

# Multinuclear Magnetic Resonance Study on Aluminium *Sec*-butoxide Chelated with Ethyl Acetoacetate in Various Amounts

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RECEIVED: September 27, 2018 \* REVISED: January 18, 2019 \* ACCEPTED: January 20, 2019

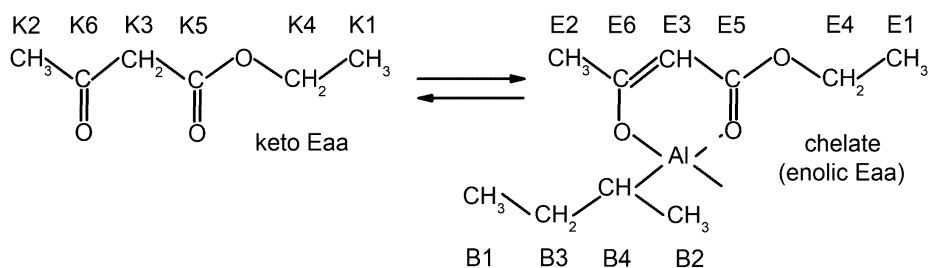
**Abstract:** Reactive aluminum alkoxide (ASB, aluminium *sec*-butoxide) was chelated using  $\beta$ -diketone (EAA, ethyl acetoacetate) in order to gain control over rapid hydrolysis in the course of the sol-gel process. Derived chelates were analysed using several NMR spectroscopic techniques: one-dimensional  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{27}\text{Al}$  NMR and two-dimensional COSY, HSQC and DOSY. The NMR analysis enabled identification of the formed chelate species, as well as determination of their quantitative relationships. Several complexation products were observed: tris-chelated monomer,  $\text{Al}(\text{EAA})_3$ , bis-chelated dimer,  $\text{Al}_2(\text{O}^i\text{Bu})_4(\text{EAA})_2$ , tris-chelated dimer,  $\text{Al}_2(\text{O}^i\text{Bu})_3(\text{EAA})_3$ , tetra-chelated dimer,  $\text{Al}_2(\text{O}^i\text{Bu})_2(\text{EAA})_4$ , and monochelated trimer,  $\text{Al}_3(\text{O}^i\text{Bu})_8(\text{EAA})$ . Of the formed oligomer compounds, this is the first evidence of  $\text{Al}_2(\text{OR})_3\text{L}_3$  in any alkoxide and  $\beta$ -ketoester or  $\beta$ -diketone combination. Aluminium *sec*-butoxide and ethyl acetoacetate complexes  $\text{Al}_2(\text{O}^i\text{Bu})_4(\text{EAA})_2$  and  $\text{Al}_2(\text{O}^i\text{Bu})_2(\text{EAA})_4$  were also observed for the first time. With the increase of the EAA/ASB ratio the coordination of aluminium shifts towards six, whereas above the EAA/ASB ratio of 2.5 solely six-coordinated aluminium exists.

**Keywords:** aluminium *sec*-butoxide, ethyl acetoacetate, NMR spectroscopy, sol-gel processes.

## INTRODUCTION

**A**LUMINA materials, especially transient forms exhibiting lower level of structural ordering are well known for their high specific surfaces. As they also display low cost, good thermal stability, surface acidity and interconnectivity with transition metals, they often find application in adsorbents, catalysts, desiccants, coatings, also as soft abrasives and advanced polycrystalline ceramics.<sup>[1]</sup> The simplest way of preparation is the thermal treatment of widely available aluminium hydroxides. However, this method often yields with particles above the nano level. On the contrary, the use of the sol-gel synthesis route was found favourable for the preparation of nanocrystalline alumina.<sup>[2]</sup> The sol-gel precursors are usually metal alkoxides, such as aluminium *sec*-butoxide,  $\text{Al}(\text{OC}_4\text{H}_9)_3$ . The structure of the alkoxide molecule enables the reactions of polymerisation and subsequent formation

of a continuous gel network. However, in case of ASB the reactivity is very high; thereof hydrolysis will occur even with air moisture, yielding with unwanted precipitation of hydroxides.<sup>[3]</sup> Such behaviour leads to difficulties in control of the sol-gel process. Thereof chelating agents are introduced in order to facilitate control over the sol-gel process.<sup>[4,5]</sup> The area of modification of various alkoxides using various chelators has been widely explored; a book by Bradley *et al.* provides a good insight in this area.<sup>[6]</sup> Normally, the chelating mechanism reposes on the affecting the availability of the alkoxy groups, where, as a consequence, hydrolytic stability is increased and condensation functionality is also altered.<sup>[3,7,8]</sup> Having in mind availability and low price,  $\beta$ -diketones and  $\beta$ -ketoesters are often used as chelating agents, ethyl acetoacetate, EAA,  $(\text{C}_6\text{H}_{10}\text{O}_3)$  being one example.<sup>[9]</sup> EAA shows characteristic movement of weakly bonded hydrogen, thereof EAA resides in equilibrium between enol



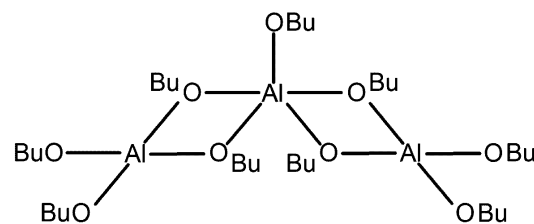
**Figure 1.** Keto-enol tautomerism and the formation of chelate. Denomination is introduced for the later interpretation of  $^1\text{H}$  and  $^{13}\text{C}$  NMR signals.

and keto form, which is known as keto-enol tautomerism (Figure 1).<sup>[10]</sup> In the enolic tautomer a reactive hydroxy group, capable of becoming a bidentate monocharged enolate ligand is present and can substitute an alkoxy group in the metal alkoxide. As a consequence, a six membered chelate ring may be formed, consequently increasing the hydrolytic stability of the alkoxide (Figure 1).<sup>[10]</sup> Normally, the keto-enol equilibrium heavily favours the keto form, yet the chelate formation will shift the keto-enol equilibrium towards the enolic form.<sup>[9,11]</sup>

As for the sol-gel process, the main issue is the control of the hydrolysis and condensation processes. This control is restored by chelation, as the availability of sites prone to nucleophilic attack by water is limited. Consequently, the chelation increases the aluminium coordination number and affects the degree of oligomerization. Generally, the favoured coordination number for aluminium in alkoxides is 6, which is achieved through the oxygen atoms of alkoxide groups.<sup>[12]</sup> The expansion of coordination is enabled *via* alkoxy bridging on behalf of which oligomeric species are formed.<sup>[13]</sup> Thereby, different metal centres, ligands and alkoxide/chelator ratios will yield different oligomers. It is important to notice that steric forces which arise for bulkier alkoxy groups hinder the oligomerization.<sup>[14]</sup> So, alkoxides having small and unbranched alkyl groups are able to achieve a higher coordination number, while the same is not possible for those having bigger and branched alkyl groups.<sup>[12]</sup> From the ASB structural models, the linear trimer is recognised as the most probable oligomer.<sup>[7,12]</sup> The linear trimer employ four alkoxy bridges connecting central aluminium reaching the coordination number of five, to two lateral four-coordinated aluminium atoms (Figure 2).

Numerous valuable investigations on the chelation of aluminum alkoxides with  $\beta$ -diketones and  $\beta$ -ketoesters have been conducted.<sup>[3,5,9,11,13,15–23]</sup> However, only few papers systematically investigated the various oligomeric compounds obtained. Wengrovius *et al.*<sup>[13]</sup> investigated complexes of  $[\text{Al}(\text{OR})_2\text{L}]_2$  and  $[\text{Al}(\text{OR})\text{L}_2]_2$  type, where OR

was *iso*-propyl, *tert*-butyl,  $\text{SiMe}_3$  and  $\text{SiPh}$ , while L was acetylacetonate or ethyl acetoacetate. They concluded that  $[\text{Al}(\text{OR})_2\text{L}]_2$  complexes are dimers containing tetrahedral and octahedral sites on a twofold axis. Two OR groups bridge the two Al sites, while the octahedral Al is additionally bound to two L groups and tetrahedral Al is additionally bound to two OR groups. Only for large OR groups the molecule was a monomer. Aging of  $[\text{Al}(\text{O}-i\text{-Pr})_2\text{acac}]_2$  over a period of several weeks yielded a linear trimer having two octahedral Al, one bound to two acetylacetonate groups, other bound to one acetylacetonate group, and one tetrahedral Al bound to two terminal isopropoxide groups, with four bridging isopropoxide groups joining all metal centres. For the  $[\text{Al}(\text{OR})\text{L}_2]_2$  complexes they proposed centrosymmetric dimer structure having two possible isomers for symmetric L, *meso* and *d,l*, distinguishable by NMR only at low temperatures. They also noted that compounds of the  $[\text{Al}(\text{OR})\text{L}_2]_2$  type decompose in a solution *via* ligand disproportionation to  $\text{AlL}_3$  and  $[\text{Al}(\text{OR})_2\text{L}]_2$  and that when L=ethyl acetoacetate, the  $[\text{Al}(\text{OR})_2\text{L}]_2$  complex is more stable. Finally, Wengrovius *et al.*<sup>[13]</sup> noticed that in the prepared molecules, aluminium prefers the coordination numbers of 6 and 4. On the contrary, the occurrence of coordination 5 is scarce.<sup>[13]</sup> Complexes of the  $[\text{Al}(\text{O}^i\text{Pr})_2\text{L}]_2$  and  $\text{AlL}_3$  type with L as methyl, ethyl, *iso*-propyl, *tert*-butyl, allyl and 2-(methacryloyloxy)ethyl acetoacetate, were investigated by Lichtenberger *et al.*<sup>[22]</sup> They managed to



**Figure 2.**  $\text{Al}_3(\text{O}^t\text{Bu})_9$  linear trimer.

prepare  $AlL_3$  derivatives at room temperature and  $[Al(O^iPr)_2L]_2$  derivatives by heating of the reaction solution. They observed that the asymmetric substitution takes place in the prepared dimers with the appearance of tetrahedral Al bound to two terminal alkoxy and two bridging groups, and octahedral Al bound to two bridging alkoxy groups and two chelating  $\beta$ -ketoesterate ligands. Three possible isomers exist as a consequence of the asymmetric nature of  $\beta$ -ketoesterate ligands, one being asymmetric  $C_1$  and second symmetric  $C_2$ , each forming a pair of enantiomers, giving 6 stereoisomers overall. The tri-substituted monomeric  $AlL_3$  complexes have two isomers, asymmetric  $C_1$  where keto and ester oxygen atoms are in *mer* arrangement, and symmetric  $C_3$  complex with keto and ester oxygen atoms in *fac* arrangement, each forming a pair of enantiomers<sup>[22]</sup> In another paper Lichtenberger *et al.*<sup>[23]</sup> investigated the complexes of  $[Al(OR)_2L]_2$ ,  $[Al(OR)L_2]_2$  and  $AlL_3$  type, where L was dimethyl, diethyl, di-*iso*-propyl, di-*tert*-butyl malonate, while R was ethyl, *iso*-propyl, *tert*-butyl. Malonates show symmetry; thereof the number of possible isomers is low in comparison with  $\beta$ -ketoester derivatives. Namely, only one  $AlL_3$  and one  $[Al(OR)_2L]_2$  isomer exist. For  $[Al(OR)L_2]_2$  two isomers, *meso* and *d,l*, are possible. Lichtenberger and Schubert<sup>[24]</sup> presented a review on chemistry of various pure and chemically modified aluminium alkoxides. They pointed out the dependence of the degree of oligomerization on the type and size of the alkoxy group. Also, they observed that the modification with the chelating ligand tends to have minimal effect on the change of the degree of oligomerization. Recently, our group<sup>[25]</sup> managed to determine the crystal structure of aluminium tris(ethyl acetoacetate). Using XRPD the crystallised molecule of three ethyl-acetoacetate *O,O*-bidentately linked ligands in octahedral coordination with aluminium centre connected into 1D chains by two hydrogen bonds was assigned to the monoclinic space group  $P2_1/n$ .

The physical properties of the final material are strongly influenced by the structure of the gel. The gel formation is critically influenced by the hydrolysis and polycondensation processes, which are in turn under heavy influence of the modifiers, *i.e.* the chelation control agents.<sup>[9]</sup> Hence, the alteration of the degree of oligomerization, coordination number, ligand occurrence and distribution yielding various compounds, would enable better control and understanding of the sol-gel process. On behalf of the former, properties of the sol-gel derived alumina-based materials could be improved. For this reasons, aluminium *sec*-butoxide ( $Al(O^iC_4H_9)_3$ , ASB) / ethyl acetoacetate ( $C_6H_{10}O_3$ , EAA) system has been investigated in a systematic manner. Sols, *i.e.* chelation products of ASB/EAA in different ratios were analysed by nuclear magnetic resonance techniques in order to structurally identify, quantify and report the occurring species.

## EXPERIMENTAL

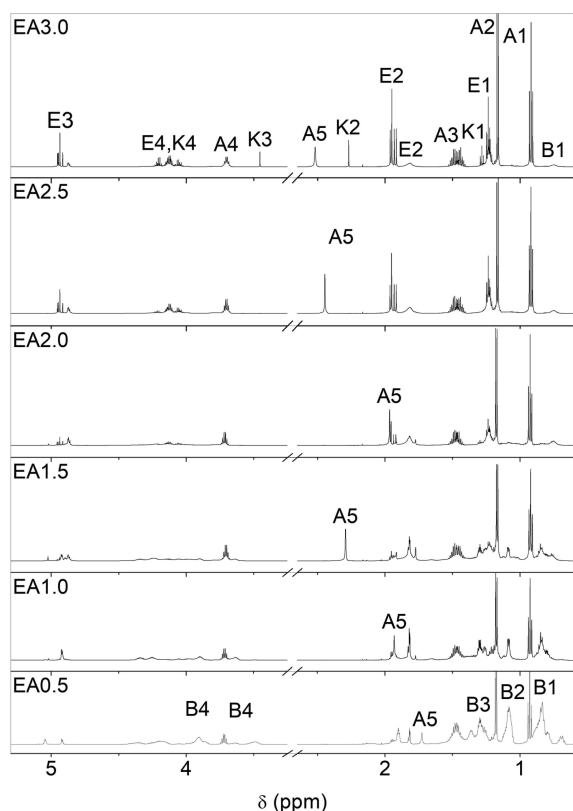
Reactants for the sol-gel reaction were aluminium *sec*-butoxide, ASB,  $Al(O^iBu)_3$ , 97 %, Aldrich, Great Britain and ethyl acetoacetate, EAA,  $C_6H_{10}O_3$ , 99 %, Fluka, Germany. Sols having different EAA/ASB molar ratios of 0.5, 1, 1.5, 2, 2.5 and 3 were prepared, denoted accordingly EA0.5, EA1.0, EA1.5, EA2.0, EA2.5 and EA3.0, respectively. Uniform amount of ASB was added to the appropriate amount of EAA using a syringe to minimize exposure to air humidity. Thereafter the mixtures were stirred in a closed reactor at room temperature for 24 h, during which no precipitation occurred. All chemicals were used as received. All subsequent spectroscopic analyses were performed within the next 24 h.

For the NMR measurements the samples were dissolved in  $CDCl_3$  and the spectra were recorded from 5 mm NMR tubes. High-resolution NMR spectrometer Bruker Avance 300 was used for scans of 1D  $^1H$  and  $^{13}C$  spectra; operating at 298.64 MHz for  $^1H$  NMR and at 75.10 MHz for  $^{13}C$  resonance. Agilent Technologies DD2 spectrometer was used for scans of 1D  $^{27}Al$  NMR spectra; operating at 78.95 MHz. The structural features of various aluminium complexes were analysed by different 1D  $^1H$ ,  $^{13}C$  and  $^{27}Al$  NMR techniques as well as 2D NMR correlated spectroscopy (COSY), heteronuclear single quantum correlation (HSQC) and diffusion-ordered spectroscopy (DOSY) measured with Bruker standard pulse sequences.

All  $^1H$  and  $^{13}C$  NMR chemical shift values ( $\delta$ ) are expressed in ppm relatively to the internal standard tetramethylsilane (TMS). The signals in the NMR spectra were deconvoluted using the Lorentz function.

## RESULTS

Figure 3 presents the  $^1H$  NMR spectra of samples EA0.5–EA3.0, where hydrogen atoms are labelled according to Figure 1. The spectra showed the presence of chelate, *i.e.* *sec*-butoxide and ethyl acetoacetate, both bound to aluminium, as well as *sec*-butanol released in the course of the chelation. As mentioned before, EAA is capable of undergoing keto-enol tautomerism (Figure 1). In such manner EAA becomes a bidentate monocharged ligand, substitutes an alkoxy group of the alkoxide and forms a complex having both oxygen atoms bound to the metal (Figure 1). Therefore, while the keto tautomer shows methylene protons signal at 3.45 ppm (K3), the enolic tautomer at this position has a single proton, whose signal appears at 4.8–5.1 ppm (E3).<sup>[10,22]</sup> In such manner the two tautomers are easy to discern and thereof it is clearly possible to monitor the extent of the chelation on behalf of the enolic-EAA content.



**Figure 3.**  $^1\text{H}$  NMR spectra of samples EA0.5–EA3.0 in  $\text{CDCl}_3$ . Resonance signals are labelled according to Figure 1. *Sec*-butanol peaks are labelled with the letter A, while the number is analogous to butoxide, hydroxyl group protons are labelled A5.

The  $^1\text{H}$  NMR spectra of all six samples exhibit signals due to the enolic-EAA: at 4.8–5.1 ppm methyne protons singlet occurs (E3), at 4.0–4.25 ppm methylene protons quartet occurs (E4), at 1.7–2.0 ppm methyl protons singlet occurs (E2) and at 1.2–1.3 ppm methyl protons triplet occurs (E1). Yet, the sample EA3.0 shows spectra where also free keto-EAA occurs in traces: at 3.45 ppm methylene protons singlet occur (K3), at 2.27 ppm methyl protons singlet occur (K2) and at 1.24 ppm methyl protons triplet occurs (K1). The weak quartet of methylene protons (K4) is overlapped with E4. According to these observations, complete chelation occurs in all samples except in the sample EA3.0, where only a minor part of EAA is free. The intensity of resonances due to EAA increases from sample EA0.5 to sample EA3.0 as the amount of EAA in the samples increases. In addition, for each of the EAA group multiple sets of resonance peaks were recorded. Such spectral features point out that the molecules of the chelating agent are bound to inequivalent chelating sites,<sup>[4]</sup> either in a

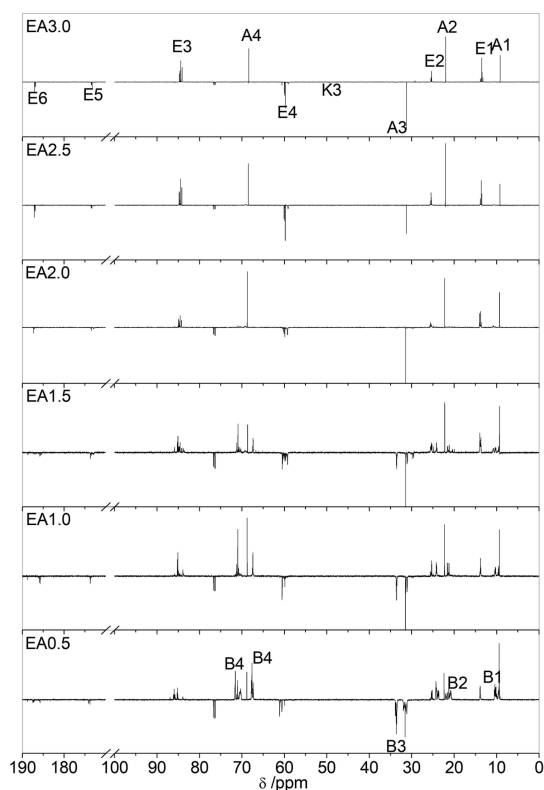
single molecule having no isomers, a molecule with different isomers or different molecules. The vast number of peaks suggests that all of the above would be the most probable outcome.

In the course of the chelation process a part of butoxy groups has been replaced with the EAA molecule. Therefore, signals assigned to butoxy group protons in ASB, as well as protons of butanol released in the course of the chelation process, could be observed in the  $^1\text{H}$  NMR spectrum. Due to the changes in intensity, it is easy to discern between those two sets of resonances. Of course, the intensities of the butoxide protons resonances decrease, while the intensities of the butanol protons resonances increase from sample EA0.5 to sample EA3.0. Additionally, the butoxide protons resonances occur as multiple overlapped peaks due to different inequivalent butoxide groups' position. At the same time, the butanol protons resonances are well defined occurring at constant chemical shifts.

Therefore, characteristic signals of the butoxy group occur at 3.4–4.0 (B4), 1.2–1.4 (B3), 1.0–1.15 (B2) and 0.65–0.9 (B1) all in ppm. At the same time, the resonances of butanol released in the course of the chelation can be observed at 3.65–3.75 (A4), 1.4–1.55 (A3), 1.15–1.2 (A2) and 0.9–0.95 (A1) all in ppm. Additional resonance signals at 1.73 (EA0.5), 1.93 (EA1.0), 2.29 (EA1.5), 1.97 (EA2.0), 2.45 (EA2.5) and 2.52 ppm (EA3.0) can be attributed to the protons of the hydroxyl group from the released butanol.

These observations are additionally confirmed by the analysis of the DOSY spectra of samples EA1.5 and EA3.0 (Figure S1). In the DOSY spectrum of EA3.0, peaks corresponding to the free *sec*-butanol and ethyl acetoacetate in the keto form decay faster than the peaks of the enol form of ethyl acetoacetate in the chelate.

The  $^{13}\text{C}$  NMR spectra of samples EA0.5–EA3.0 are presented in Figure 4. The samples display signals originating from the enolic-EAA bound to Al: at  $\approx 13$  and  $\approx 25$  ppm methyne carbon occurs (E1, E2), at  $\approx 60$  ppm methylene carbon occurs (E4), at  $\approx 85$  ppm methyne carbon occurs (E3) and at  $\approx 173$  and  $\approx 187$  ppm quaternary carbons occur (E5, E6). From the  $^{13}\text{C}$  NMR results it is also obvious that the entire EAA (or at least the vast majority) was present as the enol tautomer coordinated to aluminium. Namely, quaternary carbons showed shifts of  $^{13}\text{C}$  signals from 167 and 201 ppm (characteristic for the uncoordinated keto-form) to 173 and 187 ppm (characteristic for the coordinated enolic-form).<sup>[5,11]</sup> Only in the EA3.0 sample a weak methylene carbon signal at 49 ppm (K3), *i.e.* weak keto-EAA could be observed. Other signals of this tautomer in EA3.0 are too weak to be observed or are completely overlapped. In the  $^{13}\text{C}$  NMR spectra, signals originating from the butoxy group are observed:  $\approx 9.5$ – $10.8$  ppm (B1),  $\approx 20.3$ – $22.2$  (B1), 33.0–34.4 (B3),  $\approx 67.0$ – $67.9$  and

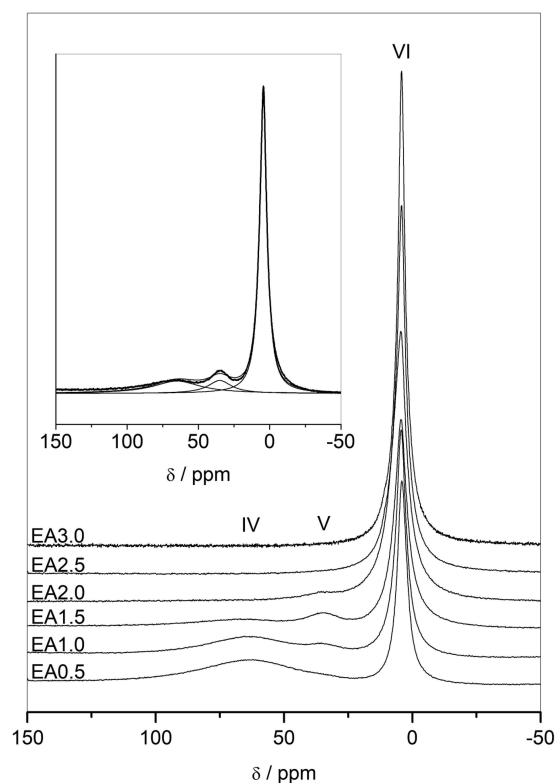


**Figure 4.**  $^{13}\text{C}$  NMR spectra of samples EA0.5–EA3.0 in  $\text{CDCl}_3$ . Resonance signals are labelled according to Figure 1. Butanol peaks are labelled with the letter A, while the number is analogous to butoxide.

$\approx 70.0$ – $71.9$  (B4); butanol:  $\approx 9$  (A1),  $\approx 22$  (A2), 31 (A3), 68 (A4), and  $\text{CDCl}_3$  ( $\approx 76$  ppm). The  $^{13}\text{C}$  NMR spectra are in accordance with the  $^1\text{H}$  NMR spectra.

The HSQC spectra of the sample EA3.0 (Figure S2) enabled a deeper insight in the relations between initially assigned proton resonances and corresponding carbon atoms. Thus, the HSQC spectrum of the sample EA3.0 exhibited correlations of carbon with directly attached protons: C-E3 at 88 ppm with methyne proton (E3) at 4.9 ppm, C-E4 at 64 ppm with methylene protons (E4) at 4.0–4.2 ppm, C-B4 at 72 ppm with methyne proton B4 at 3.7 ppm, C-E2 at 29 ppm with methyl protons E2 at 1.9 ppm, C-B3 at 1.4 ppm with methylene protons B3 at 35 ppm, C-E1 at 16 ppm with methyl protons E1 at 1.2 ppm, C-B2 at 25 ppm with methyl protons B2 at 1.1 ppm and C-B1 at 12 ppm with methyl protons B1 at 0.9 ppm.

The  $^{27}\text{Al}$  spectra of the samples EA0.5–EA3.0 are presented in Figure 5. The  $^{27}\text{Al}$  spectra gave a good insight in the coordination state of Al. Generally, peaks at about 0–10 ppm are assigned to the six-coordinated Al atoms, peaks



**Figure 5.**  $^{27}\text{Al}$  NMR spectra of samples EA0.5–EA3.0 in  $\text{CDCl}_3$ . Resonance signals are labelled with the appropriate coordination number. Inset: The deconvolution of  $^{27}\text{Al}$  NMR resonances for the sample EA1.5.

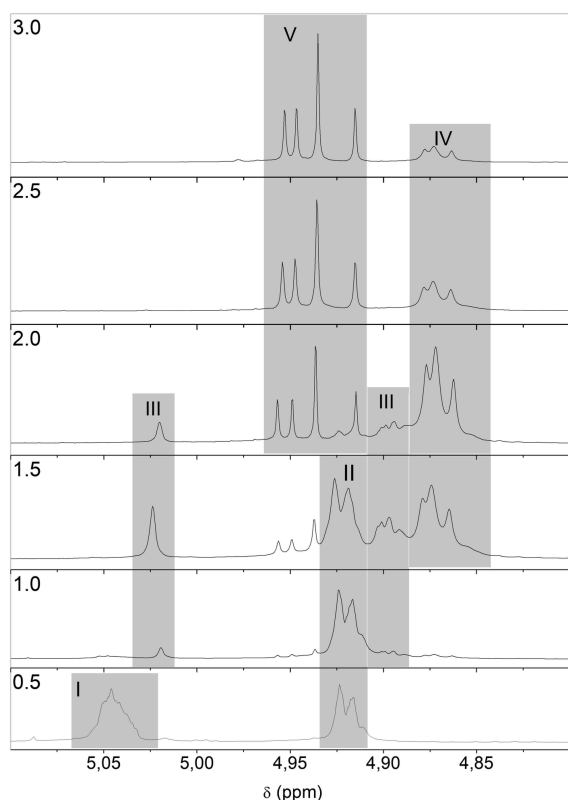
between 30 and 40 ppm to the five-coordinated Al and peaks between 60 and 70 ppm to the four-coordinated aluminium atoms.<sup>[7,11,12,13,15,22]</sup> As can be seen, the spectrum of the sample EA0.5 shows a sharp peak at  $\approx 4$  ppm due to the six-coordinated Al, and a broad peak centred at  $\approx 63$  ppm due to the four-coordinated aluminium atoms. While the sharp peaks are attributed to the uniform hexacoordinated Al environment, the broad peaks are a consequence of various geometrical arrangements around the tetraordinated Al,<sup>[12]</sup> *i.e.* the coexistence of different tetrahedral Al centres.<sup>[23]</sup> In the spectra of samples EA1.0 to EA2.0, beside the peaks due to the six- and four-coordinated structural units, a shoulder at 34 ppm, which is the consequence of the five-coordinated aluminium atoms, could be observed. The spectra of samples EA2.5 and EA3.0 show only strong and sharp peaks due to the six-coordinated aluminium atoms. The deconvolution of the peaks using the Lorentz function yields fractions of aluminium atoms in various coordination (Table 1). The trends displayed in Figure 5 and Table 1, *i.e.* the decrease

**Table 1.** Share of aluminium atoms in various coordinations for samples EA0.5–EA3.0 calculated through deconvolution of  $^{27}\text{Al}$  NMR spectra

Sample	Al(IV)	Al(V)	Al(VI)
EA0.5	0.57	0	0.43
EA1.0	0.39	0.05	0.56
EA1.5	0.19	0.10	0.71
EA2.0	0	0.05	0.95
EA2.5	0	0	1.00
EA3.0	0	0	1.00

of the tetracoordinated aluminium share and the increase of the hexacoordinated aluminium share, clearly occur on behalf of the replacement of alkoxide groups with the bidentate ligand. While it could be argued that such trends are a consequence of the alterations of quantitative relationships between various oligomeric compounds in the mixture, the appearance of the pentacoordinated aluminium seems correlated with one oligomeric compound.

Parts of the  $^1\text{H}$  NMR spectra, where characteristic E3 ring methyne proton of EAA resonances occurs, are given in Figure 6. As discussed before, such spectra, exhibiting



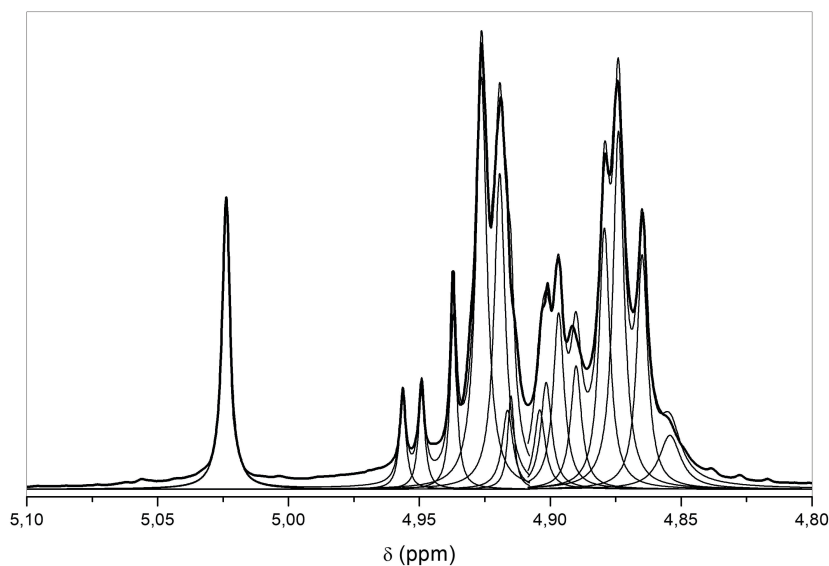
**Figure 6.** Segment of  $^1\text{H}$  NMR E3 resonances in the spectra of samples EA0.5–EA3.0 in  $\text{CDCl}_3$ .

multiple resonances, point out to the existence of inequivalent chelating sites.<sup>[4]</sup> As expected, with the increase of the  $\text{EAA}/\text{Al}(\text{O}^i\text{Bu})_3$  molar ratio, the EAA resonances intensities in the chelate also increase. But their relative intensities, characteristic for EAA present in various isomers, change considerably. Some resonances occur only for the higher  $\text{EAA}/\text{Al}(\text{O}^i\text{Bu})_3$  molar ratios, while other at higher ratios completely disappear. These characteristic signals change their intensity as a function of the EAA amount, which could aid the deduction of the presence of the coordinated compounds. Based on the intensity changes, peaks due to E3 resonance could be sorted into five groups (I – V): broad peak between 5.03 and 5.06 ppm (I), group of three peaks in the range 4.90–4.93 ppm (II), four peaks where one is between 5.01 and 5.03 ppm and the other three in the range 4.88–4.91 ppm (III), five peaks between 4.84 and 4.88 ppm (IV), and four peaks in the range 4.91–4.96 ppm (V) (Figure 6).

Similar sets could be observed in the area characteristic for E2 (Figure 3). Unfortunately, for the samples EA1.0 and 2.0 an overlapping of hydroxyl hydrogen signal with E2 resonances of the EAA occurs, making the spectra less resolvable.

On the basis of appearance of those peaks it was established that five kinds of chelate species are present in the sol (I–V), yet some of them are present as different isomers. From the intensities of the peaks it is quite obvious that the ratio of EAA to Al increases from compound I to compound V. The  $^1\text{H}$  NMR spectra are useful in providing quantitative data, as on behalf of the areas of the characteristic signals, the share of protons present in a particular environment could be determined. Such data could again aid the deduction of the presence of coordinated compounds. Therefore, the Lorentz function was used to deconvolute parts of the spectra containing E3 resonance signals. In Figure 7 the deconvolution for the sample EA1.5 is shown as an example. The sums of the integral area of the peaks' groups attributed to certain chelate compounds are given in Table 2.

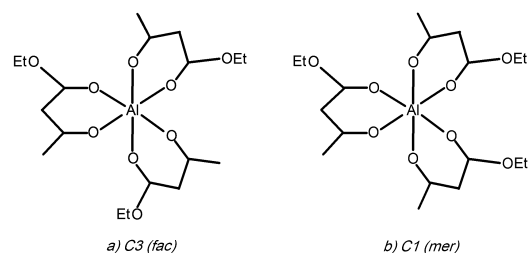
Although some information could be gained with the number of associated peaks, their relationships and relative areas, in such manner it is not possible to deduce



**Figure 7.** The deconvolution of E3  $^1\text{H}$  NMR resonances for the sample EA1.5.

compounds present in the sol and their relative amounts with certainty. However, if the assumptions on compounds are made, they can be checked with mass balancing. In order to make proper assumptions, the tendency of aluminium alkoxides toward the formation of oligomers is of utmost importance. Then one has to bear in mind that the desired coordination of aluminium cannot be achieved in alkoxides, since the oxidation state of aluminium of 3 does not meet its usual coordination number of 6. Yet the coordination is met *via* alkoxy bridging, on behalf of which oligomeric species are formed. According to Wengrovius *et al.*,<sup>[13]</sup>  $\beta$ -diketone chelates show preference for tetrahedral and octahedral coordination around the aluminium atom and eschew geometries with the coordination number of five. The chelates properties are ligand dependent, since different bulkiness of the ligands causes steric hindrance that may prevent oligomerization.<sup>[23]</sup> Therefore, taking into consideration the tendency of ASB to the formation of oligomeric species and the obvious fact that the EAA/Al ratio increases from compound I to compound V, the assumptions on oligomeric compounds were made as follows.

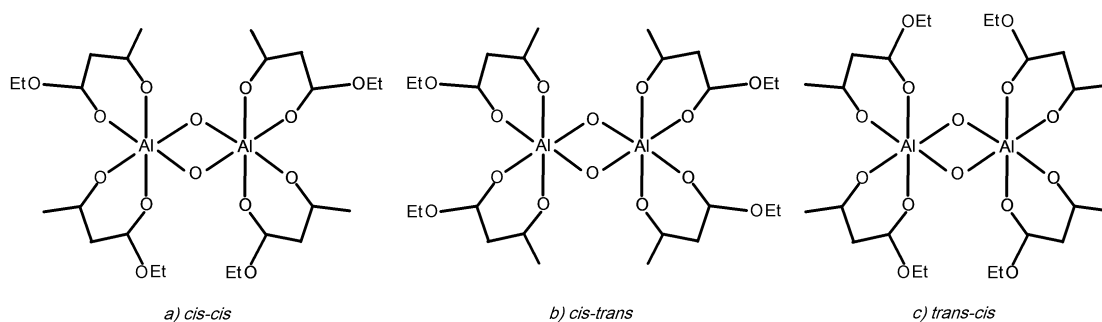
As can be seen in Figure 6, four distinct signals due to compound V can be observed. It was established<sup>[10]</sup> that these signals are consistent with the tris-chelated monomer  $\text{Al}(\text{EAA})_3$ , whereas four signals arise on behalf of the coexistence of different isomers in the solution. The trisubstituted Al ( $\beta$ -ketoesterate)<sub>3</sub> compounds are mononuclear octahedral complexes with asymmetric chelating ligands.<sup>[22,25]</sup> They display two stereoisomers (Figure 8) due to non-equivalent oxygen atoms (close to the ethoxy and methyl group); facial (*fac*) and meridional



**Figure 8.** Schematic representation of the proposed structures of a) *fac* and b) *mer* isomers of  $\text{Al}(\text{EAA})_3$  complex.

**Table 2.** Sum of area of five resonance sets for samples EA0.5–EA3.0 calculated through the deconvolution of  $^1\text{H}$  NMR spectra

Sample	A(I)	A(II)	A(III)	A(IV)	A(V)
EA0.5	55	43	0	0	0
EA1.0	14	136	26	16	14
EA1.5	0	86	76	103	30
EA2.0	0	21	64	212	83
EA2.5	0	0	0	181	265
EA3.0	0	0	0	156	386



**Figure 9.** Schematic representation of the proposed centrosymmetric structures of a) *cis-cis*, b) *cis-trans* and c) *trans-cis* isomers of  $\text{Al}_2(\text{OBu})_2(\text{EAA})_4$  complex. First prefix is omitted since the bridging butoxide groups are fixed in *cis* position.

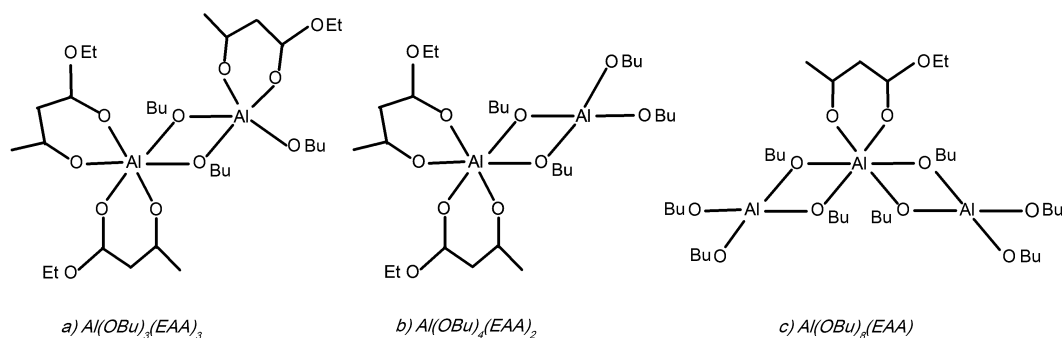
(*mer*).<sup>[22,25]</sup> Since the *fac* isomer is characterised by threefold rotational axis (point group  $C_3$ ), all of the three ligands are magnetically equivalent, on behalf of which a single E3 resonance occurs in their  $^1\text{H}$  NMR spectra. On the contrary, the *mer* isomer (point group  $C_1$ ) contains no symmetry element, thus three E3 resonances appear due to non-equivalent ligands. Obviously, three equally intense resonances belong to the *mer* isomer, while the intense single resonance belongs to the *fac* isomer. The fitted E3 signals gave the approximate ratio of 1:1:2:1, pointing out to the *fac* to *mer* isomer ratio of 2:3. The trisubstituted monomeric  $\text{AlL}_3$  compounds have been described previously for this<sup>[25]</sup> and other alkoxide/chelating agent systems.<sup>[22,23,26]</sup>

The compound IV resonances are consistent with the tetra-chelated dimer,  $\text{Al}_2(\text{O}^n\text{Bu})_2(\text{EAA})_4$ . Molecules of this type have been first described by Wengrovius *et al.*,<sup>[13]</sup> while Lichtenberger *et al.* recently reported on  $[\text{Al}(\text{O}^i\text{Pr})(\text{di-isopropyl malonate})_2]_2$ <sup>[23]</sup> and  $[\text{Al}(\text{O}^s\text{Bu})(\text{acetyl acetate})_2]_2$ .<sup>[24]</sup> Those compounds display binuclear complexes with asymmetric alkoxide bridges. In the  $\text{Al}_2(\text{O}^n\text{Bu})_2(\text{EAA})_4$  structure, the octahedral aluminium centre is coordinated by two EAA ligands and two alkoxy groups (Figure 9). The dimeric structure occurs *via* the alkoxy bridges, which in turn enables for each aluminium atom to reach the preferred coordination number six. In analysing the possible isomers of this compound various facts have to be taken into consideration: If a symmetric diketone<sup>[13]</sup> or dialkyl malonate was employed as a chelating agent, there would be two possible isomers for a symmetric dimer, *meso* and *d,l*. Since  $\beta$ -ketoester was used, while considering possible isomers, the asymmetric structure of the chelate molecule has to be taken into consideration. In the binuclear dimer each aluminium atom is octahedrally coordinated with oxygens; two oxygens are from  $\text{O}^n\text{Bu}$  ligands, and the other four from  $\beta$ -ketoester ligand. Oxygens from the  $\beta$ -ketoester ligand

differ due to the relative orientations of the ethoxyde and methyl group. Prefixes (normally *cis* or *trans*) are used to distinguish species in the abovementioned configuration, where the first specifies the relative position of the  $\text{O}^n\text{Bu}$  ligands, while the second and the third specify the positions of the ethoxyde and methyl group, respectively. The number of possible configurations in this case would be five, but in fact it is reduced to three, since the bridging butoxide groups are fixed in *cis* position. Therefore, *cis-cis-cis*, *cis-cis-trans* and *cis-trans-cis* configurations at each side of the molecule are possible. A single set of resonances should be observed for symmetrical *cis-trans-cis* and *cis-cis-trans* configurations.<sup>[22]</sup> On the other hand, *cis-cis-cis* configuration has magnetically non-equivalent protons and may yield two methyl, two methylene and two ring proton resonances.<sup>[22]</sup> As can be observed in  $^1\text{H}$  NMR (Figure 7), ring methyne protons ( $-\text{CH}=\text{}$ ) show four distinguishable signals, two of them of equal intensity consistent to the existence of the three configurations around the aluminium atom in the tetra-chelated dimer. It seems that two of the three possible configurations, one of them can be assigned as *cis-cis-cis* with certainty, occur in similar amounts, while the third can barely be observed. Tetra-chelated dimers have been described before for other alkoxide/chelating agent systems,<sup>[12,23]</sup> but not for this particular system.

The chelate compound III is characterized by a heavily overlapped group of four peaks in the range 4.88–4.91 ppm, as well as a singlet between 5.01 and 5.03 ppm. The first set of ring proton resonances is similar to those of the compound IV, only the small fourth peak was not observed due to an overlapping with the compound IV peaks. A single resonance between 5.01 and 5.03 ppm has an area equal to  $\frac{1}{2}$  of the sum of resonances in the range 4.88–4.91 ppm. This is consistent with a dimer having two EAA molecules bounded to one aluminium atom and a single EAA molecule bounded to another aluminium atom,





**Figure 10.** Schematic representation of the proposed structure of a) one possible isomer of  $Al_2(OBu)_3(EAA)_3$  complex, b) one possible isomer of  $Al_2(OBu)_4(EAA)_2$  complex and c)  $Al_3(OBu)_8(EAA)$  complex.

$Al_2(OBu)_3(EAA)_3$ , (Figure 10a). According to Wengrovius *et al.*<sup>[13]</sup> and Tadanaga *et al.*,<sup>[7]</sup> the structure expected at this chelate to butoxide ratio is  $[Al(OBu)_2(EAA)]_3$  linear trimer. It is worth noting that the intensities of  $^1H$  NMR resonances characteristic for the compound III change in a similar manner as the  $^{27}Al$  NMR resonance of the pentacoordinated aluminium (Figures 6 and 5). Therefore, the  $^{27}Al$  NMR spectra also point out to the dimeric  $Al_2(OBu)_3(EAA)_3$  structure having one six- and one five-coordinated aluminium atom. No literature reference on a compound of this type has been found. However,  $(CL)_2Al(\mu-O^iPr)_2Al(O^iPr)L$  compounds, where CL was acetyl acetonate or ethyl acetoacetate and L was 8-hydroxyquinoline or 2-pyridylmethanol, having similar structure, were described.<sup>[24]</sup>

The chelate compound II shows three peaks in  $^1H$  NMR assigned to the asymmetric bis chelated dimer,  $Al_2(OBu)_4(EAA)_2$ , with one octahedral aluminium atom bounded to two EAA ligands and one tetracoordinated aluminium atom bounded to terminal and bridging *sec*-butoxide groups. As described before, such a configuration can be defined by three prefixes (*cis* or *trans*). Again, three configurations, *cis-cis-cis*, *cis-cis-trans* and *cis-trans-cis* are possible (Figure 10b). Single set of resonances in the  $^1H$  NMR spectrum should be observed for *cis-trans-cis* and *cis-cis-trans* symmetric  $C_2$  configurations.<sup>[22]</sup> On the other hand, *cis-cis-cis*  $C_1$  configuration has magnetically non-equivalent protons and may yield with two methyl, two methylene and two ring proton resonances in the  $^1H$  NMR spectrum.<sup>[22]</sup> However, in this case only three peaks having different intensities are observed. For the complex with ethyl acetoacetate to Al ratio equal to 1 Tadanaga *et al.*<sup>[7]</sup> proposed a structure of a trimer which contains two six-coordinated Al atoms, one being coordinated by two EAA and two bridging *sec*-butoxide groups, the other being coordinated by one EAA and four bridging butoxide groups, and one four-coordinated Al atom surrounded by two bridging and two terminal butoxy groups. The same

structure has been described for other alkoxide/chelating agent combinations.<sup>[13,22]</sup> However, by analogy with the compounds III and I, in  $^1H$  NMR spectrum of such an oligomer a resonance above 5.0 ppm, due to a ring proton of EAA bounded to the central aluminium atom, should appear, which was not observed for the chelate compound II. The asymmetrically substituted alkoxy bridged dimers have been described before for various alkoxide/chelating agent combinations,<sup>[13,22,23]</sup> but not for ASB/EAA.

Finally, monochelated linear trimer,  $Al_3(OBu)_8(EAA)$ , with EAA bounded to the central aluminium atom (Figure 10c) is assumed to be compound I. Compound I shows only one broad resonance maximum due to a ring proton in a range of 5.03 to 5.06 ppm. Namely, from the structural models proposed for ASB- $\beta$ -diketones chelates, it is clear it most likely exists as a linear trimer.<sup>[7,13]</sup> According to our results, in the system EAA/ASB this holds true for EAA/ASB ratio of 0.5. The chelated trimeric structure enables the central aluminium atom to reach the coordination number of six, while other two aluminium atoms remain four-coordinated. The  $^{27}Al$  NMR spectrum of the sample EA0.5 shows almost no resonance due to pentacoordinated Al atoms, as in the chelate compound I one of the five butoxy groups (five-coordinated aluminium) in the linear trimer is replaced with EAA to yield six-coordinated aluminium.<sup>[7]</sup>

It is obvious that in some of the described cases more than one possible compound exists, e.g. apart with the bis-chelated dimer compound II, the  $^1H$  NMR spectrum could also be consistent with the trimer having two EAA molecules bounded to the terminal aluminium atom. However, the five selected compounds are most consistent with both,  $^1H$  and  $^{27}Al$  NMR spectroscopy. The assumptions on the compounds type could be confirmed or denied with mass balancing. By mass balancing based on  $^1H$  NMR one can calculate the overall composition for known compounds (assumed compositions) and relative amounts. If proper assumptions were made, then the EAA/Al ratio

**Table 3.** Share of five compounds in samples EA0.5–EA3.0 calculated using data in Table 1 and assumed compounds compositions

Sample	x(I)	x(II)	x(III)	x(IV)	x(V)
EA0.5	0.721	0.279	0	0	0
EA1.0	0.137	0.691	0.087	0.039	0.046
EA1.5	0	0.416	0.242	0.248	0.094
EA2.0	0	0.093	0.189	0.471	0.247
EA2.5	0	0	0	0.339	0.661
EA3.0	0	0	0	0.233	0.767

matching the initial stoichiometry would be obtained. Also, the calculated butanol to butoxide share would match the share determined by  $^1\text{H}$  NMR. Finally, the calculated proportions of aluminium with various coordination numbers would match those determined by  $^{27}\text{Al}$  NMR. Therefore, the integral areas of the E3 resonance (Table 2) have been deconvoluted, taking into consideration the assumed oligomers in order to yield the molar fraction of the compounds. The results are presented in Table 3.

The EAA to Al ratio was determined by multiplying the share of the specific compound with the corresponding relative number of EAA groups bounded to Al. Specifically, the relatively bounded-EAA numbers are; 1/3 for  $\text{Al}_3(\text{O}^i\text{Bu})_8\text{EAA}$ , 1 for  $\text{Al}_2(\text{O}^i\text{Bu})_4\text{EAA}_2$ , 3/2 for  $\text{Al}_2(\text{O}^i\text{Bu})_3\text{EAA}_3$ , 2 for  $\text{Al}_2(\text{O}^i\text{Bu})_2\text{EAA}_4$  and 3 for  $\text{AlEAA}_3$  (Table 4). Similarly, the relative number of butoxide groups bounded to aluminium has been obtained (Table 4), while the coordinations of aluminium atoms were obtained by balancing differently coordinated aluminium atoms in each compound (Table 4).

The right assumption of the type of compounds should give proper EAA to ASB and butanol to butoxide share, as well as proportions of aluminium with various coordination numbers. As can be seen from Table 4, the EAA/Al ratios fairly close to the true stoichiometric ratios have been obtained, except for the sample EA3.0, as in this sample some of the EAA remained unbound to aluminium, *i.e.* in the keto-form. The share of butoxide has been obtained by integration of methyl protons resonances of butoxide (B1) and butanol (A1). The shares of 0.81 (EA0.5), 0.66 (EA1.0), 0.51 (EA1.5), 0.35 (EA2.0), 0.17 (EA2.5) and 0.08 (EA3.0) have been obtained. As can be seen, a very good agreement between the calculated (Table 4) and the

measured shares has been obtained. Finally, the shares of aluminium atoms in various coordination, calculated on the basis of the  $^1\text{H}$  NMR spectra (Table 4) were compared with the shares obtained through the deconvolution of the  $^{27}\text{Al}$  NMR spectra (Table 1). Again, closely matching numbers were obtained. Therefore, the comparison of results obtained by spectra deconvolutions confirmed the assumptions on oligomer structures.

The COSY spectra of samples EA1.5 and EA3.0 (Figure S3) enabled further confirmation of previous findings due to certain important coupling interactions of hydrogen atoms in correlation with neighbouring hydrogens. The COSY spectrum of EA3.0, as shown in Figure S3b, contains cross peaks which indicate couplings between two multiplets up to three or four bonds away. Thus, the COSY data for EA3.0 exhibits off-diagonal correlations attributed to the structures V and IV: methyl protons (E2) at 1.8 ppm with methyne proton (E3) at 4.9 ppm, methyl protons (E1) at 1.25 ppm with methylene protons (E4) at  $\approx 4$  ppm, methylene protons (B3) at 1.5 ppm with methyne proton (B4) at 3.7 ppm. The COSY spectrum of EA1.5 revealed cross peaks of structures IV and V, as well as additional cross peaks, which suggested the presence of proposed structures II and III.

Similarly, in the DOSY spectrum of the sample EA3.0 (Figure S1a), the diffusion coefficient scale shows that the structure V prevails in the system, while the DOSY spectrum of EA1.5 (Figure S1b) shows peaks corresponding to the proposed structures II–V, which do not decay.

Four of five compounds established in this investigation have been reported previously for other aluminium alkoxide and  $\beta$ -ketoester or  $\beta$ -diketone combinations. To the best of our knowledge, a compound

**Table 4.** EAA/Al ratio, share of butoxide and share of aluminium atoms for samples EA0.5–EA3.0 calculated using data in Table 3 and assumed compounds compositions

Sample	EAA/Al	x(B)	Al(IV)	Al(V)	Al(VI)
EA0.5	0.520	0.827	0.632	0	0.368
EA1.0	1.083	0.639	0.461	0.042	0.497
EA1.5	1.558	0.481	0.218	0.127	0.655
EA2.0	2.059	0.314	0.053	0.108	0.839
EA2.5	2.661	0.113	0	0	1
EA3.0	2.767	0.078	0	0	1

of type  $Al_2(OR)_3L_3$  has not been described previously. As far as aluminium *sec*-butoxide and ethyl acetoacetate combination is concerned, of the compounds established in this investigation the only compound previously described was  $Al_3(OBu)_8(EAA)$ .<sup>[7]</sup>  $Al(EAA)_3$  complex has been described previously by Wengrovius *et al.*,<sup>[13]</sup> Lichtenberger *et al.*<sup>[22]</sup> and our group.<sup>[10,25]</sup>

## CONCLUSION

The reactivity of aluminium *sec*-butoxide was controlled by chelation with ethyl acetoacetate in the course of the sol-gel process. Prepared sols were analysed using different homonuclear and heteronuclear one-dimensional and two-dimensional NMR spectroscopies:  $^1H$ ,  $^{13}C$ ,  $^{27}Al$  NMR and COSY, HSQC and DOSY. The  $^1H$  NMR spectra revealed five sets of signals for the ligands: tris-chelated monomer,  $Al(EAA)_3$ , bis-chelated dimer,  $Al_2(O^iBu)_4(EAA)_2$ , tris-chelated dimer,  $Al_2(O^iBu)_3(EAA)_3$ , tetra-chelated dimer,  $Al_2(O^iBu)_2(EAA)_4$ , and monochelated trimer,  $Al_3(O^iBu)_8(EAA)$ . Formation of the chelates was evidenced as the majority of ASB reacted with EAA. Using  $^{27}Al$  NMR it was observed that the coordination of aluminium shifts towards six-coordinated aluminium with the increase of the EAA/ASB ratio, whereas solely six-coordinated aluminium exists above the EAA/ASB ratio of 2.5. The deconvolutions of the obtained spectra and the calculations based on those results confirmed the assumptions on oligomer structures. Other NMR spectra analyses confirmed the structure of different chelated compounds. Of the formed oligomers compounds, this is the first evidence of  $Al_2(OR)_3L_3$ , while aluminium *sec*-butoxide and ethyl acetoacetate complexes  $Al_2(O^iBu)_4(EAA)_2$  and  $Al_2(O^iBu)_2(EAA)_4$  were also observed for the first time.

**Acknowledgment.** The financial support received within the framework of the Croatian-Slovenian bilateral project "NMR characterization of aluminium *sec*-butoxide modified with ethyl acetoacetate at different ratios" is gratefully acknowledged.

**Supplementary Information.** Supporting information to the paper is attached to the electronic version of the article at: <https://doi.org/10.5562/cca3426>.

PDF files with attached documents are best viewed with Adobe Acrobat Reader which is free and can be downloaded from [Adobe's web site](https://www.adobe.com/acrobat/readstep2.html).

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