The Structures of Complexes of Ethylenediamine with Some Aluminum Alkoxides

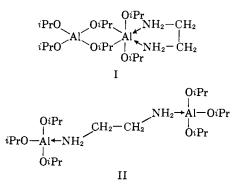
V. J. Shiner, Jr., and D. Whittaker

Contribution No. 1264 from the Department of Chemistry of Indiana University, Bloomington, Indiana. Received July 8, 1964

The structure of the complex of aluminum isopropoxide and ethylenediamine has been studied by proton magnetic resonance spectroscopy. The results are consistent with either of two possible structures, one of which involves pentacoordinated aluminum, and also indicate that the complex undergoes rapid intramolecular alkoxide exchange and rapid intermolecular alkoxide exchange with any isopropyl alcohol present. At room temperature the complex reacts with ketones, displacing isopropyl alcohol, but shows no sign of reducing activity with ketones. In solution aluminum t-butoxide and ethylenediamine form a complex which dissociates into its components on attempted isolation.

Introduction

Bains and Bradley¹ recently reported that aluminum isopropoxide forms a stable complex with hydrazine, containing two molecules of alkoxide monomer to one of hydrazine. In a later publication² they reported the isolation of an aluminum isopropoxide complex with ethylenediamine, having the same alkoxide-amine ratio. Molecular weight measurements showed this complex to be monomeric in dilute solution but to increase in molecular weight with increasing concentration. They suggest that the monomeric form may have either of the structures



Results

The Reaction between Aluminum Isopropoxide and Ethylenediamine. The addition of a tenfold molar excess of ethylenediamine to a 20% solution of tetrameric aluminum isopropoxide³ in benzene causes the proton magnetic resonance spectrum of the alkoxide to undergo considerable change. The peaks due to the methyl protons of the tetramer, at 102, 96, 86, 80, and 74 c.p.s., are replaced by two fairly broad peaks at 83 and 77 c.p.s. from tetramethylsilane. The complex spectrum of the single protons of the isopropyl groups is reduced to a septet, though very poorly resolved. The peak due to the methylene protons of the amine is only slightly shifted, but the amine proton peak is shifted downfield and becomes very broad. These changes occur in less than 1 hr. at room temperature. The volatile components of the solution contain only a trace of isopropyl alcohol, together with some ethylenediamine, showing that the complex is not formed by displacement of alcohol from the alkoxide.

The effect of adding gradually increasing amounts of ethylenediamine to a solution of tetrameric aluminum isopropoxide in benzene has been investigated. When the alkoxide is present in excess, it is only partially converted to the complex. Under these conditions, the methylene proton peak in the spectrum of the diamine is very broad, and the amine proton peak is not visible. This may result from extreme broadening of the peak, or it may be concealed by the methyl proton peaks. The amount of tetramer converted into complex increases with increasing amounts of ethylenediamine until the molar amount added is twice that of the alkoxide (calculated as tetramer), at which point all the alkoxide is changed. This result is to be expected from the report² that the complex has the molecular formula $[Al(OiPr)_3]_2 \cdot H_2N(CH_2)_2NH_2$. Further addition of ethylenediamine causes only small shifts of peak positions and a gradual sharpening of the methylene proton peak of ethylenediamine.

Structure of the Aluminum Isopropoxide-Ethylenediamine Complex. The effect of solvent on the positions of the peaks of the complex is shown in Table I. The difference in the peak positions relative to tetramethylsilane in the aromatic and nonaromatic solvents is similar to that observed with aluminum isopropoxide trimer³ and near the average of that observed for the bridging and nonbridging isopropoxide units in the tetramer.

Table I.Position of Methyl Proton Peaks in N.m.r.Spectrum of Complex in Various Solvents at 31°

Solvent	Peak positions ^a		
Benzene	83, 77		
Carbon tetrachloride	67, 61		
Toluene	80, 74		
Dioxane	68, 62		

^a Peak positions are in c.p.s. from TMS.

The septet of peaks resulting from the single protons of the isopropyl groups is very poorly resolved in the first three solvents, and probably also in dioxane, although the effect is obscured by the dioxane peak. The resolution is not affected by removal of all traces of iso-

⁽¹⁾ M. S. Bains and D. C. Bradley, Can. J. Chem., 40, 1350 (1962).

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⁽³⁾ V. J. Shiner, Jr., D. Whittaker, and V. P. Fernandez, J. Am. Chem. Soc., 85, 2318 (1963).

propyl alcohol from the solution, indicating that it is not caused by intermolecular alkoxide exchange.

On cooling a solution of aluminum isopropoxide $(0.85 \ M, \text{ calculated as monomer})$ and ethylenediamine $(2.50 \ M)$ in toluene, the proton spectrum of the solution is changed in several ways, summarized in Table II.

 Table II.
 Effect of Temperature on N.m.r. Spectrum of Mixture of Complex and Excess Ethylenediamine in Toluene

Temp., °C.	—Peak po CH ₂ of ethylene- diamine	CH₃ of isoprop- oxide	Amine protons
31	152	80, 74	68 (shoulder)
0.0	151	84,78	68
-18	164, 150	85, 79	72
-30	164, 149	86, 80	75

^a Peak positions in c.p.s. from TMS.

On further cooling, the solution set to a gel. The septet of peaks due to the single protons of the isopropyl group was sharpened by cooling to 0° and remained sharp on further cooling. These results indicate that the exchange of free and complexed ethylenediamine is rapid at room temperature but is slowed sufficiently on cooling to give separate peaks due to the free and complexed amine.

The Effect of Excess Isopropyl Alcohol on the Aluminum Isopropoxide-Ethylenediamine Complex. On adding isopropyl alcohol to a solution of aluminum isopropoxide and excess ethylenediamine in benzene, the isopropyl groups of the complex and the alcohol become spectroscopically equivalent, giving only one pair of methyl proton peaks. The single protons of the isopropyl groups give a broad, smooth hump. The amine protons of ethylenediamine and the hydroxyl protons of isopropyl alcohol give a single peak, and the peak resulting from the methylene protons of ethylenediamine is sharpened. The effect of increasing alcohol concentration on peak positions is summarized in Table III.

Table III. Effect of Isopropyl Alcohol on the N.m.r. Spectrum of the Complex^a

Al(OiPr) ₄	—Molar ratio- Ethylene- diamine	Isopropyl alcohol	Peak p Methyl protons, isopropyl group	ositions ^b Methylene protons, ethylene- diamine
1	0.60	0	83, 77	154
1	0.60	0.69	83, 77	172
1	0.60	1.25	82, 76	177
1	0.60	1.70	81,75	177
1	0.60	2.77	79, 73	177
1	0.60	8.07	76, 70	175

^a Aluminum isopropoxide concentration is 0.99 *M*, calculated as monomer. ^b Peak positions in c.p.s. from TMS.

Resolution of the methyl proton peaks decreases with increasing alcohol concentration until the concentration of the alcohol is about twice that of the alkoxide (calculated as monomer). Above this point, further increase of alcohol concentration improves the resolution.

On adding isopropyl alcohol to a solution of ethylenediamine and excess aluminum isopropoxide similar results are obtained. The methylene proton peak of the diamine, which is very broad in the absence of alcohol, is sharpened. The shift of the methyl proton peaks of the isopropoxide groups as the alcohol concentration is increased reveals that the spectrum of the uncomplexed aluminum isopropoxide has extra peaks at 82 and 76 c.p.s., indicating that it is a mixture of the tetramer and "melt" forms of the alkoxide.³ In the absence of aluminum isopropoxide, ethylenediamine does not affect the resolution of any part of the proton spectrum of a solution of isopropyl alcohol in benzene.

A solution of aluminum isopropoxide (0.56 M, calculated as monomer), ethylenediamine (2.80 M), and isopropyl alcohol (4.05 M) in toluene showed two peaks (at 71 and 77 c.p.s. from TMS) due to the methyl protons of the isopropyl groups at 31.4°, but on cooling to 0.0° these separated into peaks due to the alcohol, at 68 and 74 c.p.s. from TMS, and the alkoxide, at 81 c.p.s. from TMS. This latter peak is presumably one of a pair, the other obscured by the alcohol peak. The absorption due to the single protons of the isopropyl groups was a broad hump at 31.4° but separated into two partially superposed septets on cooling to 0.0°. On further cooling, resolution of the methyl proton peaks improved, the second of the alkoxide peaks separating from the alcohol peaks at -37° . Further cooling resulted in a loss of resolution of the alkoxide methyl proton peaks, the pair forming a single broad peak at -62.0° , although the isopropyl alcohol peaks remained sharp at this temperature. On cooling below this temperature, the solution formed a gel.

There is no evidence of separation of the methylene proton peak of ethylenediamine into free and complexed amine peaks on cooling the solution. It is possible that the two peaks may be coincident, but unlikely, as the peak due to the methylene protons of ethylenediamine occurs at 147 c.p.s. from TMS in a similar solution from which the aluminum isopropoxide is omitted. These results indicate that at room temperature the complex undergoes rapid intramolecular exchange of isopropoxide groups and rapid intermolecular exchange of isopropoxide groups with isopropyl alcohol. Isopropyl alcohol apparently accelerates the exchange between free and complexed ethylenediamine.

Reaction of Aluminum Isopropoxide with Other Amines. The proton spectrum of a solution of tetrameric aluminum isopropoxide in benzene was unchanged over a period of one week at room temperature by the addition of *t*-butylamine, piperidine, pyridine, trimethylamine, triethylamine, or N,N,N',N'tetramethylethylenediamine.

Reaction of the Aluminum Isopropoxide-Ethylenediamine Complex with Ketones. On adding acetone or acetophenone to a solution of aluminum isopropoxide and excess ethylenediamine in benzene, the methyl proton peak of the ketone disappeared within 10 min. at room temperature, and isopropyl alcohol was displaced from the complex. The acetophenone could be recovered by hydrolysis of the complex, indicating that a reaction other than reduction involving amine and ketone had taken place. Benzophenone gave a similar reaction, indicating that the alkoxide was not reacting with the enol form of the ketone.

Reaction between Aluminum t-Butoxide and Ethylenediamine. On adding a tenfold molar excess of ethylenediamine to a 20% solution of aluminum t-butoxide in benzene, the proton spectrum of this alkoxide also changes. The peaks at 91 and 84 c.p.s. are replaced by a single peak at 86 c.p.s. from TMS. The amine proton peak becomes very broad and shifts downfield, while the peak due to the methylene protons of the amine is only slightly shifted. These changes occur in less than 1 hr. at room temperature.

Attempts to isolate a sample of the complex were not successful. On freezing a sample, prepared as described above, then pumping off the solvent, a white solid was left which, after pumping for 3 hr., was shown spectroscopically to be a mixture of free and complexed alkoxide. After pumping for 7 hr. all trace of the complex had disappeared.

The complex decomposed in solution over a period of days, turning brown at first, and finally forming a sticky brown tar.

Structure of the Aluminum t-Butoxide-Ethylenediamine Complex. In an attempt to determine the ratio of amine to alkoxide in the complex, solutions containing known amounts of each were prepared and the spectra measured. The fraction of alkoxide converted to complex was measured from the spectra, and from this the ratio of amine to alkoxide in the complex was calculated assuming that all the amine is complexed. The results are given in Table IV.

Table IV. Composition of the Aluminum *t*-Butoxide– Ethylenediamine Complex in Benzene Solution

Aluminum t-butoxide, M	Ethylene- diamine, M	% Alkoxide complexed	Molar ratio amine/ alkoxide in complex ^a
0,189	0.170	35.3	2.55
0.189	0.481	80.3	3.17
0.351	0.274	37.6	2.08
0.351	0.414	55.2	2.14
0.351	0.644	77.2	2.38
0.578	0.408	41.8	1.69
0.578	0.945	81.8	2.00
0.755	0.801	61.2	1.73

^a Assuming all the amine to be complexed.

The results indicate that the assumption that all the amine is complexed is probably incorrect, so that the solution must be regarded as containing the equilibrium

aluminum *i*-butoxide + ethylenediamine \implies complex

in which appreciable amounts of all three species are present.

The effect of solvent on the positions of the peaks of the proton spectrum of the complex is shown in Table V. Solutions contained a tenfold molar excess of amine over alkoxide to force the equilibrium toward the complex.

Table V.	Effect	of Solvent	on the H	Proton	Magnetic	Resonance
Spectrum	of the	Aluminum	t-Butoxid	le-Ethy	lenediamir	ne Complex

	-Peaks of complex ^a Methyl proton peaks ^a				
Solvent	Methyl proton	Methylene proton	Aluminum <i>t</i> -butoxide	<i>t</i> -Butyl alcohol	
CCl ₄	71	160	90, 74	72	
Benzene	86	149	91, 84	70	
Toluene	83	151	91, 83	69	

^a Peak positions in c.p.s. (at 60 Mc.) from internal TMS.

On cooling a solution of the complex in carbon tetrachloride to -10° , the proton spectrum was unchanged, except for sharpening the amine proton peak. Similarly, a solution of the complex in toluene was unchanged on cooling to -20° , except for sharpening the amine proton peak; on cooling to -25° , it formed a gel.

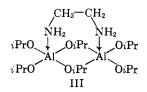
On adding *t*-butyl alcohol to a solution of the complex, the methyl proton peak of the alcohol remained separate from that of the complex, indicating that intermolecular alkoxide exchange is slower in this complex than in the aluminum isopropoxide complex. The alcohol has no effect except for small solvent shifts of less than 1 c.p.s. on either the methyl or methylene proton peaks of the complex.

Discussion

Aluminum Isopropoxide-Ethylenediamine Complex. The suggested explanation of the results described above involves the assumption that three chemical exchange reactions, whose rates can be described as "fast" or "slow" relative to the pertinent nuclear relaxation process, are in operation: (1) Intramolecular exchange of isopropoxy groups in the complex is fast in all solutions examined except at -62° in the presence of excess ethylenediamine and excess isopropyl alcohol, where it is slow enough to broaden but not split the bands due to methyl hydrogen absorption. (2) Intermolecular exchange between the complex and ethylenediamine is slowed by cooling to -18° in the absence of isopropyl alcohol, but is fast even at -62° in the presence of excess isopropyl alcohol. (3) Intermolecular exchange between the complex and isopropyl alcohol is slow below but fast above 0° in the presence of excess ethylenediamine.

The broadening and eventual fusion of the methyl proton peaks of the isopropyl groups of the complex on cooling its solution in isopropyl alcohol and toluene indicate that the complex contains more than one type of methyl group and hence probably more than one type of isopropoxide group undergoing rapid intramolecular exchange.⁴ This conclusion would rule out structure II, in which the isopropoxide groups are identical, but is consistent with structure I or structure Other unsymmetrical structures involving five II. and six coordinated aluminum atoms, bridged by two or three alkoxy groups, cannot be ruled out on the basis of the n.m.r. evidence. Structure III is preferred, however, because of its close relationship to the known fairly stable structure of the dimeric aluminum alkoxides.

⁽⁴⁾ As the referee pointed out, this explanation involves the assumption that the same species is present at both low and room temperatures. The structural conclusion, drawn from the observed broadening, that there are two different kinds of isopropoxide groups might be invalidated if polymerization took place at -62° .



Pentacoordination is a relatively uncommon state of aluminum, but it has been claimed to obtain in aluminum isopropoxide- β -dicarbonyl complexes,⁵ and evidence to support its existence has been obtained from studies of complexes between aluminum hydride and amines⁶ and complexes of trialkylaluminum with diamines⁷ and with tetramethyltetrazene.⁸ If structure III is correct, then the rapid intermolecular and intramolecular alkoxide exchange reactions may result from the tendency of the aluminum to change its coordination number to six. It is not possible to decide whether structure I or structure III is correct on the evidence currently available, although the lack of evidence for the formation of a 1:1 complex involving two molecules of ethylenediamine and two aluminum isopropoxide monomer units favors structure III.

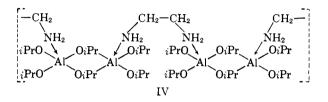
In the presence of isopropyl alcohol, each aluminum atom of structure III may possibly coordinate weakly with a molecule of isopropyl alcohol, thus raising its coordination number to six. Although there is no evidence of coordination of a second ethylenediamine molecule in this way, steric limitations appear to be important, e.g., N,N,N',N'-tetramethylethylenediamine does not form a complex with aluminum isopropoxide, and an -OH group can probably approach the aluminum atom more readily than an -NH₂ group. The change from pentacoordinate aluminum to hexacoordinate aluminum will then result in a reduction in the angles between the groups attached to the aluminum. If this postulate is correct, then the extra shielding of the diamine molecule by the isoproposide groups may be responsible for the large shift in position of the methylene proton peak in the n.m.r. spectrum of the complex when isopropyl alcohol is added to a solution of the complex in benzene. This is in agreement with the observation that the shift of this peak reaches a maximum when 2 moles of alcohol per mole of complex has been added to the solution and also with the observation that *t*-butyl alcohol, which does not exchange rapidly with the *t*-butoxide complex, does not affect the position of the methylene proton peak in the spectrum of the *t*-butoxide complex. Coordination of isopropyl alcohol to the aluminum atom of the complex may also be responsible for the observation that the resolution of the methyl proton peaks of the solution of the complex and isopropyl alcohol reaches a minimum when 2 moles of alcohol per mole of complex has been added to the solution of the complex.

(5) R. K. Mehrotra and R. C. Mehrotra, *Can. J. Chem.*, **39**, 795 (1961).

Resolution should decrease as more molecules of the complex assume the hexacoordinate structure, but improve if the rate of exchange increases as more free alcohol is made available.

The poor resolution of the methine proton peaks of the complex in the absence of isopropyl alcohol may be due to unresolved splitting caused by spin coupling with the aluminum atoms.

The spectra show no sign of changing with increasing concentration of the complex, indicating that the increase in molecular weight with increasing concentration of the complex, reported by Bains and Bradley,² may not involve such a drastic rearrangement as they suggest. The increase in molecular weight may result from linking of dimeric isopropoxide molecules by ethylenediamine molecules, forming a chain of alternant dimeric aluminum isopropoxide and ethylenediamine molecules as shown in structure IV.



Aluminum t-Butoxide-Ethylenediamine Complex. The positions of the methyl proton peaks in spectra of the complex in different solvents favor a structure in which all the t-butoxy groups are nonbridging, but on account of the instability of the complex insufficient data have been obtained to allow definite conclusions about its structure. The observed decomposition of the complex on removal of the solvent is consistent with the earlier observation¹ that aluminum t-butoxide does not form a stable complex with hydrazine.

Purification of Materials. A commercial sample of aluminum isopropoxide was purified by distilling at $108.5-109.5^{\circ}$ at 0.4 mm., then storing in a desiccator for four weeks at room temperature to allow complete conversion to the tetrameric form. Aluminum *t*-butoxide was prepared as described by Wayne and Adkins⁹ and purified by recrystallization from benzene. Commercial samples of amines were dried over potassium hydroxide pellets and then distilled.

Nuclear Magnetic Resonance Spectroscopy. Nuclear magnetic resonance spectra involving the study of temperature effects were recorded with a Varian D.P.-60 n.m.r. spectrometer. All peak positions are in c.p.s. (at 60 Mc.) from internal tetramethylsilane reference. Peak positions quoted are considered accurate to ± 1 c.p.s.

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