$(DPE)_2$, 56195-86-9; $Mo(N_2)(2\text{-}CH_3C_6H_4CN)(DPE)_2$, 56195-87-0; $Mo(N_2)(CH_3CN)(DPE)_2$, 56195-88-1; $Mo(N_2)(C_2H_5CN)(DPE)_2$, 56195-89-2; $[Mo(N_2)(DPE)_2]_2(1,4\text{-}NCC_6H_4CN)$, 56195-90-5; $MoCl(N_2COPh)(DPE)_2$, 56210-38-9; $MoCl_2(N_2HCOPh)(DPE)_2$, 56271-04-6; benzoyl chloride, 98-88-4.

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Preparation and Properties of a Neutral, Chelated Four-Coordinate Organoaluminum–Nitrogen Derivative[1]

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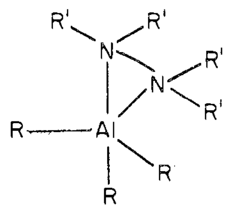
Received February 5, 1975 AIC50088J

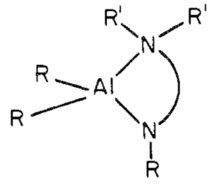
The new compound $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2$ has been prepared from trimethylalane and $H(C_2H_5)NC_2H_4N(CH_3)_2$ by pyrolysis at 100°. This compound represents the first example of a neutral four-coordinate organoaluminum–nitrogen derivative in which the nitrogen-containing ligand is chelated to the aluminum. The material has been thoroughly characterized according to its elemental analysis, cyroscopic molecular weight in benzene (+5°) and chlorobenzene (−46°), ^1H NMR spectrum, and infrared spectrum. All of our data are consistent with the hypothesis that $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2$ is a monomeric species in aromatic solvents. However, in aliphatic solvents such as cyclopentane, an equilibrium between the monomeric chelate and a dimeric species exists. This equilibrium is shifted toward the dimer at lowered temperatures. The reactions of the new compound as an acid and a base are also considered.

Introduction

There are very few examples of organo- or hydridoaluminum compounds containing chelated ligands. Those that have been reported can be described as five-coordinate adducts or four-coordinate derivatives. These two classes of chelated compounds can be distinguished by the coordination number of the aluminum and the ligand atoms. In the case of an aluminum–nitrogen five-coordinate adduct, the aluminum is five-coordinate and both nitrogen atoms of the ligand are four-coordinate. For the classification "four-coordinate derivative" the aluminum is four-coordinate and one nitrogen of the chelating ligand is three-coordinate while the second nitrogen is four-coordinate. There are several good examples of five-coordinate adducts but there are no well-characterized four-coordinate chelated aluminum–nitrogen derivatives. The complexes[2] tetramethylmethylenediamine–alane ($H_3Al\cdot N(CH_3)_2CH_2N(CH_3)_2$) and tetramethylpropanediamine–alane ($H_3Al\cdot N(CH_3)_2C_3H_6N(CH_3)_2$) have been thoroughly characterized and represent five-coordinate aluminum species. Other compounds which have been reported to involve chelated ligands are the adducts of trimethylalane with tetramethylhydrazine,[3] tetramethyltetrazine,[4] and tetramethylmethylenediamine.[5] However, the evidence for chelation in these compounds is less complete. Prior to this research there were no known examples of neutral four-coordinate derivatives of aluminum involving chelated nitrogen ligands. This type of derivative is a possible product of the reaction between an alane and a dibasic ligand which contains one acidic hydrogen. The compound dimethylaluminum acetylacetonate[6,7] might be included in the classification "four-coordinate derivative", but both ends of the ligand are identical after chelation. Other attempts have been made to prepare chelated aluminum derivatives,[8] but in all previous cases, association with dimer formation occurred rather than chelation. For example, dimethylaluminum 2-methyoxymethoxide[9] $[(CH_3)_2AlOC_2H_4OCH_3]_2$ forms a four-membered aluminum–oxygen ring and the methoxy oxygen is not coordinated.



five-coordinate adduct



four-coordinate derivative

In this paper we report the preparation of the first example of a neutral, chelated four-coordinate organoaluminum–nitrogen derivative, $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2$. This compound has been thoroughly characterized by cryoscopic molecular weight measurements in a variety of solvents and by low-temperature and concentration-dependent ^1H NMR data.

Experimental Section

All compounds described in this investigation were manipulated in a vacuum line or a purified nitrogen atmosphere. The solvents and reagents were purified by conventional means. Aluminum compounds were analyzed for aluminum by EDTA titration[10] and for nitrogen by the standard Kjeldahl method and by hydrolyzable methyl content.

Preparation of $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2$. This compound was prepared by reaction of trimethylalane (10.0 mmol) with *N*,*N*-dimethyl-*N*'-ethylethylenediamine (10.0 mmol) without solvent in a sealed flask equipped with a break-seal side arm. The mixture was heated at 100° for 24 hr to allow complete reaction. The noncondensable gas produced was measured (9.82 mmol) and identified as methane by its vapor pressure (10 mm) at −196°.[11] The product, obtained in greater than 90% yield, was purified by vacuum fractionation using 0 and −196° traps. The organoaluminum derivative $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2$, a slightly volatile colorless liquid at room temperature, was isolated in the 0° trap. Anal. Calcd: Al, 15.68; N, 16.27; hydrolyzable CH_3, 17.47. Found: Al, 16.20; N, 16.11; hydrolyzable CH_3, 17.51.

Infrared Spectrum. The infrared spectrum of $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2$ was recorded in the range 4000–400 cm^{-1} by means of a Perkin-Elmer Model 457 spectrometer. A sample was observed as a neat liquid between KBr plates. Absorption intensities were measured using the method of Durkin, Glore, and DeHayes.[12]

Following are the spectral data for $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2$ [frequency, cm^{-1} (intensity: s, strong; m, medium; w, weak; sh, shoulder)]: 3002 (m), 2950 (vs), 2915 (vs), 2880 (s), 2870 (sh, s), 2850 (m), 2800 (vs), 2780 (vs), 2730 (m), 2700 (m), 2670 (w), 2650 (w), 2575 (w), 1650 (vw), 1488 (sh, w), 1470 (s), 1462 (s), 1452 (sh, m), 1410 (w), 1394 (sh, w), 1387 (w), 1368 (m), 1344 (m), 1332 (s), 1307 (m), 1285 (m), 1232 (m), 1245 (m), 1232 (m), 1208 (s) 1185–1178 (vs), 1147 (s), 1105 (w), 1059 (m), 1025 (m), 1015 (m), 950 (m), 883 (m), 850 (w), 785 (m), 710 (s), 660 (vs), 610 (m), 508–495 (w), 456 (w).

Nuclear Magnetic Resonance Spectra. The ^1H NMR spectra were recorded at 100 MHz using a JEOLCO MH-100 spectrometer equipped with variable-temperature capability. All chemical shifts are given in ppm and are referenced to tetramethylsilane as 0.00 ppm. Upfield shifts are denoted as + and downfield shifts as −. The chemical shifts observed for 10% cyclopentane solutions of $H(C_2H_5)NC_2H_4N(CH_3)_2$ and $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2$ at ambient temperatures are given here (s = singlet, t = triplet, m = multiplet). $H(C_2H_5)NC_2H_4N(CH_3)_2$: −1.03 (t), $C\mathit{H}_3CH_2$; −2.15 (s), $(CH_3)_2N$; −2.62 (m), C_2H_4 and $CH_3C\mathit{H}_2$. $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2$: +0.94 (s), $(CH_3)_2Al$; −2.37 (s), $(CH_3)_2N$; −2.88 (m), C_2H_4 and $CH_3C\mathit{H}_2$. Variable-temperature and concentration-dependent data are given in the Results and Discussion.

Molecular Weight Measurements. Molecular weight measurements were obtained cryoscopically in benzene (+5°) and chlorobenzene (−46°) using an apparatus similar to that described by Shriver.[13] The molecular weight data for $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2$ (calculated mol wt 172) were essentially invariant over the concentration ranges studied. In benzene, molecular weights in the range of 183–189 were observed for 0.0344–0.103 *m* solutions (calculated based on monomer). Molecular weights in the range of 179–183 were observed for 0.118–0.229 *m* chlorobenzene solutions.

Attempted Reaction between $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2$ and $N(CH_3)_3$. The reagents $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2$ and $N(CH_3)_3$ were combined in an attempt to determine if the base $N(CH_3)_3$ could displace the $-N(CH_3)_2$ end of the chelating ligand at 25°. By use of a tensimetric titration technique, $N(CH_3)_3$ was added to 1.130 mmol of $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2$ in increments of 0.528 mmol. No reaction was observed at 25°.

Competition Reaction between $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2$ and $N(CH_3)_3$ with $Al(CH_3)_3$. Trimethylalane was added to an equimolar mixture of $N(CH_3)_3$ and $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2$ in an attempt to compare the basicity of $N(CH_3)_3$ with the three-coordinate nitrogen bound to the aluminum in the chelated derivative. Trimethylamine (3.70 mmol) and $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2$ (3.70 mmol) were dissolved in 25 ml of toluene. Trimethylalane (3.70 mmol, $Al(CH_3)_3$) was added to the base mixture by means of a vacuum distillation using a −196° bath. After the mixture was warmed to room temperature and stirred for 1 hr, the volatile components were removed and fractionated using −78 and −196° traps. The −196° trap contained 2.77 mmol of $N(CH_3)_3$, whereas the solvent and a trace of a colorless, slightly volatile liquid were observed in the −78° trap. A yellow material, which remained in the initial reaction flask, was purified by sublimation in vacuo at 90° to give a white solid. This white solid had a melting point of 50–54° and was soluble in toluene but insoluble in aliphatic solvents. On the basis of the observed reaction stoichiometry, molecular weight measurements of the product in benzene, and ^1H NMR data, the product is believed to be $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2\cdot Al(CH_3)_3$. The data suggest that the monomeric chelate is a stronger base than $N(CH_3)_3$ toward $Al(CH_3)_3$.

Reaction between $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2$ and $N(CH_3)_2H$. Dimethylamine was treated with $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2$ (1.130 mmol) in order to determine if an amine-exchange reaction could occur. The addition of the 0.528-mmol increment of $N(CH_3)_2H$ produced a white solid. There was no $N(CH_3)_2H$ pressure above the reaction mixture. After an excess of $N(CH_3)_2H$ had been added, a solid–liquid mixture was present at room temperature which could not be completely separated. Spectral data are interpreted to suggest that an amine-exchange reaction occurred and an equilibrium mixture—the chelate, $[(CH_3)_2AlN(CH_3)_2]_2$, and $H(C_2H_5)NC_2H_4N(CH_3)_2$—was the product.

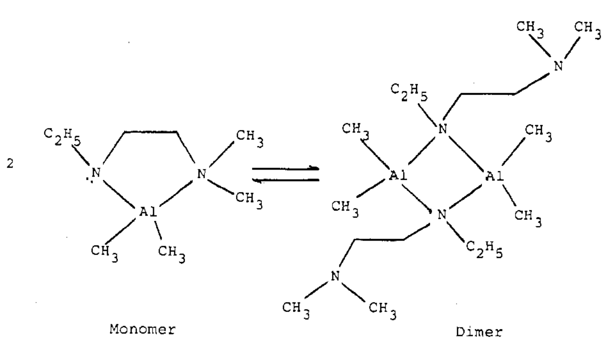


Figure 1. Monomer and dimer structures for $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2$.

Results and Discussion

The compound $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2$, a slightly volatile liquid at room temperature, exists as a monomeric species in the aromatic solvents (benzene, toluene, and chlorobenzene) but as an equilibrium mixture of monomeric and more associated, probably dimeric, species in the aliphatic solvent cyclopentane. Cryoscopic molecular weight data in benzene (+5°) and chlorobenzene (−46°) show a degree of association of 1.10 or less and there is no significant molecular weight dependence on concentration. The ^1H NMR spectrum in toluene-d_8 is also completely consistent with the presence of only a monomeric species. However, the NMR spectrum in the aliphatic solvent cyclopentane is very different, as it is both temperature and concentration dependent. These observations in cyclopentane suggest an equilibrium between a monomer and more associated species, probably a dimer. The most likely structure for the monomeric species involves chelation of the nitrogen ligand to form a four-coordinate derivative. A more associated species could be a dimer with bridging nitrogen atoms. These structures and the proposed equilibrium in cyclopentane are shown in Figure 1.

The ^1H NMR spectrum of $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2$ in toluene-d_8 is shown in Figure 2. The two singlets in approximately equal intensity have been assigned to the $N(CH_3)_2$ group protons and the $(CH_3)_2Al$ group protons as shown. The highest field triplet is due to the methyl protons of the $N(C_2H_5)$ group. The other two triplets at lower field are assigned to the ethylene protons. The quartet is due to the methylene protons of the $N(C_2H_5)$ group. The spectrum does not change with concentration nor does it change as the temperature is lowered to −80°. These observations are all consistent with the existence of only a monomeric species of the structure shown in Figure 1. In view of the propensity of aluminum to complete its octet and the presence of so strong a base as the dimethylamino group of the ligand, the aluminum is most likely four-coordinate and the nitrogen ligand is chelated to the aluminum.

The NMR data for $(CH_3)_2Al(C_2H_5)NC_2H_4N(CH_3)_2$ in cyclopentane solution are strikingly different from those observed in aromatic solvents. At room temperature the spectrum is similar to that observed in toluene-d_8 except that the triplet of the $N(C_2H_5)$ group is obscured by the solvent side bands and the methylene and ethylene protons are not resolved. As the temperature is lowered, the spectrum changes. New lines grow in at the expense of the initial room-temperature lines. The original lines due to the $(CH_3)_2Al$

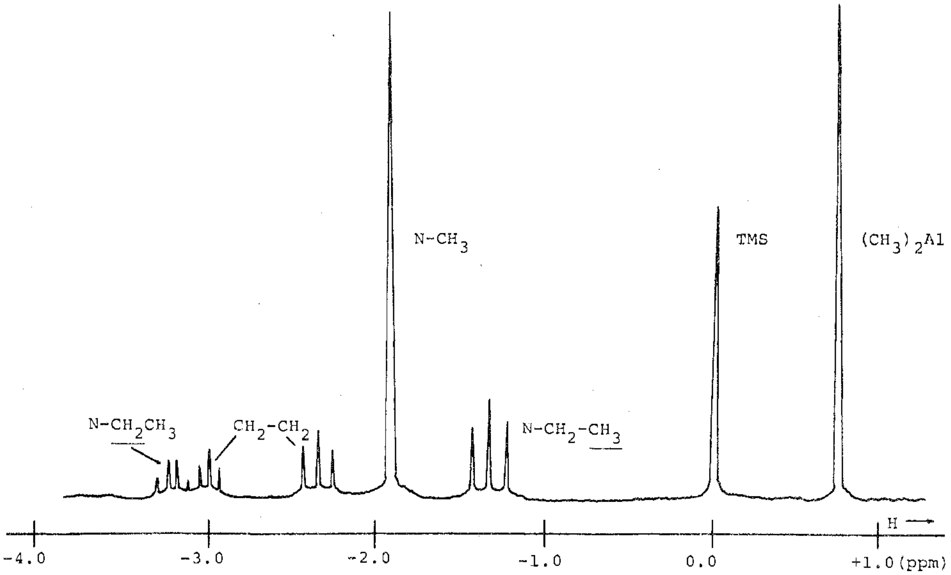


Figure 2. The 100-MHz NMR spectrum of $(CH_3)_2Al(C_2H_5)NC_2H_4N(CH_3)_2$ in toluene-d_8.

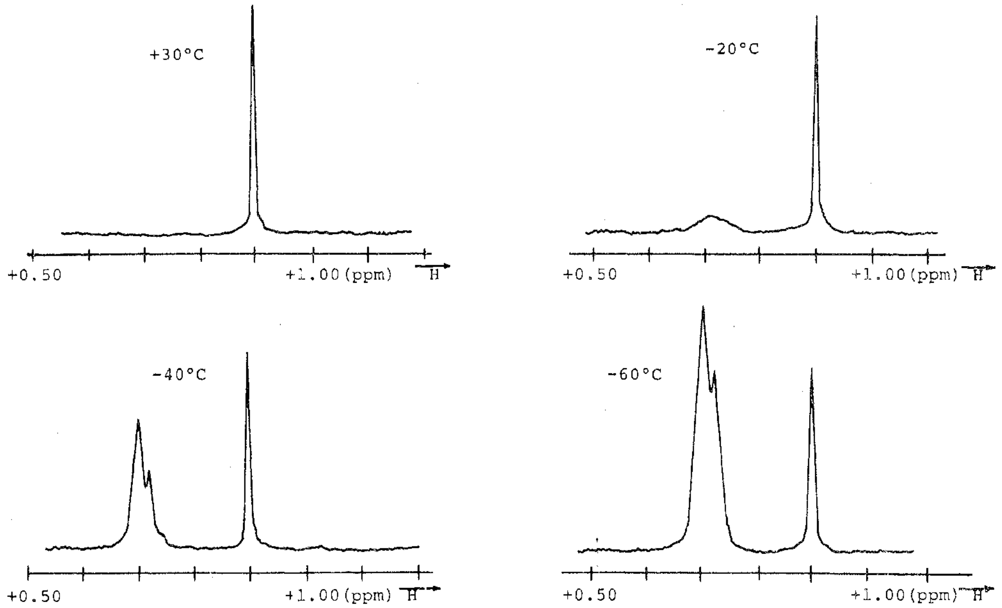
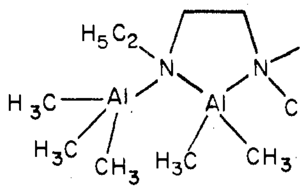


Figure 3. Temperature variation of the $(CH_3)_2Al$ NMR line of $(CH_3)_2Al(C_2H_5)NC_2H_4N(CH_3)_2$.

protons (+0.94 ppm) and $N(CH_3)_2$ protons (−2.37 ppm) decrease in intensity and new lines appear at +0.70 and −2.17 ppm. These new lines are always broader than the initial room-temperature lines. At −40° the new $N(CH_3)_2$ line at −2.17 ppm and the new $(CH_3)_2Al$ line at +0.70 ppm appear to consist of two or more overlapping lines. This multiplicity is more apparent in dilute solutions but the lines are never well resolved. The temperature variation of the $(CH_3)_2Al$ group spectrum is shown in Figure 3. The most plausible explanation for the growth of the new lines is a shift of an equilibrium between monomer and dimer toward the dimer at lower temperatures. This equilibrium must be slow enough to permit observation of both species by NMR. As the temperature is lowered, the equilibrium is shifted to the right until sufficient dimer is present to observe it in the NMR spectrum. The field position of $N(CH_3)_2$ group protons of the dimer (the new line at −2.17 ppm) is close to that observed for the $N(CH_3)_2$ group protons of the pure ligand (−2.15 ppm). This would be expected if the $N(CH_3)_2$ ends of the ligand in the dimer were unbound as they are shown in Figure 1. It is unlikely that these $N(CH_3)_2$ groups are bound to the aluminum in the dimer as that would make the aluminum five-coordinate with three bulky nitrogen groups and two methyl groups bound to it. Methylaluminum–nitrogen compounds with five-coordinate aluminum have not been previously observed. The field position of the new $(CH_3)_2Al$ line (0.70 ppm) is close to that observed for other compounds in which aluminum and nitrogen exist in a similar dimeric structure. An example is the four-membered aluminum–nitrogen ring compound dimethylaminodimethylalane $[(CH_3)_2AlN(CH_3)_2]_2$ for which the $(CH_3)_2Al$ chemical shift is +0.75 ppm. The broadness and multiplicity noted for the dimer $(CH_3)_2Al$ line may be related to the possibility of geometrical isomers.

To substantiate further the monomer–dimer equilibrium proposed for $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2$ in cyclopentane the influence of concentration on the NMR spectra was investigated. If an equilibrium between monomer and dimer existed, the NMR spectra would have to be dependent on concentration as well as temperature. While holding the temperature of the NMR probe constant, the spectra of samples of various concentrations were observed. As the concentration of the sample was increased, the relative intensity of the line assigned to the dimer also increased as would be expected from the proposed equilibrium. It should be noted that the $N(CH_3)_2$ lines were also dependent on concentration but integration was more difficult due to solvent side bands and underlying methylene protons. Integration, at various concentrations and temperatures, of the $(CH_3)_2Al$ lines due to the monomer and dimer allowed the relative amounts of monomer and dimer and consequently the equilibrium constants to be calculated. Values of $\Delta H°$ and $\Delta S°$ for the proposed equilibrium were obtained from a plot of log K vs. $1/T°K$. Difficulties of temperature control and the possibility of small amounts of more associated species require these values for K, $\Delta H°$, and $\Delta S°$ be taken as approximations. However, these values are useful in that they do show the interplay between $\Delta H°$ and $T\Delta S°$ for the monomer–dimer equilibrium of this compound and the importance of these factors to chelation in general. If one uses the values determined ($\Delta H° = -39.3$ kJ mol^{-1}; $\Delta S° = 166$ J deg^{-1} mol^{-1}) to calculate $\Delta G°$ for the reaction $2A \rightleftarrows A_2$, the values obtained are as follows: $\Delta G°_{300°K} = +10.5$ kJ mol^{-1}; $\Delta G°_{233°K} = -0.622$ kJ mol^{-1}. These values indicate that it is the large negative entropy associated with the dimer formation that predominates at room temperature to favor the monomeric chelate. As the temperature decreases, this effect becomes less important and enthalpy favors the formation of the dimer.

The chemical properties of the chelate $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2$ suggest that it can behave as a very weak Lewis acid and a Lewis base. Dimethylamine reacts to give an equilibrium mixture with the products $[(CH_3)_2AlN(CH_3)_2]_2$ and the dibasic ligand $H(C_2H_5)NC_2H_4N(CH_3)_2$. Trimethylamine, however, does not react with the chelate, possibly due to the entropy effect or to the fact that the ligand nitrogen atoms of the chelate are stronger bases than $N(CH_3)_3$. The competition reaction between the chelate and $N(CH_3)_3$ for trimethylalane suggests that the chelate is a stronger base than $N(CH_3)_3$. Approximately 75% of the $N(CH_3)_3$ was recovered unreacted. The major aluminum-containing product from the competition reaction had a molecular weight in benzene of 287. The following adduct, the most likely potential product, has a molecular weight of 244.



The product, formed by the chelate coming apart and the dimethylamino end of the ligand binding the $Al(CH_3)_3$, would be expected to dimerize through the $N(C_2H_5)$ and form a four-coordinate $Al(CH_3)_2$ group. A mixture of these two species would lead to a molecular weight greater than 244. Dissociation to give the chelate and $Al_2(CH_3)_6$ would give a lower molecular weight. The ^1H NMR spectrum of the adduct in toluene-d_8 shows two or more lines in the Al–CH_3 region and two lines of equal intensity for the $N(CH_3)_2$ protons. These data are not inconsistent with the type of adduct postulated. If the postulated adduct is indeed the product, it provides evidence for the polarization of the Al–N bond and the increased basicity of the nitrogen bound to the aluminum. Considering only steric factors one would have expected the trimethylamine to be a stronger base than the ethylamino group of the chelate toward trimethylalane.

Acknowledgment. We wish to thank the National Science Foundation, Grant No. GP-20200, for financial support of this research.

Registry No. $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2$(monomer), 55975-87-6; $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2$(dimer), 55975-89-8; $Al(CH_3)_3$, 75-24-1; $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2 \cdot Al(CH_3)_3$, 55975-88-7; $N(CH_3)_2H$, 124-40-3; $[(CH_3)_2AlN(CH_3)_2]_2$, 22450-81-3.

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Nitrosodisulfonates and Hydroxylamine-*N*,*N*-disulfonates. IV. Crystal Structure of Sodium Nitrosyl-*N*,*N*-disulfonate Trihydrate

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The crystal structure of $Na_3[ON(SO_3)_2] \cdot 3H_2O$ has been determined by Patterson methods and refined by full-matrix least squares to a weighted residue of 0.033 using 928 independent reflections. The crystals are orthorhombic, of space group $Cmc2_1$ with $a = 14.234$ (2) Å, $b = 11.052$ (1) Å, $c = 5.8607$ (5) Å. The $[ON(SO_3)_2]^{3-}$ anion, which contains a crystallographic mirror plane passing through the NO group, has a pyramidal coordination at nitrogen and an N–O bond length of 1.427 Å, both features distinguishing it from the radical nitrosodisulfonate $[ON(SO_3)_2]^{2-}$, where the N–O bond length is 1.28 Å. In the present structure the N–O bond is directed at the centroid of a triangle formed by the three Na atoms, which have coordination numbers of 6, 6, and 7 respectively.

Previous articles[1,2] in this series have discussed the preparation and characterization of a number of alkali metal salts of hydroxylamine-*N*,*N*-disulfonate and related anions. In particular, the crystal structure of a rubidium salt, $Rb_5\{H[ON(SO_3)_2]_2\} \cdot 3H_2O$, was determined[2] and led to the suggestion that in alkaline solution, pH 11–12, at which that salt crystallizes, the $[HON(SO_3)_2]^{2-}$ ion coexists with nitrosyl-*N*,*N*-disulfonate $[ON(SO_3)_2]^{3-}$ in solution. This latter