Inorganica Chimica Acta, *122* (1986) 225–228

Reactions of Dichloroaluminium Acetylacetonate with Lewis Bases. 2. Ionic Complexes of Cl_2Alacac with Dimethoxyethane and Dimethylformamide

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(Received July 8, 1986)

Abstract

Dichloroaluminium acetylacetonate reacts with dimethoxyethane (DME) forming a complex $[(acac)_2Al\cdot DME][AlCl]_4$ (2:1), irrespective of the reactant mole ratio. The $[(acac)_2Al\cdot 2DMF][AlCl]_4$ (1:1) ionic complex is the only product for the equimolar ratio of reactants in the case of dimethylformamide (DMF). The structure of complexes has been investigated by the variable-temperature ^{1}H NMR method and ^{27}Al NMR technique. The cationic complex $[(acac)_2Al\cdot DME]^+$ is exclusively of the *cis* form, while the $[(acac)_2Al\cdot 2DMF]^+$ is predominantly *cis* with a small amount of the ***trans*** form. The mechanism of stereochemical arrangements in the cationic complexes is discussed.

Introduction

The reaction of dichloroaluminium acetylacetonate Cl_2Alacac with tetrahydrofurane (THF) has been described earlier [1]. The ionic complex $[(acac)_2Al\cdot 2THF]^+[AlCl]_4^-$ results from that reaction. From ^{1}H and ^{13}C NMR studies it appears that the complex $[(acac)_2Al\cdot 2THF]^+$ is predominantly *trans* in a dichloromethane solution with a small amount of the *cis* form. In the presence of an excess of THF a fast exchange occurs between the complexed and free THF at room temperature. A stereochemical rearrangement of ligands also takes place in the complex.

The results of the reaction of Cl_2Alacac with dimethoxyethane (DME) and dimethylformamide (DMF) are now presented. The use of DME, a bidentate Lewis base, was interesting for explaining the structure of the complex formed and course of site interchanges in the octahedral cation. In order to study the influence of the Lewis acid strength on the reaction course and structure of the complex DMF, as a stronger base than THF and DME, was chosen. Such a choice also permitted a comparison of these results with those of Movius and Matwiyoff [2], who postulated on the basis of ^{1}H NMR studies, the formation of the cation $[(acac)_2Al\cdot 2DMF]^+$ in a DMF solution containing $Al(DMF)_6(ClO_4)_3$ and $Al(acac)_3$.

Experimental

All reactions were carried out in an atmosphere of dry, deoxidized nitrogen. Cl_2Alacac was prepared as described previously [1]. Methylene chloride was dried over molecular sieves type 4 A and distilled from P_2O_5. DME was distilled from a sodium-benzophenone ketyl. DMF was predried (molecular sieves 4 A) and distilled from P_2O_5.

^{27}Al NMR spectra were recorded on a Bruker WM 250 spectrometer and ^{1}H NMR spectra on a Tesla 80 MHz spectrometer.

$[(acac)_2Al\cdot DME][AlCl]_4$ (I)

A solution of 1.67 g (8.5 mmol) of Cl_2Alacac in 7 ml of CH_2Cl_2 was introduced to a Schlenk vessel, to which 1 ml (about 10 mmol) of DME was dropped in while stirring at room temperature. The reaction was carried out for 20 min. The unreacted DME and CH_2Cl_2 were removed by vacuum evaporation at room temperature. The complex **I** was obtained as a white crystalline solid, very soluble in CH_2Cl_2 but insoluble in DME and toluene. *Anal.* Found: Al, 9.91; C, 45.53; H, 7.21. Calc. for $C_{18}H_{34}Al_2Cl_4O_6$: Al, 9.96; C, 45.57; H, 7.17%.

$[(acac)_2\cdot 2DMF][AlCl]_4$ (II)

The synthesis was carried out as described above. 2.25 g (11.42 mmol) of Cl_2Alacac, 0.83 g (11.42 mmol) of DMF and 8 ml of CH_2Cl_2 as a solvent were used. Complex **II** is a thick oily liquid, very soluble in CH_2Cl_2 and insoluble in DME, diethyl ether and toluene, *Anal.* Found: Al, 9.98; C, 35.48; H, 5.24; N, 5.15. Calc. for $C_{16}H_{28}N_2Al_2Cl_4O_8$: Al, 10.00; C, 35.55; H, 5.18; N, 5.18%.

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Results and Discussion

Cl_2Alacac reacts with DME yielding a 2:1 complex irrespective of the reactant mole ratio (reaction 1). No 1:1 complex was found.

$$2Cl_2\text{Alacac} + \text{DME} \longrightarrow [(\text{acac})_2\text{Al}\cdot\text{DME}][\text{AlCl}]_4 \qquad (1)$$

In the ^{27}Al NMR spectrum of I in CH_2Cl_2 two signals of identical intensity appear. The sharp signal at 102.6 ppm corresponds to the aluminium atom in $[AlCl]_4^-$, and the signal at 4.5 ppm to that in the octahedral $[(acac)_2Al\cdot DME]^+$ cation [1].

In the ^{1}H NMR spectrum of I at room temperature single signals of acetylacetonate protons, CH_3-chelate and CH-ring, are observed as well as two singlets of the complexed DME protons (Fig. 1, Table I). A broadening of the CH_3-chelate signal is observed with decreasing the temperature below +5 °C, followed by its splitting at 0 °C into two signals of identical intensity.

Simultaneously at the same temperature range the singlet of the CH_2(DME) protons broadens and splits into a multiplet. The signals of the CH-ring and CH_3(DME) protons do not change their character and remain singlets. The course of changes observed in the spectra with a decreasing of temperature indicates that the cation complex $[(acac)_2Al\cdot DME]^+$ formed has the *cis* structure, as expected. In such a structure the CH_3-chelate protons of the acetylacetonate ligand and the CH_2(DME) protons are magnetically non-equivalent. The presence of individual signals for the particular groups of protons at room temperature indicates that the studied cationic complex with three bidentate ligands is stereochemically non-rigid at that temperature. The changes of signals described are caused by a stereochemical rearrangement of ligands, which is practically stopped at −5 °C.

No exchange occurs between complex I and free DME at room temperature, and in the ^{1}H NMR spectrum different proton signals corresponding to the complexed and free DME are present (Fig. 1).

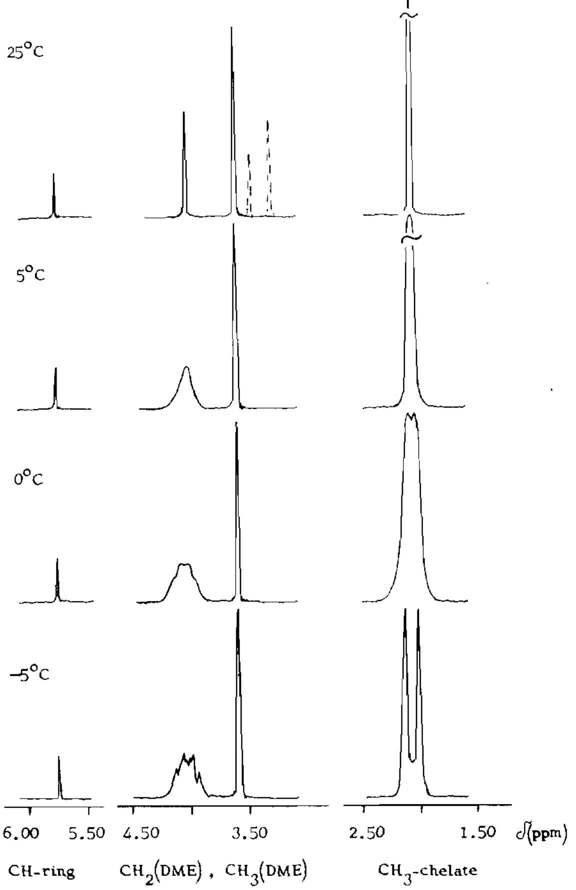


Fig. 1. Temperature dependence ^{1}H NMR 80 MHz spectra of $[(acac)_2Al\cdot DME][AlCl]_4$ in CH_2Cl_2 solution; positions of free DME present in the spectrum recorded with an excess of the base at 25 °C is marked with dashed line.

A variable-temperature ^{1}H NMR study for I together with the earlier presented [1] results for the $[(acac)_2Al\cdot 2THF][AlCl]_4$ complex permit a broader analysis of the mechanism of stereochemical rearrangement processes and donor exchange in the octahedral cation complex. The rapidly occurring

TABLE I. ^{1}H NMR Chemical Shifts for Complexes of Cl_2Alacac with DME and DMF in CH_2Cl_2 as an Internal Standard δ(H) = 5.33[a]

Complex	Temperature (°C)	acac		DME		DMF	
		CH-ring	CH_3-chelate	CH_2	CH_3	CH	NCH_3
$[(acac)_2Al\cdot DME][AlCl]_4$ I	25	5.74	2.03	4.03	3.60		
	−30	5.77	2.15; 2.04	4.08 m	3.62		
$[(acac)_2Al\cdot 2DMF][AlCl]_4$ II	25	5.60	1.94			7.95	3.11; 2.93
	−30	5.59	2.03; 1.92			8.05; 7.91	3.10; 2.91 3.04; 2.87

[a] Values in ppm. m, multiplet.

stereochemical rearrangements in the $[(acac)_2Al\cdot DME]^+$ cation at a retarded exchange of molecules of the complexing base indicate an intramolecular mechanism of rearrangements. In the case of the $[(acac)_2Al\cdot 2THF]^+$ cation an exchange between the free and complexed THF molecules occurred simultaneously with the stereochemical rearrangements. The coalescence temperature for both processes was equal to 0 °C, which shows that they occur much faster than for Al(III) tris-β-diketonates. Hence an assumption was drawn that the rupture of the donor–acceptor bond between the aluminium atom and oxygen atom in THF without a cleavage of the diketonate oxygen–aluminium bond is responsible for the exchange of THF molecules and stereochemical rearrangements. The $[(acac)_2Al\cdot DME]^+$ cation has a structure similar to that of tris-β-diketonates. The rate of stereochemical rearrangements in this cation, however, is comparable with the rate of those in the $[(acac)_2Al\cdot 2THF]^+$ cation. Thus it can be assumed that one of the aluminium–oxygen bonds in DME undergoes cleavage easier in comparison to the diketonate oxygen–aluminium bond and the rupture of that bond is the rate determining step of site interchanges (Scheme 1).

Further rearrangements proceed via an intermediate stage with a five-coordinative aluminium atom and a repeated closing of the DME ring [3, 4]. In the case of the octahedral complex with DME (bidentate ligand), the retardment of stereochemical rearrangements takes place at a much higher temperature (*ca.* −5 °C) than for the analogous complex with THF (monodentate ligand) (*ca.* −30 °C). From the results obtained for **I** it also appears that in the case of a bidentate ligand the rupture of the first aluminium–oxygen bond, which is decisive of the site interchanges in the octahedral cation, proceeds easier than the rupture of the second Al–O bond leading to the exchange of DME

$Cl_2Alacac$ reacts with DMF yielding a 1:1 mole complex at an equimolar ratio of reactants (reaction 2)

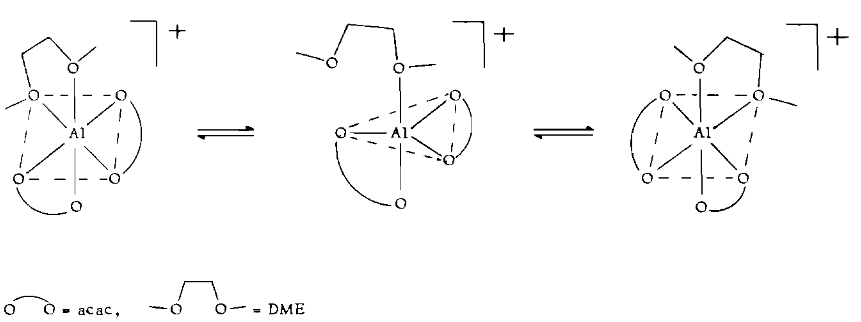
$$2Cl_2Alacac + 2DMF \longrightarrow [(acac)_2Al\cdot 2DMF]^+[AlCl]_4^- \qquad (2)$$

II

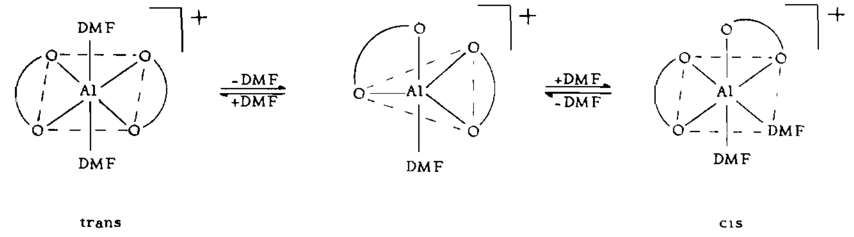
In the presence of an excess of DMF the $Cl_2Alacac$ reaction proceeds differently and is now being studied. Complex **II** is a thick, oily liquid very soluble in CH_2Cl_2 and insoluble in DME and toluene.

The structure of complex **II** has been determined on the basis of NMR studies. In the ^{27}Al NMR spectrum of **II** in a CH_2Cl_2 solution a sharp signal at 102.6 ppm, typical for the $[AlCl]_4^-$ anion, was observed, as well as a signal at 3.6 ppm corresponding to the octahedral $[(acac)_2Al\cdot DMF]^+$ cation. The stereochemistry of the $[(acac)_2Al\cdot 2DMF]^+$ cation was analyzed on the basis of variable-temperature ^1H NMR spectra (Fig. 2, Table I). In the spectrum at room temperature singlets of the acetylacetonate CH_3-chelate and CH-ring protons are present, as well as a doublet and singlet corresponding to the N-CH_3 and CH protons, respectively, of DMF. Decreasing the temperature below 0 °C causes a gradual broadening of the CH_3-chelate protons signal. At −7 °C this signal splits into two peaks, which slowly sharpen with a decrease in temperature. From the integration of these signals at −30 °C it appears that their mutual ratio is 1.55:1. The signal of the CH-ring protons does not change within the temperature range studied. The signals corresponding to the DMF protons change similarly within the temperature range studied. Below 0 °C the signals in the doublet of the N-CH_3 protons and the CH protons signal broaden at the base. At −20 °C new signals of those protons can be distinguished in the higher field; their full formation appears at about −30 °C. New signals in the higher field are much less intense. The mutual intensity ratio of corresponding pairs of signals in the N-CH_3 and CH range is 3.5:1.

On the basis of the comparison of changes observed in the spectra of **II** with the results described



Scheme 1



Scheme 2.

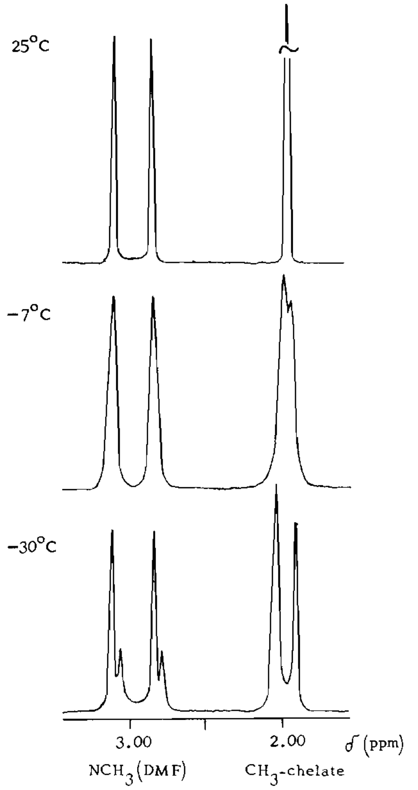


Fig 2. Temperature dependence ^1H NMR 80 MHz spectra of $[(acac)_2Al{\cdot}2DMF][AlCl]_4$ in CH_2Cl_2 solution in the NCH_3-(DMF) and CH_3-chelate region

earlier for the $[(acac)_2Al{\cdot}2THF][AlCl]_4$ complex [1] and complex **I** it appears that the $[(acac)_2Al{\cdot}2DMF]^+$ cation occurs in two forms *cis* and *trans* The different intensity of signals in the CH_3-chelate doublet (Fig. 2) is probably caused by the overlapping of the *trans* form protons signal on one of the *cis* form proton signals lying in the lower field. At low temperature a separation of the signals of the *cis* and *trans* isomers is observed in the DMF protons range The changes observed in the spectra are the result of the gradual retardment of the rate of stereochemical rearrangements in the cation with decreasing temperature. From the comparison of the intensity of signals corresponding to the *cis* and *trans* structures of the $[(acac)_2Al{\cdot}2DMF]^+$ cation it appears that the share of the *cis* form is *ca.* 78% and that of the *trans* one is *ca.* 22%. For the $[(acac)_2Al{\cdot}2THF]^+$ cation the amounts were reversed (75% *trans* and 25% *cis*).

Movius and Matwiyoff [2] suggested on the basis of ^1H NMR spectra the formation, in the reaction of $Al(acac)_3$ with $Al(DMF)_6(ClO_4)_3$ in DMF, of an identical cation to the one observed by us in **II**. On the basis of variable-temperature ^1H NMR spectra they concluded that the $[(acac)_2Al{\cdot}2DMF]^+$ cation occurs in the form of the *cis* and *trans* isomers at a comparable ratio 1.1.2 respectively. This conclusion resulted from the inappropriate interpretation of the CH_3-chelate protons signals. The signal in the doublet lying at a higher filed was assigned to the *cis* form, and the second signal of a somewhat greater intensity to the *trans* form. They also do not distinguish the separated signals of the $N\text{-}CH_3$ protons to the *cis* and *trans* structures.

From the analysis of variable-temperature ^1H NMR spectra of **II** it appears that the rate of stereochemical rearrangements of the cation is comparable to those observed for complexes with THF and DME. It should be presumed that the rupture of the Al–O bond in DMF is the stage decisive of the rearrangement rate and the mechanism of rearrangements is similar to that described [1] for the $[(acac)_2Al{\cdot}2THF][AlCl]_4$ complex (Scheme 2). For the reaction studied it was not possible to investigate the exchange of DMF molecules in the cation due to the occurrence of further reactions with an excess of DMF and formation of new reaction products

Acknowledgements

The authors wish to thank the Polish Academy of Sciences for financial support of this work and the Inorganic Group of Universiteit van Amsterdam (especially to Dr. D. Grove and Mr J. M. Ernsting) for enabling one of the authors (J.L) to perform ^{27}Al NMR.

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