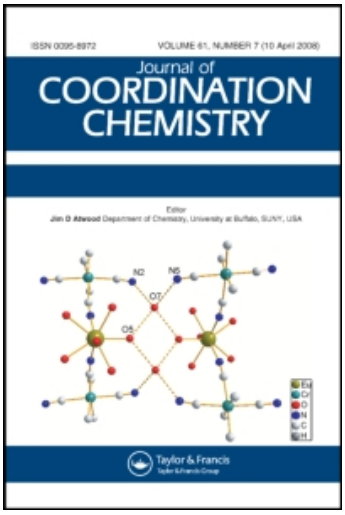

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Aluminum 2-Methoxyethoxide: An Internally Coordinated Aluminum Alkoxede

A. Alipour[a]; H. Jazayeri[a]; M. Mohammadpour Amini[b]
[a] Faculty of Chemistry and Chemical Engineering, Iran University of Science and Technology, Tehran, Iran [b] Materials Division, AEOI, Karadj, Iran

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Note

ALUMINUM 2-METHOXYETHOXIDE: AN INTERNALLY COORDINATED ALUMINUM ALKOXIDE

A. ALIPOUR [a], H. JAZAYERI [a] and
M. MOHAMMADPOUR AMINI [b,*]

[a] *Faculty of Chemistry and Chemical Engineering, Iran University of Science and Technology, Tehran, Iran;* [b] *Materials Division, AEOI, P.O. Box 31585-4395, Karadj, Iran*

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Aluminum 2-methoxyethoxide was isolated and characterized by ^{1}H, ^{13}C and ^{27}Al NMR. The ^{27}Al NMR and mass spectra show that the compound is an internally coordinated dimer. This aluminum alkoxide is less susceptible to hydrolysis in comparison to other aluminum alkoxides.

Keywords: Aluminum alkoxide; ^{27}Al NMR; sol–gel

During the last two decade the sol–gel process for the preparation of thin films, fibres and highly pure oxides from metal alkoxides have attracted considerable interest.[1] In this regard, syntheses and characterization of metal alkoxides have extensively been investigated.[2,3] However, most of the alkoxides are very reactive to moisture and due to the significant differences in reactivity, preparation of homogenous multi-component ceramic oxides is a difficult task.[4] Structural modification of metal alkoxides with complexing agents such as β-diketones and alkanolamines has been effective for the control of hydrolysis–condensation of metal alkoxides.[5–7] In the sol–gel alumina process, chemical modifications of aluminum alkoxides with β-diketones have been carried out.[8] Interestingly, it was found that the

* Corresponding author.

reactivity of aluminum sec-butoxide with β-diketones towards water decreases and subsequently affects the structure of the derived gel.[9,10] The structures of modified aluminum alkoxides have been investigated by IR, ^{1}H, ^{13}C and ^{27}Al NMR spectroscopies,[3] and ^{27}Al NMR is now the most convenient tool for following structural changes of aluminum alkoxides. Depending on the bulkiness of associated alkyl groups, aluminum alkoxides can exist as dimers, trimers and tetramers. Four-coordinate aluminum in ^{27}Al NMR appears in the range 60–70 ppm, five-coordinate in the range 30–40 ppm and six-coordinate in the range 0–10 ppm.[11]

It was of interest to investigate structural modification which may take place by coordination of the oxygen atom of the 2-methoxyethoxy group to aluminum and to examine modifications of hydrolysis and condensation. We report here the structure of aluminum 2-methoxyethoxide, $(CH_3OCH_2CH_2O)_3Al$, on the basis of mass, ^{1}H, ^{13}C and ^{27}Al NMR spectroscopy, interpreted in light of previous work.[12]

Aluminum 2-methoxyethoxide was prepared from aluminum and 2-methoxyethanol according to the general procedure used for the preparation of aluminum alkoxides.[2] In contrast to aluminum isopropoxide or butoxide, attempts to purify aluminum 2-methoxyethoxide by vacuum distillation, resulted in its decomposition. Therefore, aluminum 2-methoxyethoxide was purified by extraction with benzene in several stages. The ^{27}Al NMR spectrum was recorded on a JEOL-90 spectrometer, and ^{1}H and ^{13}C NMR were obtained on a Bruker Advance DRX-500 MHz spectrometer. Mass spectrometry was performed on a Hewlett Packard 597B instrument at 70 eV. ^{1}H NMR (CD_3Cl): δ 3.35 (t, CH_2); 3.39 (s, CH_3O); 3.43 (t, CH_2); 3.46 (s, CH_3O); 3.47–3.75 (m, CH_2) and 3.75–4.04 (m, CH_2) ppm relative to TMS. ^{13}C NMR ($CDCl_3$): δ 58, 59, 60, 61, 62, and 72 ppm. The ^{27}Al NMR in $CDCl_3$ (1 : 1 vol%) shows a single peak at 7 ppm with respect to $AlCl_3/D_2O$ as external standard. Mass spectrum, *m/e* 489 $[Al_2(CH_3OCH_2CH_2O)_5(OCH_2CH_2O)]^+$, 429 $[Al_2(CH_3OCH_2CH_2O)_5]^+$ and 207 $[Al(CH_3OCH_2CH_2O)_2(CH_2O)]^+$. *Anal.* calcd. for $C_9H_{21}O_6Al$ (%): C, 43.75; H, 8.62. Found C, 42.96; H, 8.40.

The ^{27}Al NMR spectrum of Al(O-*sec*-Bu)$_3$ shows 3 peaks due to four-, five- and six-coordinate aluminum atoms. After modification of this alkoxide with ethylacetoacetate only a single peak was observed in the range characteristic of six-coordinate aluminum with significant reduction in line width.[9] In contrast to other aluminum alkoxides, the ^{27}Al NMR spectrum of aluminum 2-methoxyethoxide (Figure 1) shows only one peak in the range of six-coordinated aluminum. Interestingly, qualitative observations made during experiments indicated that aluminum 2-methoxyethoxide is

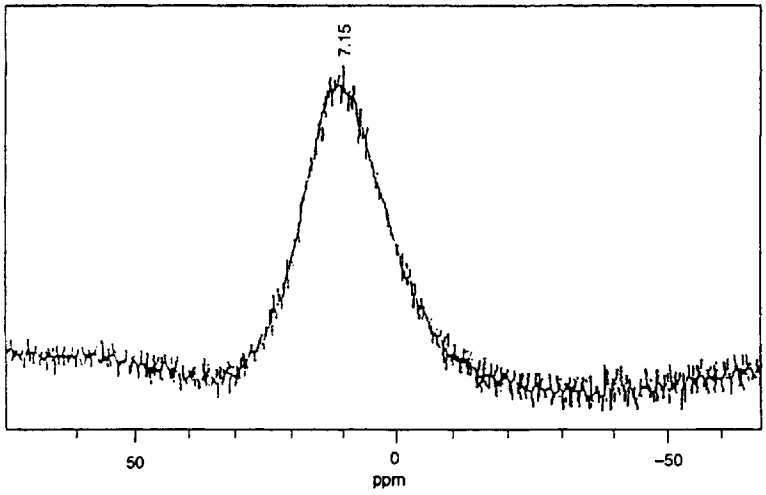
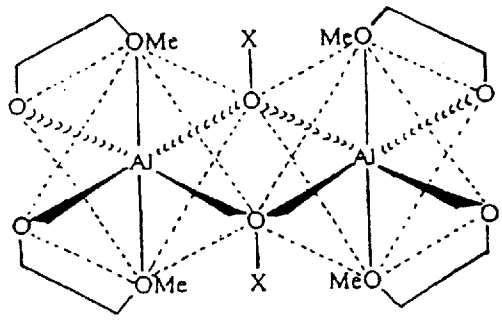


FIGURE 1 The ^{27}Al NMR spectrum of aluminum 2-methoxyethoxide.



X = $-CH_2CH_2OCH_3$

FIGURE 2 Proposed structure of aluminum 2-methoxyethoxide.

less susceptible to hydrolysis. For instance, a 0.1 M solution of aluminum 2-methoxyethoxide in 2-methoxyethanol tolerated three-mol equivalents of water without any change in appearance of solution in comparison to aluminum 2-butoxide that gelled immediately in a similar hydrolysis condition. The lower hydrolysis rate of aluminum 2-methoxyethoxide could be due to the lower susceptibility of six-coordinate aluminum to nucleophilic attack. The largest fragment in the mass spectrum (*m/e* 489) revealed a dimeric species for aluminum 2-methoxyethoxide and from ^{1}H, ^{13}C, and ^{27}Al NMR data we propose following structure, Figure 2, for it. This is an aluminum alkoxide that displays a unique structural motif in solution.

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