CONTRIBUTION TO THE STRUCTURE OF ALUMINIUM CAPROLACTAMATE BASED ON THE STUDY OF INFRARED AND PROTON MAGNETIC RESONANCE SPECTRA

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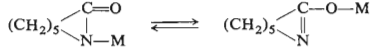
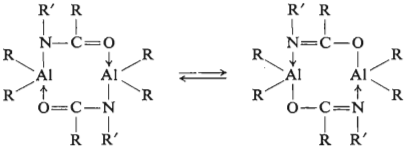
Aluminium caprolactamate (*I*) was prepared by the reaction of ε-caprolactam with isopropyliminoalane (*II*) in benzene. IR and ^{1}H-NMR spectra of *I* in various solvents are described as well as low-temperature ^{1}H-NMR spectra in hexane and dichloromethane. On the basis of these results together with the determination of molecular weights, structural arrangement was proposed for the dimer of *I* containing an eight-membered ring formed by two —O—C—N— bridges between aluminium atoms and two caprolactam ligands on each aluminium atom bonded through oxygen atom of carbonyl.

Lactams form, similarly to the primary amides of carboxylic acids, salts with alkali metals, alkyl- or halogenmagnesium and aluminium compounds; in most cases, an unambiguous determination whether the metal is primarily bonded to the nitrogen or oxygen atom only, is very difficult. Alkaline salts of lactams exist evidently in a tautomeric equilibrium (*A*) (refs[1,2]) whereas dimeric organoaluminium derivatives of amides of carboxylic acids occur in equilibrium (*B*) (ref.[3]). In general, it holds that the oxygen–metal bond in these compounds is stronger and consequently more probable than the nitrogen–metal bond[4–8] even though exceptions are known[9]. When the amide or lactam forms a complex with Lewis acid[6,10,11], or when it is present as a ligand in the transitional element complex[12–14], the bond between the oxygen of the carbonyl and the central metal atom has been always observed.



(*A*)



(*B*)

Aluminium caprolactamate (*I*) was prepared by Komoni and Tani[15] from triethylaluminium and ε-caprolactam (further only caprolactam) according to equation (*C*). For the completion of the reaction it is necessary to heat the reaction mixture up to 120°C. The authors did not isolate *I* for the study of the mechanism of polymerization, nor did they study its properties. As it has been found in our laboratory, caprolactam yields quantitatively *I* with isopropyliminoalane (*II*) according to the equation (*D*).

$$3\,(CH_2)_5CONH + (C_2H_5)_3Al \xrightarrow[20\ min]{120°C} Al[NCO(CH_2)_5]_3 + 3\,C_2H_6 \quad (C)$$

$$3\,(CH_2)_5CONH + HAlNCH(CH_3)_2 \rightarrow$$
$$\xrightarrow[2\ hod]{80°C} Al[NCO(CH_2)_5]_3 + H_2NCH(CH_3)_2 + H_2 \quad (D)$$

DISCUSSION

Aluminium caprolactamate is a solid white substance, sensitive to air moisture or to the presence of oxygen, easily soluble in aromatic and aliphatic hydrocarbons, dichloromethane, and cyclic or acyclic ethers.

Fig. 1 demonstrates the concentration dependence of the molecular weight of *I* in benzene, dioxan, cyclohexane, and dichloromethane. It is evident that the association degree depends to the small extent on concentration, on temperature (molecular weight in benzene was determined by cryoscopy and ebuliometry), but it considerably depends on the used solvent. *I* is practically a dimer in cyclohexane,

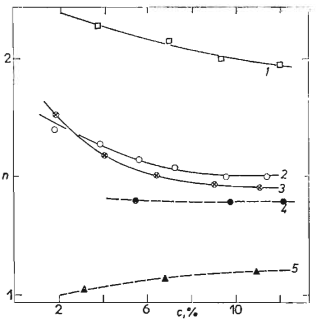


FIG. 1

Degree of Association (*n*) of Aluminium Caprolactamate (*I*) as Determined by Cryoscopy in Benzene *2*, Cyclohexane *1*, Dioxan *3* and by Ebulioscopy in Benzene *4* and Dichloromethane *5*

a monomer in dichloromethane, and an equilibrium between monomeric and dimeric compounds evidently exists in benzene and dioxan.

Infrared spectrum of caprolactam exhibits a very strong band at 1660 cm^{-1} in the solid state or at 1672 cm^{-1} in benzene solution, that can be assigned to the amide group[10]. Between 1500 and 1700 cm^{-1}, alkali metal caprolactamates[2,4] or adducts of isocyanates with triethylaluminium[16,17] exhibit two bands: one band in the region of higher wavenumber (>1640 cm^{-1}) and one band in the range of lower wavenumber (<1600 cm^{-1}), that are assigned to ν(C=O) and ν(C=N) vibrations, respectively. According to some new results[13,18], it seems that the band at wave number exceeding 1650 cm^{-1} corresponds to the free lactam or to the amide resulting from the hydrolysis of the sample; when working in completely inert atmosphere, the band is not observed in the spectrum. Aluminium caprolactamate acts in all studied solvents in an analogical way (Table I). Between 1450 and 1750 cm^{-1}, the spectrum exhibits two very strong bands with one or two shoulders. The spectra of the solutions of pure caprolactam are for comparison listed in the Table, too. The position of the single band of caprolactam in this region is practically identical in all studied solvents except for dichloromethane and pyridine. An analogical situation is observed in the solution of *I*; neither here a more expressed dependence of the band position or intensity on solvent polarity is observed. The band in the region of free caprolactam about 1675 cm^{-1} appears only in these cases, where the unreacted caprolactam was not completely removed during the desolvation or when it did not polymerize due to the high temperature (over 100°C), or due to the presence of oxygen.

With lactams forming complexes with Lewis acids or acting as ligands in complexes of transitional elements, oxygen atom behaves as electron donor and the

TABLE I

Infrared Absorption Bands[a] of Caprolactam (*V*), Aluminium Caprolactamate (*I*) and Adducts of *V* and *I* with $AlCl_3$ in the Region of 1500—1700 cm^{-1}

Solvent	*V*	*V*.$AlCl_3$	*I*	*I*.$AlCl_3$
Cyclohexane	1682 (*vs*)		1585 (*sh*), 1601 (*vs*), 1613 (*sh*)	
Benzene	1674 (*vs*)	1643[b]	1582 (*sh*), 1598 (*vs*), 1612 (*sh*)	1564 (*w*), 1593 (*s*)
Dichloromethane	1668 (*vs*)	1539 (*vs*)	1568 (*sh*), 1584 (*vs*), 1606 (*sh*)	1573 (*s*)
Dioxan	1673 (*vs*)		1585 (*sh*), 1600 (*s*), 1613 (*sh*)	
1,2-Dimethoxyethane	1676 (*vs*)		1582 (*sh*), 1597 (*vs*), 1612 (*sh*)	
Pyridine	1667 (*vs*)		1570 (*s*), 1583 (*sh*)	

[a] *vs* very strong, *s* strong, *w* weak, *sh* shoulder, [b] According to the literature[10].

delocalization of the non-bonding nitrogen electron pair to the π-molecular orbital including O, C, and N appears. The coordination of oxygen becomes evident in the IR spectrum through the shift of the band of the amide group to lower wavenumbers. On the other hand, when the coordination between nitrogen and Lewis acid exists, the absorption may be supposed to be shifted towards higher wavenumbers[10,12]. When adding $AlCl_3$ to free caprolactam in 1 : 1 ratio, the band of amide stretching is shifted by 30 cm^{-1} towards lower wavenumbers, which indicates the caprolactam coordination to aluminium atom through oxygen atom of the carbonyl group. When adding gradually $AlCl_3$ to the solution of aluminium caprolactamate, first it appears a strong band at higher wavenumbers (which may be explained by the $AlCl_3$—N coordination); when further $AlCl_3$ is added, a band at lower wavenumbers appears ($AlCl_3$—O coordination is formed) – Fig. 2.

The presented results may be easily explained in the following way: the caprolactam ligand is bonded to the aluminium atom predominantly through the oxygen atom. When aluminium caprolactamate dimer is supposed to form a structure analogous to amide adducts or to the adducts of isocyanate with organoaluminium compounds[3,16,19], *i.e.* a structure with an eight-membered ring with $\geq$Al—O═C═N$\leq$ arrangement (equilibrium (*B*)), then one of the absorption spectrum bands corresponds to the caprolactam ligand forming the bridge, the other one to the terminal ligand. The band at approx. 1 600 cm^{-1} is suppressed and that at approx. 1 585 cm^{-1}

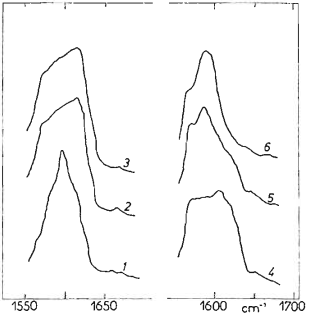


FIG. 2

Infrared Spectra in the Region of 1 500 to 1 700 cm^{-1} of 2% Benzene Solution of Aluminium Caprolactamate (*I*) *1* and Mixture of *I* and $AlCl_3$ in Ratio 8 : 1 *2*, 4 : 1 *3*, 2 : 1 *4*, 1 : 1 *5* and 1 : 2 *6*

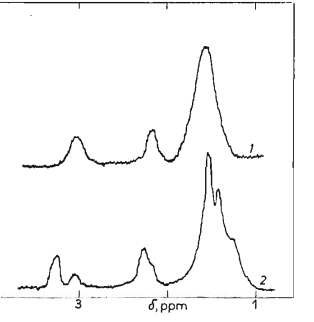


FIG. 3

^{1}H-NMR Spectra of 5% Solution of Aluminium Caprolactamate (*I*) *1* in Dichloromethane, *2* in Benzene

dominating in the spectrum of aluminium caprolactamate dimer in which a part of the caprolactam ligands is replaced by either ethyl or isopropyl imine group[20], corresponds very likely to the bridge arrangement.

^{1}H-NMR spectra of aluminium caprolactamate at room temperature in various solvents exhibits, similarly to pure caprolactam[10,21], three broad peaks belonging to the protons of ε-methylene group, α-methylene group, and β–δ-methylene groups (Table II). The spectrum in aromatic hydrocarbons shows a distinct solvent induced shift and, moreover, a splitting of the signals of ε-methylene as well of β–δ-methylene groups, to "doublets" in which the integral intensities of both peaks are 5 : 1 (Fig. 3).

As mentioned above, caprolactam in all caprolactam complexes with Lewis acid is evidently bonded through the oxygen atom of the C=O group. Similar conclusions may be drawn from the change in the chemical shifts of the signals of caprolactam in the presence of aluminium chloride (Table II). In dichloromethane, the signals of all methylene groups of solvated caprolactam were found, as expected, in the lower field. The largest change in the chemical shift is observed with the signal of the α-CH_2 group ($\Delta\delta$(ε-CH_2) = 0·38 ppm, $\Delta\delta$(α-CH_2) = 0·42 ppm, $\Delta\delta$(β–δ-CH_2) = 0·15 ppm). Values of $\Delta\delta$(ε-CH_2) = 0·30 ppm, $\Delta\delta$(α-CH_2) = 0·33 ppm, and $\Delta\delta$(β–δ-CH_2) = 0·12 ppm are presented in ref.[10] for the caprolactam–BF_3 complex.

TABLE II

^{1}H-NMR Spectra of ε, α and β-δ-CH_2 Group of Caprolactam (*V*), Aluminium Caprolactamate (*I*) and Adducts of *V* and *I* with $AlCl_3$ (chem. shifts in ppm, δ scale)[a]

Solvent	*V*			*V* + $AlCl_3$ (1 : 1)			*I*			*I* + $AlCl_3$ (1 : 1)		
	ε	α	β–δ	ε	α	β–δ	ε	α	β–δ	ε	α	β–δ
Hexane[b]							3·16	2·34	[c]			
Benzene	2·74[d]	2·25[d]	1·25	2·37	2·15	1·08	3·34	2·38	1·56	3·22	2·46	1·50
						0·93	3·10		1·44			
Toluene							3·30	[c]	1·59			
							3·09					
Pyridine	3·07[d]	2·46[d]	1·51				3·36	2·45	1·53			
		2·49[e]					3·10	2·50[e]	1·61			
Dichloro-methane	3·20[d]	2·45[d]	1·72	3·58	2·87[d]	1·87	3·15	2·39	1·64	3·38	2·55	1·71
Dioxan							3·10	2·30	1·57			
1,2-Dimetho-xyethane	[c]	2·35[d]	1·66				[c]	2·32	1·57			

[a] The signals are broad singlets; they are in each group arranged according to falling integral intensity. [b] 95% hexane and 5% benzene. [c] Signal overlapped by the signal of the solvent. [d] Multiplet. [e] Sharp singlet in area of broad signal of α-methylene.

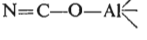
When we then compare from this viewpoint the change in chemical shift of *I* in the presence of a molar equivalent of $AlCl_3$ in dichloromethane, it is evident that Lewis acid affects to the largest extent the ε-methylene group ($\Delta\delta(\alpha\text{-}CH_2) = 0{\cdot}23$ ppm, $\Delta\delta(\alpha\text{-}CH_2) = 0{\cdot}16$ ppm, $\Delta\delta(\beta\text{-}\delta\text{-}CH_2) = 0{\cdot}07$ ppm). Aluminium chloride will be therefore coordinated in the contradistinction to free caprolactam to the nitrogen atom. When considering all the above mentioned facts about the structure of the caprolactam–Lewis acid complex, we may easily explain also this phenomenon in the following way: caprolactam ligand in *I* is at least predominantly bonded to the aluminium atom through oxygen. In benzene solution, the situation is complicated by the "solvation" by benzene, *i.e.* by the change in the shielding of single methylene groups of caprolactam and *I* thanks to a specific localization of the benzene nucleus.

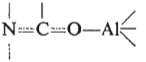
Neither at high temperatures (up to +100°C), nor at low temperatures (down to −80°C), the ^{1}H-NMR spectrum of the solution of *I* changes except for the broadening of single signals. A substantial change has been observed only in dichloromethane, where at −70°C the signal of the β–δ-methylene group is splitted to two equal peaks, whereas the signals of the ε- and α-methylene groups remain unchanged. In dichloromethane, *I* is to the contradistinction with other solvents, monomeric; that is why this phenomenon results most likely from the coordination of dichloromethane to aluminium atoms.

The presented results lead to the following preliminary conclusions about the structure of aluminium caprolactamate in a solution:

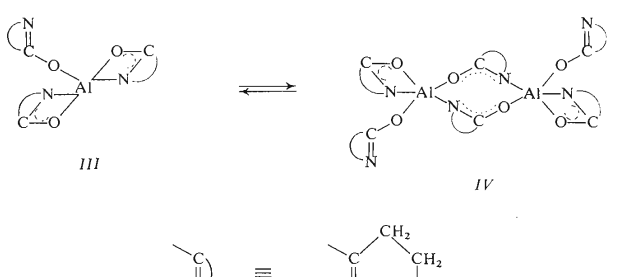
1) The non-coordinated C=O group is either not present in *I* at all, or it is present only to a small extent. The caprolactam ligand is bonded to aluminium atom through oxygen (arrangement, *E*, *F*); the arrangement of the type (*G*) is unprobable.


(*E*)


(*F*)


(*G*)

2) *I* exists in the solution as an equilibrium of monomeric (*III*) and dimeric (*IV*) form. An eight-membered ring is included evidently in the dimeric structure, which may be postulated even from analogy with the adducts of amides and isocyanates with alkylaluminium compounds of known structures[3,16,19]. Also the fact supporting this arrangement is that in ^{1}H-NMR spectra in the solution of aromatic hydrocarbon ε-methylene group expresses through two relatively distant signals in the ratio approximately 5 : 1, that evidently correspond to the terminal and bridge caprolactam ligand and where coalescence even at 100°C does not take place. The



III *IV*

gradual replacement of caprolactam ligand by ethyl or isopropylimine group in *I* becomes evident in infrared and ^{1}H-NMR spectra through the change in the ratio of the terminal and bridge ligands in favour of the bridge ligand[20]. It seems therefore reasonable at least in aromatic hydrocarbons to assume the existence of an equilibrium between aluminium caprolactamate monomer and dimer (*III* or *IV*), where both in the monomer and in the dimer further nitrogen is coordinated. Coordination number of 6 or 4 (the formation of a further Al—N bond or the rupture of the existing one) cannot be excluded with aluminium either.

EXPERIMENTAL

All preparations and measuring of aluminium caprolactamate spectra were carried out in the atmosphere of dry argon. Caprolactam was before its application vacuum distilled, isopropyliminoalane (*II*) was 96·5% (determined from the content of Al), and the ratio of Al : H : N equaled 1 : 1·002 : 1·008. The solvents were dried on molecular sieves and before their application distilled from $NaAlH_2(OCH_2CH_2OCH_3)_2$ solution, from isopropyliminoalane solution[22]–(pyridine, n-hexane, cyclohexane), or from CaH_2 suspension–(dichloromethane).

Infrared spectra of 2% solutions of *I* were measured on Beckman IR 20 A spectrometer, ^{1}H-NMR spectra were measured at 100 MHz on Varian XL-100-15. *I* Was measured at normal temperature in 5% solutions, at low temperature in 1% solution since 5% solutions gave very broad signals because of the high viscosity. Tetramethyl silane served as an internal standard. Molecular weight was determined by ebuliometry and cryscoscopy as described earlier[23].

Preparation of Aluminium Caprolactamate (*I*)

3·97 g (0·045 mol) of 96·5% isopropyliminoalane dissolved in 50 ml of benzene were dropped at simultaneous cooling within 15 minutes into 15·3 g (0·135 mol) of caprolactam dissolved in 50 ml of benzene. When the evolution of hydrogen and of isopropylamine was finished the reaction mixture was heated under reflux for 1 hour; then 50 ml of the solvent was removed from the reaction mixture by distilation and the reaction was completed during following 1 hour's

heating under reflux. After evaporating the remaining solvent the product was dried at 80°C of 10 Pa for 2 hours. Solid glassy white substance was obtained. For $Al(NCOC_5H_{10})_3$ (363·4) was calculated: 7·42% Al, 11·56% N; found: 7·24% Al, 11·26% N.

Preparation of Aluminium Caprolactamate Complex with Aluminium Chloride

The corresponding amount of 2% solution of *I* was injected into the weighed amount of aluminium chloride. Aluminium chloride was dissolved under stirring in benzene, trichloromethane, and dichloromethane solution of *I*.

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