensities has dropped to 1 1 5 Below −50 °C the intensity of signals does not change, which indicates a slowdown of reaction (6) From the known solution composition, relative signal areas, and their temperature dependence over the temperature range −5 to −40 °C, the thermodynamic parameters for reaction (6) were calculated They are $\Delta H° = -11 9 \pm 1 2$ kJ mol^{-1}, $\Delta S° = -48 8 \pm 2$ J K^{-1} mol^{-1} and $K = 0 38 \pm 0 02$ (25 °C) A typical plot of $\log K$ versus $1/T$ derived from the temperature dependence of the relative areas of the proton methyl signals is shown in Fig 5

TABLE 5 ^{1}H NMR data (ppm) for dichloroaluminium acetylacetonate in dichloromethane[a]

Temperature (°C)	CH			CH$_3$			
	H(3′)	H(3)	H(6)	H(1′)	H(1)	H(4)	H(8)
−50	6 09	6 01	6 41	2 21	2 14	2 50	2 61
25		6 12			2 25		

[a] CH$_2$Cl$_2$ as an internal standard δ(H) = 5 33, concentration 8 4%

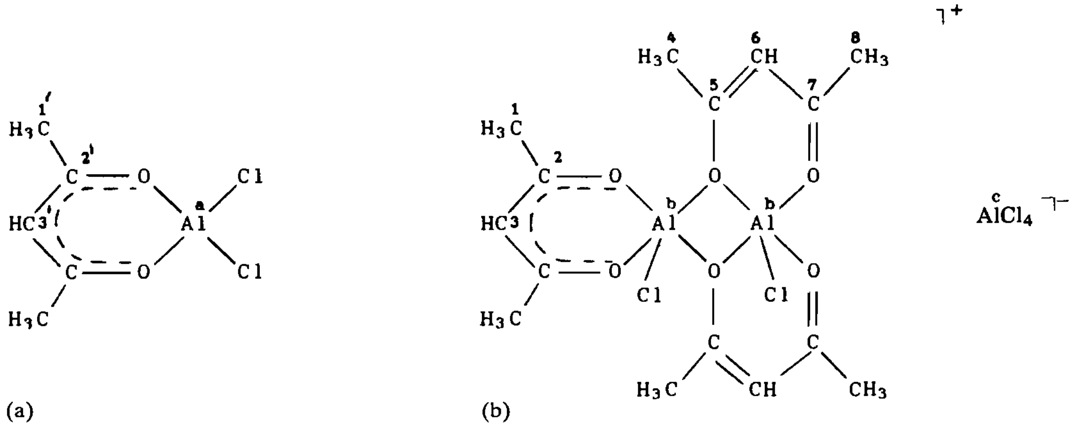

Fig 4 Schematic drawing of the two structure forms of the dichloroaluminium acetylacetonate occurring in CH$_2$Cl$_2$ solution (a) monomer Cl$_2$Alacac, (b) trimeric complex [Cl$_2$Al$_2$(acac)$_3$]$^+$[AlCl$_4$]$^-$ Designation of proton, carbon and aluminium atoms corresponds to the assignments in Tables 5 and 6 and Figs 3, 6 and 7

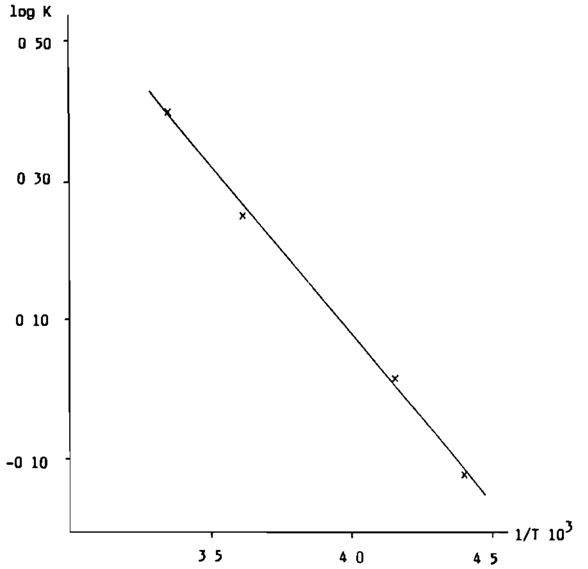

Fig 5 Plot of log K vs $10^3/T$ for reaction (6) The K values were derived from the relative areas of the CH$_3$ proton signals

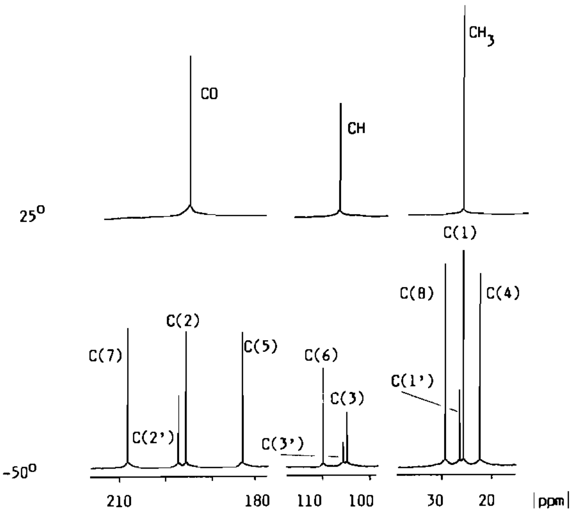

Fig 6 ^{13}C NMR (62 9 MHz) spectra of dichloroaluminium acetylacetonate in CH$_2$Cl$_2$ solution at 25 and −50 °C (conc 20%)

^{13}C NMR spectra

^{13}C NMR spectra of dichloroalumininium acetylacetonate in a CH$_2$Cl$_2$ solution at 25 and −50 °C are presented in Fig 6 The signals are assigned to the carbon sites defined in Fig 4 and in the discussion below Chemical shifts corresponding to the assignments are tabulated in Table 6

At −50 °C the CH$_3$ and CH regions consist of four and three signals, respectively, which corre-

TABLE 6 ^{13}C NMR data (ppm) for dichloroaluminium acetylacetonate in dichloromethane[a]

Temperature (°C)	CO				CH			CH_3			
	C(2′)	C(2)	C(5)	C(7)	C(3′)	C(3)	C(6)	C(1′)	C(1)	C(4)	C(8)
−50	197 5	195 7	183 5	208 4	105 8	105 5	110 1	26 5	26 3	24 9	28 8
25			196 9			106 6				26 5	

[a] C_6D_6 as an internal standard

sponds to the number of signals in the ^1H NMR spectrum Employing the considerations discussed at length for the ^1H NMR data, these signals can be readily assigned as follows C(1′) and C(3′) to the symmetrical bidentate ligand in the monomer, C(1) and C(3) to the symmetrical bidentate ligand in the trimeric complex, C(1), C(4) and C(8) to two asymmetrical ligands (bridging ligands) in the trimeric complex One methyl carbon signal and one methine carbon signal correspond to each of the symmetrical bidentate ligands However, two methyl carbon signals and one methine carbon signal correspond to two asymmetrical ligands in the trimeric complex The relative intensities of methyl carbon signals C(1) C(4) C(8) in the trimeric complex are close to 1 1 1 and of the methine carbon signals C(3) C(6) are close to 1 2

In addition, four signals due to carbon atoms bonded to oxygen atoms occur in the spectrum Signals C(2′) and C(2) at chemical shifts comparable to those of CO carbons in chelated acetylacetonate complexes of aluminium [2a], were assigned to bidentate symmetrical ligands in the monomer and trimeric complex The signal C(7) at 208 4 ppm has been assigned to the carbonyl carbon atom in the asymmetrical ligand This is a value similar to the literature data [8] The signal at 183 5 ppm has been assigned to the C(5) carbon atom in the asymmetrical ligand The shift of this signal towards a lower field in comparison to the region characteristic for carbon $=\overset{|}{C}-O$ [8] is caused by complexation of the oxygen atom by the adjacent aluminium atom and by the system of conjugated C=O and C=C double bonds

^{13}C NMR data are in agreement with those of ^1H NMR studies and confirm the presence in a CH_2Cl_2 solution of a trimer of structure shown in Fig 4(b) At room temperature only single CH_3, CH and CO signals occur and indicate facile intramolecular rearrangements in the trimeric complex and intermolecular exchanges between the monomer and the trimeric complex

^{27}Al NMR spectra

The ^{27}Al NMR spectrum of dichloroaluminium acetylacetonate in a CH_2Cl_2 solution at room temperature is presented in Fig 7 Signal (a) at 88 0 ppm predominates in the spectrum besides those of smaller intensity, (b) at 37 ppm and (c) at 102 ppm An increase in the concentration of dichloroaluminium acetylacetonate or a decrease in temperature cause a decrease in the intensity of signal (a) relative to the remaining two signals The observed dependence of the signal intensity on temperature and concentration, as well as the chemical shift position of signal (a), which is characteristic for a four-coordinated aluminium atom in inorganic compounds [9], permit us to assign this signal to the aluminium atom in the monomer (Fig 4(a)) The position of signal (b) is characteristic for a five-coordinated aluminium atom [9a] and the signal has been assigned to the central aluminium atoms in the $[Al_2Cl_2(acac)_3]^+$ cation (Fig 4(b)) Signal (c) occurs in the region typical for $[AlCl_4]^-$ [9, 10] The $W_{1/2}$ of the signal is about 100 Hz This is bigger than the typical width for the $[AlCl_4]^-$ anion ($W_{1/2}=10$ Hz [9b]) The broadening of signal (c) may be caused by rapid intermolecular rearrangements accompanying the exchange reaction (6) between the monomer and trimeric complex or (and) interaction between the $[AlCl_4]^-$ anion with the $[Al_2Cl_2(acac)_3]^+$ cation

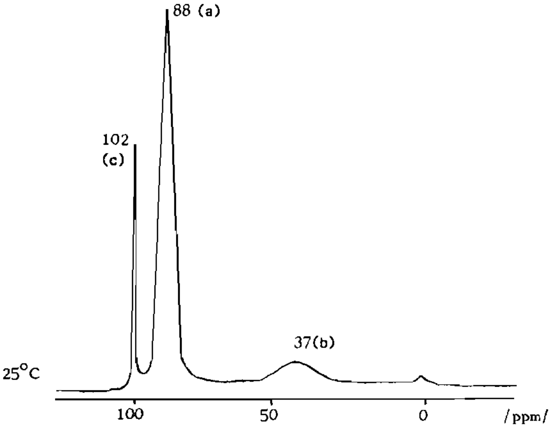

Fig 7 ^{27}Al NMR spectrum of dichloroaluminium acetylacetonate in CH_2Cl_2 solution at 25 °C (conc 20%)

A signal of a very small intensity also occurs in the ^{27}Al NMR spectrum at *c.* 3 ppm, which corresponds to the six-coordinated aluminium atom [9] and is difficult to assign.

IR spectra

Spectra of dichloroaluminium acetylacetonate in nujol and methylene chloride in the range of C=O and C=C stretching vibration are presented in Fig. 8. Measurements were performed at room temperature.

A very broad band νC=C at 1535 cm^{-1} and two bands νC=O at 1575 and 1610 cm^{-1} are present in the spectrum of a solid compound in nujol. The band at 1575 cm^{-1} corresponds to C=O stretching vibrations in the symmetrical chelating ligand [11] and the band at 1610 cm^{-1} was attributed to C=O stretching vibrations in asymmetrical ligands of the trimeric complex.

Two intense bands, νC=C at 1533 cm^{-1} and νC=O at 1560 cm^{-1} as well as a very weak band νC=O at 1700 cm^{-1} appear in a diluted solution (*c.* 2%). The intense bands were attributed to the symmetrical chelate ligand in the Cl_2Alacac monomer. An increase in the concentration of the solution (to *c.* 25%) causes the appearance of bands in the stretching vibrations range of the free, non-chelating carbonyl group (1690 and 1715 cm^{-1}) and of two shoulders (at *c.* 1580 and 1610 cm^{-1}, corresponding to the C=O bands of the trimeric complex). The appearance of two bands at 1690 and 1715 cm^{-1} indicates the presence in solution of an O-unidentate acetylacetonate ligand with a non-coordinated carbonyl group at room temperature, and suggests that the O-unidentate ligand occurs in a *s-cis* and *s-trans* configuration. The appearance of *s-cis* and *s-trans* rotamers is characteristic for unsaturated ketones [12].

MS Spectra

The parent ion of the Cl_2Alacac monomer at $m/e = 196$ and its decomposition fragments $m/e = 181$ ($Cl_2AlC_4H_4O$), 161 (ClAlacac), 97 (Cl_2Al) and 43 (CH_3CO) are present in the mass spectrum of dichloroaluminium acetylacetonate. No parent peak of the $Al_2Cl_2(acac)_3^+$ cation occurs in the spectrum but peaks resulting from its fragmentation are present; m/e: 260 (ClAl(acac)$_2$), 245 (ClAlacac($C_4H_4O_2$)), 225 (Al(acac)$_2$), 161 (ClAlacac) and 132 ($AlCl_3$).

Discussion

Reaction of aluminium trichloride with aluminium triacetylacetonate gives the same product as the reaction of alkylaluminium dichloride with acetylacetone (eqns. (3) and (4)). Similarly trialkylaluminium reacts with aluminium triacetylacetonate giving dialkylaluminium acetylacetonate (eqn. (7)) which is a monomer and does not associate [13].

$$2R_3Al + (acac)_3Al \longrightarrow 3R_2Alacac \qquad (7)$$

It appears from spectral studies of dichloroaluminium acetylacetonate that in a methylene chloride solution this compound exists in two forms: as a

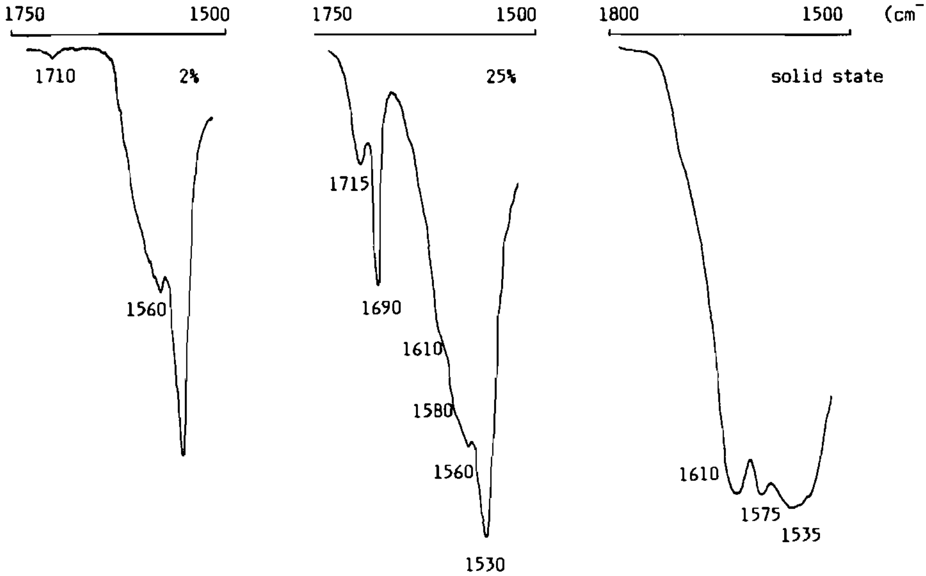

Fig. 8. IR νC=O and νC=C (cm^{-1}) spectra of dichloroaluminium acetylacetonate in CH_2Cl_2 at concentrations *c.* 2% and 25% and in the solid state in nujol.

monomer Cl_2Alacac and as a trimeric complex $[Al_2Cl_2(acac)_3][AlCl_4]$ Two groups of signals in the variable-temperature ^1H, ^{13}C and ^{27}Al NMR spectra correspond to these two forms The relative intensity of the two groups of signals depends on temperature and concentration of the compounds in solution The monomeric form dominates at temperature above 0 °C and at low concentrations Decreasing the temperature and increasing the concentration cause a trimerization of dichloroaluminium acetylacetonate

The lack of association of R_2Alacac and its facility for Cl_2Alacac can be explained by the different acidity of the aluminium atoms in those compounds and by the instability of eventually formed associates of R_2Alacac We have previously shown that dialkylaluminium acetylacetonate reacts very slowly in the liquid phase (without solvent) giving products of disproportionation [1a] The much higher acidity of the aluminium atom in Cl_2Alacac favors the acceptor–donor interaction with the oxygen atom of the acetylacetonate ligand of another Cl_2Alacac molecule It is also known from our studies [1b, c] that dichloroaluminium acetylacetonate reacts with Lewis bases to form stable ionic complexes (see eqn (2)) The complexes consist of an aluminium diacetylacetonate cation, stabilized by base molecules, and of the $[AlCl_4]^-$ anion So it can be assumed that donor–acceptor interaction between two molecules of Cl_2Alacac leads to the formation and recombination of ions (eqn (8)) These reactions probably proceed synchronously between the formed unstable complexes The existence of free ions is less probable

$$2Cl_2\text{Alacac} \rightleftharpoons \{Cl^- + Cl\text{Alacac}^+ + Cl_2Al^+ + \text{acac}^-\} \rightleftharpoons ClAl(\text{acac})_2 + AlCl_3 \qquad (8)$$

Aluminium trichloride, formed in the above reaction, reacts with the next molecule of Cl_2Alacac forming the ions ClAlacac$^+$ and $[AlCl_4]^-$, eqn (9)

$$AlCl_3 + Cl_2\text{Alacac} \rightleftharpoons Cl\text{Alacac}^+ + [AlCl_4]^- \qquad (9)$$

The unstable cation ClAlacac$^+$ is stabilized by reactions with $ClAl(acac)_2$ giving a trimeric complex, eqn (10)

$$Cl\text{Alacac}^+ + [AlCl_4]^- + ClAl(\text{acac})_2 \rightleftharpoons [Al_2Cl_2(\text{acac})_3]^+[AlCl_4]^- \qquad (10)$$

The formation of an ion pair $[(acac)_2Al]^+$ $[AlCl_4]^-$, as an intermediate species can also be expected, for example, from the reaction of $ClAl(acac)_2$ and $AlCl_3$ (analogous ions are formed in eqn (2)), eqn (11)

$$(\text{acac})_2AlCl + AlCl_3 \rightleftharpoons [(\text{acac})_2Al]^+\ [AlCl_4]^- \qquad (11)$$

Stabilization of the $[(acac)_2Al]^+$ cation by interaction with the oxygen atom of Cl_2Alacac should lead to a trimeric form, eqn (12)

$$[(\text{acac})_2Al]^+ + Cl_2\text{Alacac} + [AlCl_4]^- \rightleftharpoons [Al_2Cl_2(\text{acac})_3]^+[AlCl_4]^- \qquad (12)$$

Reactions (6) and (8)–(12) are reversible The first step of the reactions leading to the formation of the monomer from the trimeric complex involves cleavage of one oxygen-bridge in the $[Al_2Cl_2(acac)_3]^+$ cation (between ClAlacac$^+$ and $ClAl(acac)_2$ units) This is indicated by the differences in Al–O (bridging) distances in the cation Equilibrium (6) between the monomer and trimeric complex depends on the temperature and the dichloroaluminium acetylacetonate concentration in the methylene chloride solution In the solid state this equilibrium is entirely shifted to the trimer

From our results of X-ray structural analysis it appears that the differences in C–O(bridging) and C–O(non-bridging) distances are significant within acac ligands which form bridges between two Al atoms ^{13}C NMR data also confirm inequalities of C atoms adjacent to the bridging and non-bridging O atoms These differences indicate that of the two C–O bonds within the bridging ligand one is close to a single and the second to a double bond (Fig 5(b)) Similar phenomena have been observed for the $[Mn(acac)_2]_3$ trimer [7b] and the crystalline structure of acetylacetone [14]

Supplementary material

Tables of positional and thermal parameters for all atoms, observed and calculated structure factors and a complete list of bond lengths and bond angles are available from the authors on request

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