

# The Structures of Complexes of Ethylenediamine with Some Aluminum Alkoxides

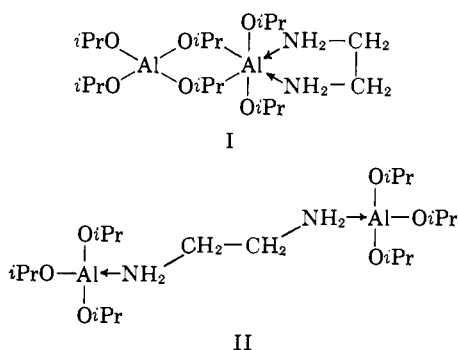
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The structure of the complex of aluminum isopropoxide and ethylenediamine has been studied by proton magnetic resonance spectroscopy. The results are consistent with either of two possible structures, one of which involves pentacoordinated aluminum, 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 Bradley<sup>1</sup> recently reported that aluminum isopropoxide forms a stable complex with hydrazine, containing two molecules of alkoxide monomer to one of hydrazine. In a later publication<sup>2</sup> 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 isopropoxide<sup>3</sup> 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 report<sup>2</sup> that the complex has the molecular formula  $[\text{Al}(\text{O}i\text{Pr})_3]_2 \cdot \text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2$ . 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 trimer<sup>3</sup> 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 <sup>a</sup>
Benzene	83, 77
Carbon tetrachloride	67, 61
Toluene	80, 74
Dioxane	68, 62

<sup>a</sup> 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).
- (2) M. S. Bains and D. C. Bradley, *ibid.*, **40**, 2218 (1962).
- (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*, 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 positions <sup>a</sup> —		Amine protons
	CH <sub>2</sub> of ethylenediamine	CH <sub>3</sub> of isopropoxide	
31	152	80, 74	68 (shoulder)
0.0	151	84, 78	68
-18	164, 150	85, 79	72
-30	164, 149	86, 80	75

<sup>a</sup> 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<sup>a</sup>

Al(OiPr) <sub>3</sub>	—Molar ratio—		—Peak positions <sup>b</sup> —	
	Ethylenediamine	Isopropyl alcohol	Methyl protons, isopropyl group	Methylene protons, ethylenediamine
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

<sup>a</sup> Aluminum isopropoxide concentration is 0.99 *M*, calculated as monomer. <sup>b</sup> 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.<sup>3</sup> 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.

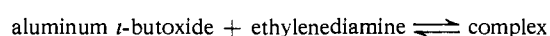
**Structure of the Aluminum *t*-Butoxide-Ethylenediamine Complex.** In an attempt to determine the ratio of amine to alkoxide in the complex, solutions containing known amounts of each were prepared and the spectra measured. The fraction of alkoxide converted to complex was measured from the spectra, 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 <i>t</i> -butoxide, <i>M</i>	Ethylenediamine, <i>M</i>	% Alkoxide complexed	Molar ratio amine/alkoxide in complex <sup>a</sup>
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

<sup>a</sup> 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



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 Proton Magnetic Resonance Spectrum of the Aluminum *t*-Butoxide-Ethylenediamine Complex

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

<sup>a</sup> Peak positions in c.p.s. (at 60 Mc.) from internal TMS.

On cooling a solution of the complex in carbon tetrachloride to  $-10^{\circ}$ , 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  $-20^{\circ}$ , except for sharpening the amine proton peak; on cooling to  $-25^{\circ}$ , 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  $-62^{\circ}$  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  $-18^{\circ}$  in the absence of isopropyl alcohol, but is fast even at  $-62^{\circ}$  in the presence of excess isopropyl alcohol. (3) Intermolecular exchange between the complex and isopropyl alcohol is slow below but fast above  $0^{\circ}$  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.<sup>4</sup> This conclusion would rule out structure II, in which the isopropoxide groups are identical, but is consistent with structure I or structure II. Other unsymmetrical structures involving five 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  $-62^{\circ}$ .

