

STRUCTURE OF SODIUM TETRACAPROLACTAMATOALUMINATE. ¹H NMR SPECTRA OF SODIUM ISOBUTYLCAPROLACTAMATO- ALUMINATES

Otomar KŘÍŽ, Jiří FUSEK and Bohuslav ČÁSENSKÝ

*Institute of Inorganic Chemistry,
 Czechoslovak Academy of Sciences, 250 68 Řež*

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Sodium tetracaprolactamboaluminate (*I*) exists in benzene solution predominantly as a dimer. Its structure was proposed on the basis of molecular weight studies, infrared, and ¹H NMR spectra of sodium isobutylcaprolactamatoaluminates (*II*). Two modes of dimerization are supposed: an eight-membered cyclic caprolactam bridge between two aluminum atoms or the coordination of the caprolactam ligands belonging to two different aluminum atoms to one sodium atom.

The structure containing an eight-membered ring in which formation participate both oxygen and nitrogen of the caprolactam ligand, was proposed¹ for the dimeric aluminum 6-caprolactamate, $\{Al[\overline{N(CH_2)_5CO}]_3\}_2$. Structure of some alkali metal alkylaluminates were determined by X-ray crystallography²⁻⁴. The crystal lattice is composed from alkali metal cations and tetraalkylaluminate anions alternating in a chain structure. The covalent metal-to-alkyl group bond was considered for the lithium cation only. Degree of association in these compounds is markedly concentration and solvent dependent; with sodium tetra-*n*-butylaluminate in cyclohexane solution increases with increasing concentration from two to six⁵. Presence of tetrahydrofuran perturbs the stability of the aggregate and decreases its molecular weight. The magnitude of this effect increases with increasing concentration of tetrabutylaluminate and with increasing tetrahydrofuran to tetrabutylaluminate ratio.

Separated ion pairs have to be considered⁶ in the case of sodium alkylcaprolactamatoaluminate and sodium tetracaprolactamatoaluminate $NaAl[\overline{N(CH_2)_5CO}]_4$, *I*. The degree of association of compound *I* exhibit a negligible concentration dependence ($n = 2.10 - 2.05$ in concentration range 1.5–20%). The probability that a tight ion pair exist in dimeric *I* is decreased by the possibility of sodium atom solvation due to the presence of oxygen and nitrogen donor atoms in the lactam ligand.

The maximal number of tetrahydropyran molecules solvating the sodium cation varies between 2 and 4 in the system tetrahydrofuran–sodium tetra-*n*-butylaluminate-

–cyclohexane at the $\text{NaAl}(\text{n-C}_4\text{H}_9)_4$ concentrations above 0.01 mol l^{-1} , as inferred from the study of $\nu_{(\text{COC})}$ vibrations of tetrahydrofuran⁷. The number of solvating tetrahydrofuran molecules sharply decreases at solute concentrations below 0.01 mol l^{-1} . At low concentrations of tetraalkylaluminate in non-polar solvent the ion pairs are more stable, "tighter", and their solvation is more difficult. High concentration results in decreasing stability of the aggregate owing to the increasing dipole–dipole or ion–dipole interactions. The anions are easily replaceable by molecules of the solvating base.

The sodium solvation number in the presence of other donor bases varies in the range 2–6, depending on the base size, geometry, and solvation ability. It is evident from ¹H NMR and infrared spectra that the solvation number 4 is sufficient for a complete breakdown of the contact ion pairs⁸. The formation of stable complexes in which sodium or generally an alkali metal cation is solvated by one^{9,10} or two^{11–14} base donor atoms have been reported in many cases of solvation. The properties (degree of association, conductivity, infrared and ¹H NMR spectra) of these complexes in solution differ from those of corresponding non-solvated ion aggregates. π -Solvation of the sodium or potassium cation by an aromatic nucleus^{11,13,15} or by a π -system of the triple bond¹⁶ is markedly weaker than the solvation by some base having a donor oxygen or nitrogen atom. No change in chemical shift in the ¹H NMR spectra accompanies the solvation in the case of sodium tetrabutylaluminate, contrary to solvation by tetrahydrofuran or diethyl ether¹⁷. On the basis of the above mentioned facts it can be expected that during the stepwise replacement of the alkyl in sodium tetra-isobutylaluminate by 6-caprolactam the donor oxygen or nitrogen atoms in the resulting $\text{NaAl}(\text{i-C}_4\text{H}_9)_{4-x}[\text{N}(\text{CH}_2)_5\text{CO}]_x(II)$ would preferentially solvate the sodium cation.

The infrared spectra of compounds *II* confirm these assumptions even if the caprolactam for $x < 1$ in lesser extent also contributes to the solvation of the aluminum atom¹⁸. The degree of association of sodium tetra-isobutylaluminate (*II*, $x = 0$) in cyclohexane solution ($0.07\text{--}0.4 \text{ mol l}^{-1}$), determined by cryoscopy, is 2–5.5. For the same concentration range in benzene solution, where the stability of the aggregate is perturbed owing to the solvation of sodium by π -aromatic system, the degree of association of the compound *II* ($x = 0$) is substantially lower (1.55–1.70) and changes only a little. During the stepwise insertion of caprolactam ligand into the molecule of *II* up to $x = 1.7$ in benzene solution, the degree of association slowly rises and then again decreases (Table I). Compounds *I* and *II* ($x = 4$), respectively, as the end products of substitution the isobutyl for 6-caprolactam, are practically dimeric in benzene solution and exhibit only a minimal concentration dependence of the degree of association.

With compound *II* ($x < 1$), the stretching vibration region of its infrared spectrum is dominated by a single band $\nu_{(\text{NCO})}$, assigned to the caprolactam moiety solvating

the sodium atom. As the value of x increases, two other bands participate on the absorption in this region. They were assigned to caprolactam solvating aluminum and sodium and to the non-solvating ligand, the latter band with relatively high wavenumber¹⁸.

The solvation of sodium atom in sodium tetra-*n*-butylaluminate by ether⁹ and aromatic hydrocarbons¹⁷ was also studied by ¹H NMR spectroscopy. Owing to the fast exchange between free and sodium solvating molecules, only one signal of the α -protons of the corresponding ether is present in the spectrum, its chemical shift being an average of the solvating and nonsolvating ether shifts. There is an apparent flexion in the dependence of the chemical shift of the protons under discussion on the ether to solvated sodium ratio; *e.g.* in the system sodium tetra-*n*-butylaluminate-tetrahydrofuran, there are two such points at ratios 1 : 1 and 1 : 4. Similar flexions in the dependence of the chemical shift on the solvation of tetrahydrofuran have been observed in the presence of alkali metal tetrahydridoaluminates¹⁹. However, the chemical shift of β -CH₂ protons of the solvating ligand practically does not change with the varying ether-salt ratio.

Compounds of the type *II* display in their ¹H NMR spectra three broad singlets of ϵ -, α -, and β - δ CH₂ groups of the caprolactam ligand, doublets of the CH₂ and CH₃ groups and a multiplet of the isobutyl CH group (Fig. 1). Fig. 2 shows the dependence of chemical shifts on the number of caprolactam ligand x in the compounds *II* for the individual protons. All signals are slightly shifted downfield with increasing x . The curves for caprolactam α -methylene singlet and isobutyl α -methylene doublet exhibit apparent flexions at $x = 1.7$. Neither multiplicity nor signal shape are changed when varying x in the compound *II*.

TABLE I

Dependence of degree of association (n) in sodium isobutylcaprolactamatoaluminates NaAl(i-C₄H₉)_{4-x}[N(CH₂)₅CO]_x (*II*) on x (determined by cryoscopy in 0.07–0.2 mol l⁻¹ benzene solution)

x	n
0	1.55–1.65
0.33	1.65–1.70
1.01	2.50
1.53	2.85–2.95
2.03	2.30
2.51	1.90–2.10
3.00	2.00–2.10
4.00	2.10–2.05

Starting from the presented results of molecular weight determination, ^1H NMR spectroscopy, and in agreement with the assignment of the four stretching bands of the lactam moiety¹⁸ to the free caprolactam ligand or to this ligand solvating sodium or aluminum, the following assumptions concerning the structure of isobutylcaprolactamatoaluminates *II* and dimeric sodium tetracaprolactamatoaluminate (*I*) can be summarized. Sodium tetra-isobutylaluminum (*II*, $x = 0$) exist in cyclohexane solution as an associate of tight ion pairs, according to the molecular weight determination and in analogy with ref.⁶. Substantially lower degree of association was found in benzene solution of compound *II*. That indicates a large participation of benzene on the solvation of the sodium cation. The degree of association increases by stepwise replacement of isobutyl by caprolactam. The coordination $\text{C}=\text{O}\dots\text{Na}$, already proved by infrared spectroscopy¹⁸, becomes effective. This finding is consistent with the existence of tight complexes $\text{NaAlR}_4\dots$ donor solvent⁹⁻¹⁴. Low probability of coordination between the metal and the nitrogen atom of the $\text{AlN}-\text{C}=\text{O}$ moiety is confirmed by a negligible dependence of the chemical shift of the $\varepsilon\text{-CH}_2$ group in the neighbourhood of nitrogen atom on x and by the absence of any flexion on its curve (Fig. 2). A shift of the $\nu_{(\text{NCO})}$ band toward higher wavenumbers^{1,20}

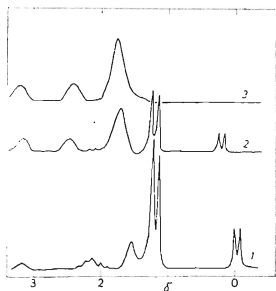


FIG. 1

^1H NMR spectra of sodium isobutylcaprolactamatoaluminates $\text{NaAl}(\text{i-C}_4\text{H}_9)_{4-x}$.

$[\text{N}(\text{CH}_2)_5\text{CO}]_x$; 1 $x = 0.71$; 2 $x = 2.03$;
3 $x = 4$

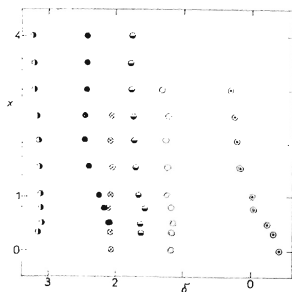


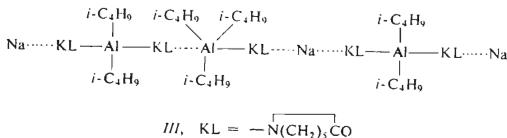
FIG. 2

Dependence of chemical shift δ on x in ^1H -NMR spectra of sodium isobutylcaprolactamatoaluminates $\text{NaAl}(\text{i-C}_4\text{H}_9)_{4-x}$.

$[\text{N}(\text{CH}_2)_5\text{CO}]_x$; \circ $-\text{CH}_2-\text{CH}$,
 \circ CH_3-CH , \otimes CH_2-CH
 $\begin{array}{l} \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$;
 \odot $\varepsilon\text{-CH}_2$, \bullet $\alpha\text{-CH}_2$, \ominus $\beta\text{-}\delta\text{-CH}_2$ of caprolactam

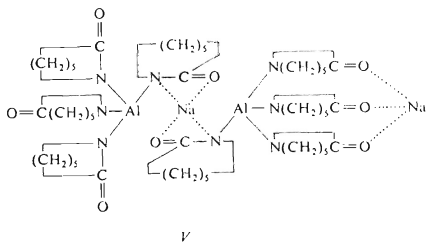
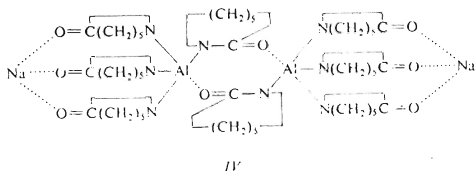
and pronounced dependence of the ϵ -methylene group chemical shift on x can be expected in the case of $N \cdots Na$ or another $N \cdots Al$ coordination, contrary to the spectra of compound *II*. The flexions in the dependence of the degree of association and the chemical shift of caprolactam α -methylene on x for compound *II* appear at $x \cong 1.7$ and correspond to a compound containing 1 to 2 $CO \cdots Na$ coordination bond, per sodium or aluminum atom. This fact is in agreement with similarly proved existence of the complexes $[C_4H_8O \cdots Na][Al(C_4H_9)_4]$ (ref.^{9,10}) or $[Na(C_4H_8O)_2]_2 \cdots [Al(CH_3)_2(C_{14}H_{10})]_2$ (ref.¹¹). Compound *II* ($x = 1.7$) corresponding to the formula $Na_3Al_3[N(CH_2)_5CO]_5(i-C_4H_9)_7$ contains according to the molecular weight determination three aluminum atoms per molecule. Judging from the assigned $\nu_{(NCO)}$ vibrations, this compound should contain a large portion ($> 20\%$) of lactam ligand solvating the aluminum atom. Thus, in the benzene solution of the mentioned composition the prevailing compound will be the aggregate *III*. All the lactam ligands in compound *III* participate on solvation of sodium or aluminum atoms. With increasing caprolactam content in the molecule, the stability of the chain made of three aluminum atoms decreases, the degree of association falls and approaches the values of 2.

Compound *I*, prepared in usual way from sodium tetraamidoaluminate using the stoichiometric or only a slight excess of caprolactam⁶, contains some residual amide groups. Its degree of association in benzene is substantially larger ($n = 3.5-4$ corresponds to summary formula $NaAl(NH)_{0.25}[N(CH_2)_5CO]_{3.5}$; for compound corresponding to summary formula $NaAl(NH)_{0.05}[N(CH_2)_5CO]_{3.9}$, the value of n is 2.8. The $Al-NH-Al$ bridges present in molecules of the above mentioned compounds do not affect substantially the relative proportions of the bands assigned to caprolactam ligand solvating sodium or aluminum, quite similarly to the $Al-O-Al$ bridges in compounds $NaAlO_{4-y/2}[N(CH_2)_5CO]_y$, obtained by partial hydrolysis of the compound *I*.



It follows from the infrared spectra¹⁸ of compounds *II* in the region $1500-1650$ cm^{-1} that the band dominating in the spectrum of *II* ($x = 1$) (1566 cm^{-1} , relative integrated intensity $B \sim 20\%$) is also present in *I* and *II* ($x = 4$), respectively. This

band can be assigned to $\nu_{(\text{NCO})}$ of caprolactam coordinated to sodium through oxygen and nitrogen simultaneously. Band at 1611 cm^{-1} (with $I, B \sim 25\%$) was assigned to lactam group forming a bridge between two aluminum atoms. Band at 1630 cm^{-1} (with $I, B \sim 12\%$) was assigned to non-solvating caprolactam ligand. All mentioned facts can be for example explained by the existence of dimeric I in two forms IV



and V in an equilibrium. Non-solvating ligand in the structure V can be engaged in further coordination with the sodium atom in the structure V or in an intermolecular coordination with the terminal sodium atom in IV ; on the other hand, not all three caprolactam ligands in IV should be coordinated to the sodium atom. The structures IV and V are of course speculative. The co-existence of monomeric I with the aggregate containing three or four aluminum atoms connected similarly to IV or V is in agreement with our conclusions.

EXPERIMENTAL

All manipulations and preparations of the mentioned compounds were performed in dry nitrogen atmosphere. Sodium tetraisobutylaluminate ($II, x = 0$) was prepared by reaction of triisobutylaluminum with sodium²¹. Sodium isobutylcaprolactamate aluminates were obtained by reaction of compound $II, n = 0$ with sodium tetracaprolactamatealuminate⁶ or with the benzene solution of 6-caprolactam as described previously¹⁸. The solvents used were dried by distillation from $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$ solution. Molecular weights were determined by cryoscopy in ben-

zene. ^1H NMR spectra of 7% benzene solutions of compounds *I* and *II* were measured on instruments Tesla BS-467 (60 MHz, 20°C) and Varian XL-100 (100 MHz, 27°C).

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