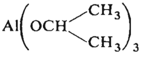
STRUCTURE OF DIMERIC MONOISOPROPOXYDICAPROLACTAMOALANE AND DIISOPROPOXYMONOCAPROLACTAMOALANE

Otomar KŘÍŽ, Bohuslav ČÁSENSKÝ and Jiří MACHÁČEK
Institute of Inorganic Chemistry,
Czechoslovak Academy of Sciences, 250 68 Řež

Received August 24th, 1979

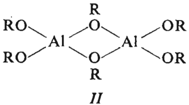
Molecular weight and ^1H-NMR and IR spectral measurements evidence that in dimeric aluminium isopropoxide in which one or two isopropoxyls have been replaced by caprolactam ligand, only the oxygen atoms of the isopropoxyl take part in the bridge formation between the two aluminium atoms.

Freshly prepared aluminium isopropoxide (*I*) is a trimer, converting slowly to tetramer if allowed to stand at room temperature[1]. This change in association (ageing effect) of aluminium alcoholates is a manifestation of the tendency to increase the aluminium coordination number from 4 to 6. Solid aluminium isopropoxide heated to 130 – 140°C is predominantly dimeric (*II*, $R = i\text{-}C_3H_7$), and the dimeric structure remains preserved for some time after rapid cooling of the hot benzene solution[2]. Based on ^1H-NMR spectroscopic investigation of this solution, the dimeric structure of *II* was confirmed; it is analogous to that of aluminium tert-butoxide[3,4] or monoisopropoxy-ditert-pentyloxyalane[5]. Aluminium caprolactamate $Al.[OCN(CH_2)_5]_3$ (*III*) occurs in solution as a dimer, in equilibrium with the monomer. The two aluminium atoms of the dimer are interconnected by —O=C=N— bridges of the caprolactam, forming eight-membered ring[6]. The terminal caprolactam ligands in both the monomer and the dimer can take part in the further coordination of the aluminium atom.



$Al(OCH(CH_3)_2)_3$

I

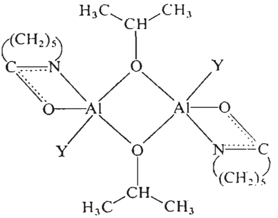


II

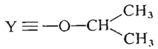
Aluminium isopropoxide *I* reacts with 6-caprolactam analogously as with other lactams[7] so that two of the three isopropoxyls are replaced by the caprolactam ligand with the formation of monoisopropoxydicaprolactamoalane (*IV*). The stage of diisopropoxymonocaprolactamoalane (*V*) is difficult to catch in this reaction;

this compound was therefore prepared by successive reaction of isopropyliminoalane, $HAlNCH(CH_3)_2$, with 6-caprolactam and 2-propanol in benzene solution.

The dicaprolactamo derivative *IV* is a white crystalline substance, well soluble in ether, considerably less soluble in aromatic hydrocarbons (max. 5% in benzene at room temperature). The molecular weight, determined ebuliometrically, decreases slightly with increasing concentration; in the concentration region 5 – 12% in benzene solution it corresponds to the association degree 2·15 – 1·9. The monocaprolactamo derivative *V* retains the honey-like consistence also in substance. It is completely miscible with aromatic hydrocarbons and ethers. Its molecular weight is independent of the concentration and corresponds to the association degree 2·18 ± 0·04 for 5 – 22% benzene solutions.



IV, $Y \equiv OCN(CH_2)_5$



V, $Y \equiv -O-CH(CH_3)_2$

Table I gives the chemical shifts in the ^1H-NMR spectra of the compounds $Al[OCN(CH_2)_5]_n(O\text{-}i\text{-}C_3H_7)_{3-n}$ for $n = 0, 1, 2, 3$ (compounds *I*, *V*, *IV*, *III*, respectively). Obviously, the bridge joining the two aluminium atoms is formed exclusively by the isopropoxyl oxygen atoms. For the aluminium-to-isopropoxyl ratio 1 : 1 (compound *IV*), the spectrum exhibits only a single methyl doublet belonging apparently to the bridge isopropoxyl and a septet of the methine hydrogen. For the aluminium-to-isopropoxyl ratio 1 : 2 (compound *V*), a doublet and a septet of the terminal isopropoxyl groups appear in addition. Signals that can be attributed to the caprolactam forming the —O ⩦ C ⩦ N— bridge between two aluminium atoms, which appear in the spectrum of the dimeric aluminium caprolactamate *III*, are absent from the spectra of the compounds *IV* and *V*. The signal of the β to δ CH_2 groups appears as a broad singlet in the spectra of compounds whose caprolactam-to-aluminium ratio is higher than unity (*III*, *IV*). In the spectrum of the compound

TABLE I

^{1}H-NMR Spectra of $Al[OCN(CH_2)_5]_n(O\text{-}i\text{-}C_3H_7)_{3-n}$, $n = 0, 1, 2, 3$ (compounds *I*, *V*, *IV*, *III*, respectively), in 5% Benzene Solution
Chemical shifts in ppm, δ scale, coupling constants in Hz; symbols: bs broad singlet, d doublet, sp septet, m multiplet.

Compound	n^a	$OCN(CH_2)_5$			$O\text{-}i\text{-}C_3H_7$	
		$\varepsilon\text{-}CH_2$	$\alpha\text{-}CH_2$	$\beta\text{-}\delta\text{-}CH_2$	CH	CH_3
I^b		—	—	—	—	1·35 (d, $J = 6$)^d, 1·27 (d, $J = 6$)^c
V	1	3·13 (bs)^c	2·30 (bs)	1·25—1·65 (m)^c	4·45 (sp, $J = 6$)^d 2·89 (sp, $J = 6$)^c	1·40 (d, $J = 6$)^d, 0·92 (d, $J = 6$)^c
IV	2	3·23 (bs)^c	2·34 (bs)	1·50 (bs)^c	4·44 (sp, $J = 6$)^d	1·52 (d, $J = 6$)^d
III	3	3·34 (bs)^c	2·38 (bs)	1·56 (bs)^c	—	—
		3·10 (bs)^d		1·44 (bs)^d	—	—

[a] Coefficient in the formula $Al[OCN(CH_2)_5]_n(O\text{-}i\text{-}C_3H_7)_{3-n}$; [b] ref.[2]; [c] terminal group; [d] bridge group.

V, with one caprolactam ligand per one aluminium atom, the protons of such methylene groups appear as a multiplet, similarly as in the case of isopropyliminomonocaprolactamoalane $Al(N\text{-}i\text{-}C_3H_7)[OCN(CH_2)_5]$ (ref.[8]). These facts can be explained, for instance, in terms of restriction to rotation of the caprolactam ligand resulting from its further coordination to the aluminium atom.

Table II lists the absorption peaks in the infrared spectra of the compounds *I*, *III*, *IV*, *V* in the regions of the Al—O and C—O ($600-1\,200\ cm^{-1}$) and caprolactam N=C=O ($1\,500-1\,700\ cm^{-1}$) stretching vibrations. The views of authors[9-12] upon the band assignment in the spectra of the tetrameric, trimeric, and dimeric aluminium isopropoxide are somewhat different. In the range $830-870\ cm^{-1}$, several bands appear in the case of compounds where the presence of bridge as well as terminal isopropoxyls can be assumed (*I*, *V*), whereas in the spectrum of *IV*

TABLE II

Infrared Absorption Bands, in the Regions 600—1 200 cm^{-1} and 1 500—1 700 cm^{-1}, of $Al[OCN(CH_2)_5]_n(O\text{-}i\text{-}C_3H_7)_{3-n}$ ($n = 0, 1, 2, 3$, compound *I*, *V*, *IV*, *III*, respectively) in Benzene Solutions

I[a]	*V*	*IV*	*III*
618 mw	640 sh	634 vs	635 vs
650 w			
688 ms	680 vs		
704 sh	705 sh	705 sh	
819 sh	799 w		
839 ms	837 ms	837 m	840 w
863 m	860 sh	881 w	881 w
	878 sh	896 w	
956 s	960 s	960 s	962 w
1 038 s	1 033 s	1 024 w	1 020 ms
	1 088 w	1 086 m	1 088 m
1 127 s	1 132 s		1 126 w
1 142 s		1 142 s	1 152 w
1 175 s	1 170 s	1 155 sh	
1 186 s	1 198 sh	1 173 sh	1 200 m
	1 524 w	1 523 w	1 529 m
		1 558 sh	1 582 sh
	1 592 s	1 598 vs	1 598 vs
			1 612 sh
	1 677 w	1 676 w	1 674 w

[a] Spectra of mixture of dimeric and trimeric aluminium isopropoxide measured in Nujol mull, according to ref.[11].

where the isopropoxyl present only takes part in the bridge formation, a single band is observed in the above region. In the 1150 cm^{-1} range, *III* does not exhibit appreciable absorption, *IV* displays one marked band at 1142 cm^{-1}, and in the spectra of *V* and *I* several bands are found. The occurrence of several distinct bands in the case of aluminium isopropoxide (*I*) is explained by Fieggen and Gerding[11] in terms of participation of both terminal and bridge isopropoxyl groups in the structure. Wilhoit and coworkers[12] attributed the band at 1033 cm^{-1} in the spectrum of *I* to the Al—O—C grouping of the terminal isopropoxyl, the band at 935 cm^{-1} to the Al—O—Al grouping. While in the spectra of *I* and *V* the two bands are comparable in intensity, in the spectrum of *IV* the band at 960 cm^{-1} is a prominent one, whereas that at 1025 cm^{-1} is substantially less intense.

The above facts comply with the general conclusion that an isopropyl bridge between aluminium atoms is stronger than a bridge constituted by the caprolactam —N⩦C⩦O— grouping. The structure of the isopropoxycaprolactamoalanes *IV* and *V* is represented by a four-membered ring composed of two oxygen and two aluminium atoms, and similarly as in *III* (ref.[6]) the caprolactam ligand is at least partly involved in the further coordination to the aluminium atom.

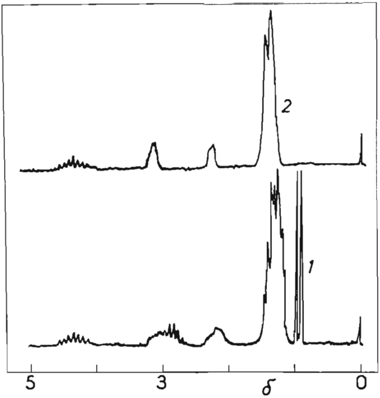


FIG. 1

^{1}H-NMR Spectra (100 MHz) of Diisopropoxymonocaprolactamoalane *1* and Monoisopropoxydicaprolactamoalane *2* in 5% Benzene Solutions

EXPERIMENTAL

All reactions and preparations of the substances examined were conducted in annealed apparatus in argon atmosphere. 6-Caprolactam was distilled prior to use; aluminium isopropoxide was prepared from 2-propanol and elemental aluminium[13], isopropyliminoalane was obtained by direct synthesis from isopropylamine, aluminium, and hydrogen[14]. The infrared spectra were measured on a spectrophotometer Beckman IR 20A in 2—4% benzene solutions, the ^{1}H-NMR spectra were scanned on a spectrometer Varian XL-100 (100 MHz) or on an instrument Tesla 60 (60 MHz) in 5% benzene solutions, using tetramethylsilane as internal standard. The molecular weights were determined ebuliometrically in benzene solutions as described previously[15]

Monoisopropoxydicaprolactamoalane

87·6 g (0·328 mol) of aluminium isopropoxide and 99·1 g (0·876 mol) of 6-caprolactam were placed in a flask fitted with a reflux condenser and a capillary reaching the flask bottom. Dry nitrogen was fed through the capillary, and the apparatus was attached to vacuum of 2500 Pa *via* the condenser. The 2-propanol formed was condensed in a freezing vessel (solid CO_2 with methanol). After 12 h heating, 50·1 g (97·3%) of 2-propanol was obtained. 150 ml of benzene was then added to the product and the mixture was boiled at normal pressure for 1 h. After cooling, the crystals were filtered out, washed twice with 100 ml of benzene, and dried at 50°C and 130 Pa. White crystalline substance (108·5 g) was obtained. For $C_{15}H_{27}AlN_2O_3$ (310·4) calculated: 8·69% Al, 9·02% N; found: 8·34% Al, 8·81% N.

Diisopropoxymonocaprolactamoalane

Solution of 6-caprolactam (15·30 g, 0·135 mol) and 2-propanol (16·25 g, 0·270 mol) in 100 ml of benzene was heated to boil for 1 h and benzene solution of isopropyliminoalane (11·90 g of 96·56% substance, 0·135 mol, in 90 ml of benzene) was added dropwise with constant stirring. 160 ml of benzene with isopropylamine was distilled off from the mixture, and the solution was diluted with 160 ml of benzene to obtain 190·5 g of a yellow-brown solution. Analysis of the solution: 1·92% Al, 0·97% N, hence Al : N molar ratio 1 : 0·97. According to the aluminium content, the solution contained 18·31% $Al[OCN(CH_2)_5](O\text{-}i\text{-}C_3H_7)_2$.

The authors wish to thank Mrs K. Procházková for the infrared spectral measurements, Dr Z. Samek and Dr F. Mareš for the ^{1}H-NMR *spectral measurements, and Mr P. Kolář for the molecular weight determinations.*

REFERENCES

1. Ulich H., Nespital W.: Z. Phys. Chem. (Leipzig) *165*, 294 (1933).
2. Kleinschmidt D. C., Shiner V. J. jr, Whittaker D.: J. Org. Chem. *38*, 3334 (1973).
3. Shiner V. J. jr, Whittaker D., Fernandez V. P.: J. Amer. Chem. Soc. *85*, 2318 (1963).
4. Mehrotra R. C.: J. Ind. Chem. Soc. *30*, 585 (1953).
5. Mehrotra R. C.: J. Ind. Chem. Soc. *31*, 85 (1954).
6. Kříž O., Čásenský B.: This Journal *44*, 2772 (1979).
7. Čásenský B., Macháček J., Kubánek V.: Czech. 186 968.
8. Kříž O., Čásenský B.: J. Organometal Chem. *161*, 273 (1978).
9. Bell J. V., Heisler J., Tannenbaum H., Goldenson J.: Anal. Chem. *25*, 1720 (1953).
10. Barraclough C. G., Bradley D. C., Lewis J., Thomas I. M.: J. Chem. Soc. *1961*, 2061.
11. Fieggen W., Gerding H.: Rec. Trav. Chim. Pay-Bas *90*, 410 (1971).

12. Wilhoit R. C., Burton J. R., Kuo F. T., Huang S., Vignesnel A.: J. Inorg. Nucl. Chem. *24*, 851 (1962).
13. Wild A. L.: Org. Reactions *2*, 178 (1974).
14. Časenský B., Macháček J., Hanslík T.: Czech. 167 751; Chem. Abstr., *84*, 58 605 (1976).
15. Kříž O., Sochor P.: This Journal *41*, 193 (1976).

Translated by P. Adámek.