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ALUMINIUM HYDRIDE

K.N. Semenenko, B.M. Bulychev, and E.A. Shevlyagina

CONTENTS

I. Introduction 649

II. Methods of making aluminium hydride and its amine complexes 650

1. Compounds of aluminium hydride with ammonia and its derivatives 651
2. Compounds of aluminium hydride with bifunctional amines 655
3. Compounds of aluminium hydride with pyridine 656
4. Alkyl-substituted complexes of aluminium hydride with tertiary amines 657
5. Quaternary ammonium salts of aluminium hydride [quaternary ammonium tetrahydroaluminates] 657

I. INTRODUCTION

Aluminium hydride is one of the least studied but most interesting hydrides and also one of the most interesting in practical respects.

The detailed investigation of aluminium hydride and its complexes can give results of considerable significance for the further development of ideas about the nature of the chemical bond in molecules constructed from atoms of light elements.

Aluminium does not react directly with hydrogen to form the simple hydride AlH_3. Reactions which would yield pure (individual) aluminium hydride by the hydrogenation of aluminium compounds or by exchange reactions with other metal hydrides in the absence of a solvent which is a donor of electrons are still not known. In practice one is usually dealing with solutions or precipitates containing onium complexes of aluminium hydride with oxygen- or nitrogen-containing molecules. When these complexes are sufficiently stable (for example, those with tertiary amines $AlH_3.NR_3$) they can be isolated from the reaction mixture and obtained in an individual state.

The sharp rise in reactivity of the compounds of aluminium in relation to hydrogenating agents in the presence of a solvent which is a donor of electrons is due to additional ionisation of the Al–X bond owing to the effect of an electronic shift in the formation of the onium bond:



Furthermore, complex formation with a solvent stabilises the hydride molecule formed by the reaction:

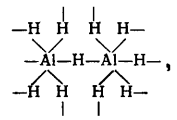
$$AlX_3 + 3MH \rightarrow AlH_3 + 3MX,$$

"clearing" the electron deficiency at the metal atom and hindering polymerisation, which leads to the formation of unstable, insoluble $(AlH_3)_x$.

The valence capacities of aluminium towards hydrogen are not determined uniquely. In alkali metal tetrahydroaluminate complexes† aluminium apparently has a coordination number of six. In support of this assumption there is the absence of isomorphism between $NaAlCl_4$ and $NaAlH_4$. According to Baenziger[1], $NaAlCl_4$ is orthorombic, with tetrahedral $AlCl_4^-$ ions at the lattice sites.

† Termed *alanates* in the Russian, presumably as derivatives of "alane", the name suggested by Wiberg for the AlH_3 unit (Ed. of Translation).

Such "ions" are either absent from the sodium tetrahydroaluminate lattice, being bound in an infinite pattern:



or are so distorted that their departure from tetrahedral symmetry leads to a different type of packing of the molecules in the crystalline lattice. From the formal point of view, octahedral coordination of the hydrogen atoms or ions around the aluminium atoms is entirely possible but the value of this conclusion, drawn on the basis of a comparison of the r_{Al}/r_H ratios with the known criteria for the stability of polyhedra with coordination number four or six, is quite relative, owing to the uncertainty in estimating the radii of the aluminium and hydrogen atoms which are specific for just this type of interaction. On the other hand, a series of derivatives of aluminium hydride are shown in which aluminium exhibits, formally at least, the coordination number of five.

Bis(trimethylamine)alane [2-trimethylamine-aluminium hydride (Ed of Translation)] $AlH_3.2N(CH_3)_3$ and the polymeric *NN'N*-tetramethylethylenediaminealane [*NN'N*-tetramethylethylenediamine-aluminium hydride (Ed. of Translation)] $AlH_3.Me_2N[CH_2]_2NMe_2$ are the only compounds of aluminium hydride for which there have been exhaustive X-ray diffraction investigations[2,3].

The bis(trimethylamine)alane molecule has a trigonal bipyramidal configuration with the hydrogen atoms situated in the equatorial plane. In the linear grouping N–Al–N the interatomic distance d_{Al-N} is 2.18 ± 0.01 Å, that is, a little greater than in aluminium nitride (1.87 Å) and considerably greater than the sum of the covalent radii (1.96 Å).

The configuration of a trigonal bipyramid with the aluminium atom at the centre of the equatorial plane is also retained in the compound of aluminium hydride with *NN'N'*-tetramethylethylenediamine. The interatomic distance d_{Al-N} is 2.195 ± 0.05 Å, and the valence angle N–Al–N is somewhat less than 180°.

It is interesting that in trimethylaminegallane $GaH_3.N(CH_3)_3$, the molecule of which apparently has a configuration[4] identical with that of $BF_3.N(CH_3)_3$, d_{Ga-N} = 1.97 Å, agreeing well with the sum of the covalent radii of Ga and N.

Apparently the increase in the coordination number of aluminium to five or six can be linked either with the participation of the 4*s*- and 3*d*-orbitals in bond formation or with a considerable ionicity of one of the Al–X bonds in the complex. In the latter instance there is some analogy with the so-called "quinquevalent" nitrogen.

II. METHODS OF MAKING ALUMINIUM HYDRIDE AND ITS AMINE COMPLEXES‡

It was mentioned above that there is not yet a method for isolating "pure" unsolvated aluminium hydride from a reaction mixture.

Attempts to obtain it by a "dry" method (without use of a solvent) have been unsuccessful or are of only theoretical significance.

In the direct reaction of metallic aluminium with hydrogen at 1500°, only physical adsorption of the gas takes place.[5] When an aluminium wire is vaporised in an atmosphere of hydrogen at 1100°, a product is formed in which the H : Al ratio fluctuates from 0.19 to 1.02.[5] It is suggested that under these conditions a mixture of aluminium and polymeric aluminium hydride is formed, but the properties of this product differ markedly from those of polymeric aluminium hydride, obtained from ethereal solution — all the hydrogen is lost on heating to ~78° whereas the "ordinary" hydride is "stable" up to 105–110°.

The probability of the formation of aluminium hydride under these conditions was shown mass-spectrometrically[6], in which study aluminium hydride monomer was formed at low aluminium concentrations (~ 0.43%) at ~ 1090°, and the formation of the dimeric molecule Al_2H_6 was observed at ~ 1170° and a higher aluminium concentration (~ 1.7%).

On treating an aluminium–cerium alloy (up to 14% Al) with hydrogen, a product is formed which shows a thermal effect at ~ 210–230° on pyrolysis.[7] Decomposition on the walls of the ampoule gives a faint metallic mirror; as cerium hydride decomposes at a much higher temperature, this effect may be connected with the decomposition of aluminium hydride.

The reduction of trimethylaluminium by hydrogen in an electric discharge leads to the formation of aluminium hydride[8,9], but in this instance a mixture of alkylaluminium hydrides and aluminium hydride is obtained.

Methods based on the reduction of aluminium compounds with various reductants in a solvent–electron donor medium have the greatest practical importance for obtaining solutions of polymeric "solvated" aluminium hydride.

1. Reduction of $AlCl_3$ by lithium hydride in ether[10,11]:

$$AlCl_3 + 3LiH \xrightarrow{20^\circ} AlH_3 + 3LiCl.$$

This reaction proceeds in two stages: initially lithium tetrahydroaluminate is formed, which with an excess of aluminium chloride gives aluminium hydride. As a result of the reaction a metastable solution of aluminium hydride in ether is formed, from which on standing the hydride is deposited as a polymer $(AlH_3)_x$.

2. Reduction of aluminium chloride by lithium tetrahydroaluminate in ether[12,13]:

$$AlCl_3 + 3LiAlH_4 \rightarrow 4AlH_3 + 3LiCl.$$

The yield of aluminium hydride here is considerably greater than in the previous method.

3. Reduction of aluminium chloride by calcium or magnesium hydrides with added aluminium in ether.[14] The yield of aluminium hydride is almost quantitative, according to information in the patent.

4. Reaction of aluminium chloride with diethylaluminium hydride in ether[15]:

$$AlCl_3 + 3Et_2AlH \rightarrow AlH_3 + 3AlEt_2Cl.$$

The yield of aluminium hydride is ~ 70% and depends on the time for carrying out the reaction since increasing the duration of the process increased the yield of a side-product of composition Al_2H_5R.

‡ For the latter, see also J.K.Ruff, "Nitrogen Compounds of Boron, Aluminium, Gallium, Indium, and Thallium", Chapter VI of "Developments in Inorganic Nitrogen Chemistry, Vol.1" (Edited by C.B.Colburn), Elsevier, Amsterdam, 1966 (Ed. of Translation).

5. An electrolytic method for obtaining aluminium hydride by the reduction of a saturated solution of sodium tetrahydroaluminate in tetrahydrofuran at a mercury cathode was recently patented.[16] After electrolysis for three hours, the Al:Na ratio was 2.7; it could be taken that the $NaAlH_4$ concentration had decreased and the aluminium hydride had been formed.

All attempts to desolvate aluminium hydride obtained from ethereal solutions have been unsuccessful. On heating, loss of ether molecules does not take place, but the Al–H bond is broken, and when a freshly prepared solution is treated with a large quantity of inert solvent (pentane or ligroin) an etherated product of composition $(AlH_3)_n \cdot .(C_2H_5)_2O$, where $n = 2.05–2.30$, is obtained[17].

The isolation of aluminium hydride from the reaction mixture and its stabilisation could be effected by treating it with substances which are stronger donors of electrons than diethyl ether. Such substances are amines forming stable amine complexes, which (unlike the oxonium solvates) are individual substances of constant composition.

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The following methods for obtaining complexes of aluminium hydride with amines are possible:

1. Direct reaction of solvated aluminium hydride with amines[18–20].

2. Reaction of an ethereal solution of aluminium hydride with the gaseous amine (trimethylamine)[8,9,12,13,21].

3. The exchange reaction of a simple amine complex of aluminium hydride (for example, $AlH_3.NMe_3$) with more complex amines[22–25].

4. The reaction of lithium tetrahydroaluminate with the amine hydrochloride.[26]

5. Direct reaction of lithium tetrahydroaluminate with the amine in ether[27]; the yield of the complex in this reaction is very small, however.

6. The reaction of aluminium, hydrogen, and amine in tetrahydrofuran under hydrogen pressure with heating.[28]

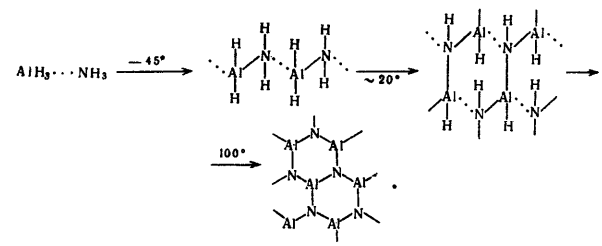
1. Compounds of Aluminium Hydride with Ammonia and Its Derivatives

The study of the reaction of aluminium hydride with ammonia began with attempts to obtain a compound analogous to borazole.[18]

On mixing a solution of aluminium in tetrahydrofuran with dry ammonia in equimolecular proportions at -80° and then heating the mixture, all the intermediate compounds analogous in composition to boron compounds were isolated, but pure alazole was not detected; the explanation given was that aluminium, unlike boron, does not tend to form Al⇄N double bonds, owing to the less electrophilic nature of the "incomplete" 3*p*-orbital.

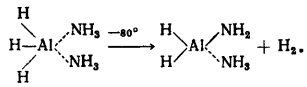
Initially at -80° a voluminous precipitate of composition $AlNH_6$ is formed, which evidently contains alazane $AlH_3 \ldots NH_3$, above -45° one mole of hydrogen is released with the formation of a highly polymeric alazene $(\ldots AlH_2–NH_2\ldots)_x$, which in turn on prolonged heating to room temperature loses a second mole of hydrogen and is converted into a highly polymeric alazyne $(AlH–NH)_x$. The formation of aluminium nitride with release of a third mole of hydrogen does not go to completion even on heating to 100°. All the products obtained are insoluble in an excess of the solvent.

In its entirety this process can be represented by the following scheme:



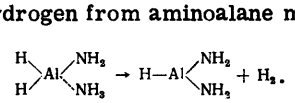
It must be noted that the release of hydrogen from the analogous boron derivatives takes place with much greater difficulty (at higher temperatures)[29,30]. The ease with which hydrogen is released from an aluminium atom was explained by its stronger electronegativity in the hydride compounds of aluminium.[18]

When aluminium hydride in ethereal solution reacts with ammonia in the molar ratio $AlH_3 : NH_3 = 1 : 4$ at -80°, an aminoalane ammine $AlH_2(NH_2).NH_3$ is formed.[18] Here the reaction evidently passes through the stage of formation of aluminium hydride–2-ammonia, $AlH_3.2NH_3$, which at the temperature of the experiment immediately loses one mole of hydrogen (above -30° almost all the hydrogen is lost):



When the reaction is carried out in similar proportions at -50° a white solid of composition $AlH(NH_2)_2$ is obtained after distilling off the excess of ether.

This suggests that diaminoalane is formed by the loss of one mole of hydrogen from aminoalane monoammine:



On heating this compound to room temperature, another mole of hydrogen is released, as a result of which a compound of composition $Al(NH)NH_2$ is formed.

Aminoalane and diaminoalane are intermediate products in the preparation of triaminoalane [aluminium amide, $Al(NH_2)_3$ (Ed. of Translation)], which is formed in the reaction of aluminium hydride with ammonia (in the proportions $AlH_3 : NH_3 = 1 : 4$) at -30°.[13,18] However, under such conditions of carrying out the reaction the theoretical atomic ratio of Al:N = 1:3 could not be reached. At best, the ratio Al:N = 1:2.84 was attained. On raising the temperature above -30°, triaminoalane decomposes to form aluminium nitride:

$$Al(NH_2)_3 \xrightarrow{-NH_3} Al(NH)NH_2 \xrightarrow{-NH_3} AlN.$$

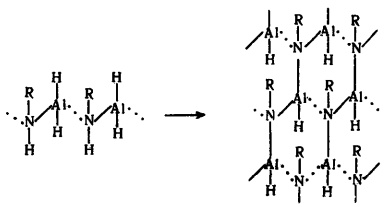
Pure triaminoalane is obtained by the reaction of an excess of liquid ammonia with diaminoalane at -50°:[18]

$$AlH(NH_2)_2 + NH_3 \rightarrow Al(NH_2)_3 + H_2.$$

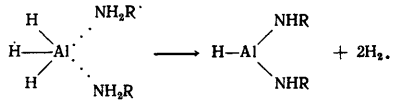
Aluminium hydride in ethereal solutions reacts with methylamine as with ammonia.[18]

When the reaction is carried out with a 1 : 1 molar ratio of the reagents in boiling dioxan a highly polymeric methylalazyne $(AlH-NR)_x$ is formed, and not a trimeric molecule corresponding to *N*-trimethylborazole. The conversion takes place in stages with the formation of *N*-methylalazane (methylamine–alane) $AlH_3 \cdot NH_2R$ and polymeric *N*-methylalazene (methylaminoalane) $(-AlH_2-NHR-)_x$.

When the reaction is carried out at -55° in ether, there is first a white precipitate of methylamine–alane $AlH_3 \cdot NH_2R$, which at -35° releases one mole of hydrogen to form methylaminoalane $AlH_2(NHR)$, converted at room temperature into *N*-methylalazyne with loss of one mole of hydrogen (released only on boiling with dioxan). All the substances thus obtained are high polymers; they are insoluble in ether and benzene and lose hydrogen with difficulty — especially in the last stage, owing to the formation of a complex network structure.



In the reaction of aluminium hydride with methylamine in ether at a reagent molar ratio of 1 : 2 and -55°, a white precipitate of $AlH_3 \cdot 2NH_2R$ is formed[18], which loses two moles of hydrogen at -35° to give bis(methylamino)alane:



Loss of the third mole of hydrogen to form Al(NHR)NR is extremely difficult, owing to the high degree of polymerisation of bis(methylamino)alane.

Bis(methylamino)alane and (methylamino)alane are intermediates in the production of a methyl derivative of triaminoaluminium, tris(methylamino)alane $Al(NRH)_3$,[18] which is a white, highly polymeric substance formed on mixing an ethereal solution of aluminium hydride with an excess of methylamine (~ 1 : 4):

$$[AlH_3] + 3NH_2R \longrightarrow Al(NHR)_3 + 3H_2.$$

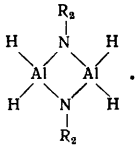
The best result is obtained by cooling the reaction mixture to -50°. The whole reaction scheme is:

$$[AlH_3] + 2NH_2R \longrightarrow AlH_3 \cdot 2NH_2R \xrightarrow{-H_2} AlH_2(NHR) \cdot NH_2R \xrightarrow{-H_2}$$
$$\xrightarrow{-H_2} AlH(NHR)_2 \xrightarrow{+NH_2R} AlH(NHR)_2 \cdot NH_2R \xrightarrow{-H_2} Al(NHR)_3.$$

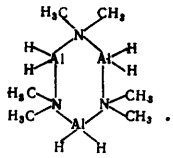
On mixing an ethereal solution of aluminium hydride with dimethylamine in the molar rato $AlH_3 : NHR_2 = 1 : 1$ at -30° and then warming to room temperature, hydrogen is liberated and (dimethylamino)alane AlH_2NR_2 is formed[18]:

$$[AlH_3] + NHR_2 \longrightarrow AlH_2(NR_2) + H_2.$$

This is readily purified by distillation in a vacuum at 40–60°. An ebullioscopic measurement of the molecular weight in ether showed that (dimethylamino)alane is dimeric and its structure evidently corresponds to the formula:



However, a cryoscopic determination of the molecular weight in benzene showed[26] that the degree of association is not 2.16,[18] but 2.99, therefore the formation of a trimeric molecule must be proposed, in which the aluminium atom has a coordination number of four and the association takes place by formation of Al–N bonds (by analogy with boron compounds[31]):



This substance melts without decomposition at 89–90°, is soluble in benzene and ether, and reacts vigorously with water with liberation of hydrogen.

(Dimethylamino)alane can be obtained by reaction of trimethylamine–alane with tris(dimethylamino)alane[32]:

$$2AlH_3 \cdot NMe_3 + (NMe_2)_3Al \rightarrow 3AlH_2(NMe_2) + 2NMe_3$$

and by reaction of lithium tetrahydroaluminate with dimethylamine in equimolecular proportions[27].

(Di-isopropylamino)alane and (diethylamino)alane are obtained in the reaction of the corresponding dialkylammonium chlorides with lithium tetrahydroaluminate[26,32]:

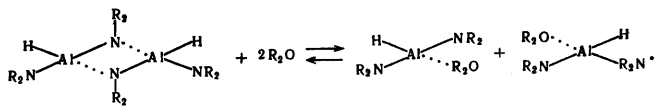
	M.p., °C	Sublimation temp., °C	Degree of association
$[(CH_3)_2CH]_2NAlH_2$	130–131	90	2.16
$(Et_2N)AlH_2$	42	—	2.12

The molecular weights of the two compounds were measured cryoscopically in benzene.

On mixing an ethereal solution of aluminium hydride with dimethylamine in the molar ratio 1 : 2 at -30°, then after the liberation of hydrogen had ceased and distillation under high vacuum at 35–50°, bis(dimethylamino)alane was obtained as colourless crystals[18]:

$$[AlH_3] + 2NHR_2 \rightarrow AlH(NR_2)_2 + 2H_2.$$

According to Wiberg and May[18], bis(dimethylamino)alane melts at 63–65° and dissolves in benzene and ether. An ebullioscopic determination of the molecular weight in ether showed that the substance is partly associated into a dimeric molecule:



Hence it is thought that the introduction of the NR_2 group diminishes the tendency to polymerisation.

Bis(dialkylamino)alanes can be isolated (in high yield) from the reaction of trimethylamine–alane with the appropriate dialkylamines[32,33]:

$$AlH_3 \cdot NMe_3 + 2(Alk)_2NH \rightarrow 2H_2 + HAl(NAlk_2)_2 + NMe_3.$$

Bis(dimethylamino)alane obtained by this method has the same melting point (62°) as the compound described by Wiberg and May[18], however, the degree of its association in benzene is 2.49 (according to these authors, 1.71 in ether). The different degree of association of bis(dimethylamino)alane depending on the solvent can be explained by the formation of an ether addition compound, although it is thought[32] that the bridging bond formed by the Me_3N group is fairly stable.

Bis(dimethylamino)alane is formed also in the reaction of sodium hydride with (dimethylamino)alane[33]:

$$NaH + 2AlH_2NMe_2 \longrightarrow NaAlH_4 + HAl(NMe_2)_2.$$

The introduction of a third R_2N group suppresses the dimerisation of the molecule, according to Wiberg and May[18]; $Al(NR_2)_3$ is monomeric. Tris(dimethylamino)alane is obtained by the reaction of an ethereal solution with dimethylamine and room temperature and molar ratio AlH_3 : NHR_2 = 1 : 4. The substance sublimes in a vacuum at 60–100°, melts without decomposition at 87–88°, and reacts vigorously with water and acids.

The same compound can be obtained by other methods. Ruff[32] proposed two methods of synthesis:

(1) $$H_3Al\cdot NMe_3 + 3HNMe_2 \longrightarrow Al(NMe_2)_3 + NMe_3 + 3H_2,$$

(2) $$LiAlH_4 + 4HNMe_2 \longrightarrow LiAl(NMe_2)_4 + 4H_2,$$

(3) $$3LiAl(NMe_2)_4 + AlCl_3 \longrightarrow 4Al(NMe_2)_3 + 3LiCl.$$

Tris(dimethylamino)alane is also obtained by the reaction of tri-isobutylaluminium with dimethylamine in heptane[34]:

$$(Bu^i)_3Al + 3HNMe_2 \xrightarrow{195^\circ} Al(NMe_2)_3 + 3iso\text{-}C_4H_{10}.$$

And finally Fetter and Bartocha[25] obtained $Al(NMe_2)_3$ by the reaction of trimethylaluminium with tetramethyltetrazene. They proposed the following reaction scheme:

$$3AlMe_3 + 3Me_2HN{=}NHMe_2 \longrightarrow 2Al(Me_2N)_3 + N_2 + 6CH_4.$$

There is a considerable difference in the physical constants of tris(dimethylamino)alane obtained by various methods (see Table 1). The marked difference between the melting points of tris(dimethylamino)alane obtained by Fetter and other authors can only be explained if quite different substances were investigated. The stability of the monomeric form in ether[18,20] and the dimeric form in benzene[32] shows that tris(dimethylamino)alane can form an ether addition compound $Al(NMe_2)_3.O(C_2H_5)_2$.[32]

Tris(dimethylamino)alane reacts without a solvent with anhydrous aluminium chloride[32]; dichloro-(dimethylamino)-alane and chlorobis(dimethylamino)alane are formed:

$$AlCl_3 + 2(Me_2N)_3Al \rightarrow 3(Me_2N)_2AlCl,$$
$$2AlCl_3 + (NMe_2)_3Al \rightarrow 3(Me_2N)AlCl_2.$$

Replacement of the third NMe_2 group taking part in the formation of a nitrogen bridge does not occur.

TABLE 1.

M.p., °C	Molecular weight	Method of determination	Reference
—30	193—199	cryoscopic (cyclopentane)	25
87—88	162	ebullioscopic (ether)	18
87—89	353	cryoscopic (benzene)	32
Not given	320	cryoscopic (benzene)	34

TABLE 2.

Compound	M.p., °C	Sublimation temperature, °C	Degree of association
$(Me_2N)_2AlCl$	55—57	55	1.95
$(Me_2N)AlCl_2$	151	90	2.12

The difference in the reactivity of the bridge and terminal dialkylamino-groups was investigated in the tensimetric titration of dialkylamino-derivatives of aluminium with gaseous boron trichloride[32].

When two moles of boron trichloride are added to one mole of tris(dimethylamino)alane (under conditions such that it is dimeric, that is, a bridge bond is formed), a sharp change in vapour pressure is observed after 15 min; when an excess of boron trichloride (over three moles) is added, the change in vapour pressure occurs after 24 h. This can be explained only by a difference in the reactivity of the NMe_2 groups in tris(dimethylamino)alane.

There are other proofs of the stability of the bridge bonds formed. When (trimethylamino)alane reacts with dimethylamine, trimethylamine is quantitatively replaced by dimethylamine and hence the equilibrium of the reaction is completely displaced in favour of a compound with nitrogen bridges[33].

Tris(di-isopropylamino)alane, unlike tris(dimethylamino)alane, is monomeric[32]. This fact is apparently connected with steric hindrance to dimerisation. The difference between these compounds also appears in the conditions for their preparation — whereas $Al(NMe_2)_3$ is formed rather readily, $Al[(iso\text{-}C_3H_7)_2N]_3$ is considerably more difficult to prepare; this is linked with the necessity of breaking the nitrogen bridges in the intermediate di-isopropylamino-derivatives of aluminium — bis(di-isopropylamino)alane is dimeric.

As mentioned above, tris(dimethylamino)alane is monomeric in ether and this is apparently due to the formation of the ether addition compound $Al(Me_2N)_3.O(C_2H_5)_2$. An attempt was therefore made to obtain an amine complex of tris(di-isopropylamino)alane with trimethylamine and dimethylamine[32].

In the first instance, no reaction was observed; in the second, there was a sudden change in pressure in the system on adding two moles of dimethylamine; apparently an exchange reaction took place instead of the formation of the expected complex:

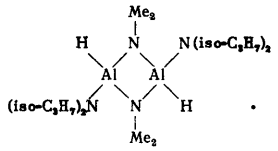
$$2(CH_3)_2NH + [(iso\text{-}C_3H_7)_2N]_3Al \longrightarrow 2(iso\text{-}C_3H_7)_2NH + (Me_2N)_2Al[N(iso\text{-}C_3H_7)_2].$$

However, (di-isopropylamino)bis(dimethylamino)alane was not isolated from the reaction products. Attempts to obtain it by the reaction of di-isopropylamine with dimethylaminoalane led to the replacement of only one hydrogen atom[32]:

$$(iso\text{-}C_3H_7)_2NH + (CH_3)_2N{-}AlH_2 \xrightarrow{36\ h} (CH_3)_2N{-}\overset{H}{\underset{|}{Al}}{-}N(iso\text{-}C_3H_7)_2 + H_2.$$

(Di-isopropylamino)(dimethylamino)alane is a solid which sublimes at 95° and its degree of association (in benzene) is 1.98. Three structural formulae for it are possible

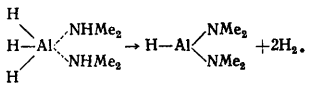
(under the conditions for the formation of nitrogen bridges), the most probable being:



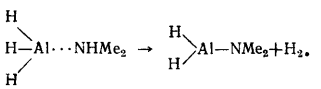
The structural formula with $(iso\text{-}C_3H_7)_2N$ bridge-forming groups is less probable, as the NMe_2 group stabilises the dimer more strongly and the molecule with a bridging bond through this group is rather stable.

As tris(di-isopropylamino)alane is monomeric and all its amino-groups are equivalent, an increase in vapour pressure is observed during tensimetric titration with boron trichloride at the molar ratio $BCl_3 : Al(NPr^i_2)_3 = 3 : 1$.[32]

To conclude this section we will consider the even less-studied bis(dimethylamine)alane and (dimethylamine)alane. Bis(dimethylamine)alane is formed in the reaction of an ethereal solution of aluminium hydride with dimethylamine at -50°.[18] It is of low stability and decomposes at -20° with loss of hydrogen and formation of bis(dimethylamino)alane:



(Dimethylamine)alane can be obtained by the action of dimethylammonium chloride on lithium tetrahydroaluminate at -40°.[26] It exists only up to -10°, above which temperature it loses one mole of hydrogen to form (dimethylamino)alane:



The amine complexes of aluminium hydride with tertiary amines in which the $[AlH_3]$ group of atoms remains unchanged are particularly interesting. Those with trimethylamine have been studied most.

These compounds are readily obtained in the reaction of freshly prepared ethereal solution of aluminium hydride with trimethylamine in the molar ratio 1:1 and 1:2 at room temperature or on coooling[8,9,12,13,20,21]. Another method of preparation is based on the reaction of lithium tetrahydroaluminate with the amine hydrochloride.[26]

Mono(trimethylamine)alane, subsequently called trimethylaminealane, distils readily in a vacuum at 60°/1 mmHg, forming colourless crystals, dissolves readily in ether, benzene, and tetrahydrofuran, reacts explosively with water, and fumes strongly in air. The pure product melts at 76° without decomposition.

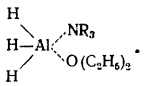
When heated rapidly to 100°, the crystals become opaque, owing to the commencement of the polymerisation of aluminium hydride:

$$x\ AlH_3 \cdot NMe_3 \rightarrow (AlH_3)_x + x\ NMe_3.$$

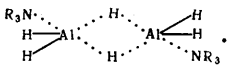
Heating on a naked flame leads to complete decomposition of the compound and the formation of an aluminium mirror:

$$AlH_3 \cdot NMe_3 \rightarrow Al + 1.5H_2 + NMe_3.$$

In determining the molecular weight (ebullioscopic method) in ether, it was found that trimethylaminealane is monomeric, but it is associated in benzene[12,13]; trimethylaminealane vapour is monomeric[35]. This difference in the behaviour of trimethylaminealane depending on the solvent was explained by the unsaturated nature of the four-coordinated aluminium atom — in ether this saturation takes place with the p-electrons of the oxygen atom:



In benzene, this propensity to saturation can be effected by the dimerisation of two molecules of trimethylaminealane with the formation of hydrogen bridges:

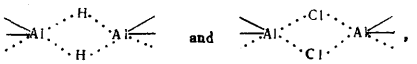


Wiberg's hypothesis of the dimerisation of trimethylaminealane received confirmation in later studies[26,36].

It can also be assumed that association of trimethylaminealane takes place by dipole–dipole interaction in the solution[36-38]. This hypothesis is based on the fact that replacement of hydrogen atoms by chlorine atoms produces a slight change in the degree of association of alane in benzene[37]:

	Degree of association
$AlH_3 \cdot NMe_3$	1.43
$H_2AlCl \cdot NMe_3$	1.32
$HAlCl_2 \cdot NMe_3$	1.46
$AlCl_3 \cdot NMe_3$	1.36

It is improbable that the stability of the rings



would be completely the same. Evidently dipole–dipole interaction is also more probable for trimethylaminealane and for an amine-complex of aluminium chloride in benzene[39].

The investigation of infrared and Raman spectra showed that the symmetry of the trimethylaminealane molecule is C_{3v} and the Al–N vibration frequency is 553 cm^{-1}.[40]

Of the other trialkylaminealanes, triethylaminealane and tri-n-propylaminealane have been obtained and studied[26,42].

Under ordinary conditions triethylaminealane is a transparent liquid, m.p. 18–19°; it is easily distilled in a vacuum at 40°.

On determining the molecular weight of this compound in benzene[26] a considerable difference from Wiberg's data[42] (determination in ether) was found. The degree of association is 1.10 according to Ruff, 1.57 to Wiberg.

With tri-n-propylaminealane steric hindrance completely prevents association into a dimer: it is difficult to distil and can be purified by recrystallisation from hexane at -80°. Its melting point is 80–81°.[26]

Bistrialkylaminealanes can be obtained by various methods which differ little in principle from one another.

When an ethereal solution of aluminium hydride is mixed with trimethylamine (1 : 2), the reaction yields a colourless solution from which, after distilling off the solvent and the excess of amine, bis(trimethylamine)alane is precipitated as a white powder; it readily sublimes in a vacuum at 30–40°/1 mmHg. The same compound can be obtained on adding an excess of trimethylamine to trimethylaminealane[13] or by the action of hydrogen chloride on lithium tetrahydroaluminate followed by addition of trimethylamine[2]:

$$LiAlH_4+HCl \xrightarrow{R_2O} H_2+LiCl+[H_3Al]\cdot R_2O,$$
$$[H_3Al]\cdot R_2O+2NMe_3 \xrightarrow{R_2O} H_3Al\cdot 2NMe_3.$$

Bis(trimethylamine)alane melts at 95° and at 100° it starts to decompose, probably with formation of a polymer of aluminium hydride and liberation of trimethylamine. The compound dissolves readily in ether, benzene, and tetrahydrofuran.

Molecular weight determinations in benzene and ether show that the substance is monomeric in these solvents[26,42]; on comparing the infrared spectra of $AlH_3.2NMe_3$ and $(AlH_3)_2(Me_2N[CH_2]_2NMe_2)_2$ it was noted that the absorption of the Al–H bond in the 5.9 μm region is the same, hence it was assumed that bis(trimethylamine)alane is partly dimerised in the gas phase[23].

Measurements of the polarisation of the molecule in benzene, cyclohexane, and dioxan did not show the presence of a dipole moment which varied in different solvents (1.2 D in benzene, 1.6 D in cyclohexane and dioxan). The existence of a dipole moment for a trigonal bipyramidal model was explained by the high atomic polarisation[38,40].

Ruff and coworkers[33] investigated the conditions for the formation and the stability of other bis(trialkylamine)alanes. The formation constants for these complexes allowed them to construct a series for the stability of alanes as a function of the alkyl group:

$$NR_3=N(CH_3)_3 > N(CH_3)_2CH_2CH=CH_2 > N(CH_3)(C_2H_5)_2 > N(C_2H_5)_3 > N(C_3H_7)_3.$$

The stability of the mixed diaminealanes changes in the sequence:

$$AlH_3\cdot N(CH_3)_3\cdot N(CH_3)(C_2H_5)_2 > AlH_3\cdot N(CH_3)_3\cdot N(C_2H_5)_3 > AlH_3\cdot N(CH_3)_3\cdot N(C_3H_7)_3,$$

that is, the stability of the complexes also depends entirely on the dimensions of the alkyl groups (mixed diaminealanes are more stable than symmetrical ones).

2. Compounds of Aluminium Hydride with Bifunctional Amines

Aluminium hydride in tetrahydrofuran reacts with hydrazine with the formation of aluminium hydrazide $Al(N_2H_3)_3$.[41] This reaction proceeds very slowly in an inert solvent whereas in tetrahydrofuran the yield approaches 94% (the isolation of this compound was carried out in a high vacuum):

$$AlH_3+3N_2H_4 \longrightarrow Al(N_2H_3)_3+3H_2.$$

The mechanism of the reaction between aluminium hydride and hydrazine is not completely clear, but it is possible that the reaction proceeds just as in the reaction of metal amides and metal alkyls with hydrazine, that is, through the formation of the ions $N_2H_3^-$ and $N_2H_5^+$, on account of a shift in the equilibrium of the protolysis of hydrazine:

$$2N_2H_4 \rightleftarrows N_2H_5^+ + N_2H_3^-.$$

The $N_2H_5^+$ ion reacts with a hydrogen ion to form a molecule of hydrazine and a molecule of hydrogen:

$$H^- + N_2H_5^+ \longrightarrow N_2H_4 + H_2,$$

and the $N_2H_3^-$ ion reacts with an aluminium ion to form aluminium hydrazide:

$$Al^{3+} + 3N_2H_3^- \longrightarrow Al(N_2H_3)_3.$$

It is interesting that in this scheme appreciable ionisation of the Al–H bond is proposed.

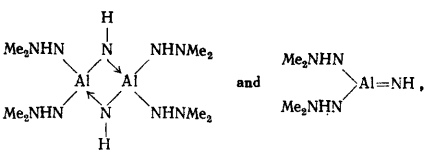
When trimethylaminealane is used instead of aluminium hydride, the reaction yields a white solid, which, when the solvent is removed, explodes at the least vibration[22]; however, this substance has not been identified.

The mechanism of the reaction of trimethylaminealane with alkyl derivatives of hydrazine and the structure of the final products of the reaction are extremely difficult to interpret and are semi-quantitative because most of the products are polymers, have a low vapour pressure, do not distil, and cannot be purified by sublimation. The direction of the reaction depends entirely on the initial proportion of the reagents, the structure of the alkyl hydrazine, and the nature of the solvent.

Methylhydrazine and trimethylaminealane (in hydrocarbon medium) give a white, stable compound[22]. On the basis of the ultimate analysis and infrared spectra of the final products the following reaction scheme was proposed:

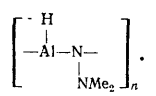
$$n\,H_3Al\cdot NMe_3 + 2n\,H_2NNHMe \longrightarrow \left[\begin{array}{l} NH{-}NHMe \\ | \\ {-}Al{-}NHNMe{-} \end{array}\right]_n + 3n\,H_2 + n\,NMe_3.$$

1,1-Dimethylhydrazine forms with trimethylaminealane a white crystalline substance which does not sublime in a vacuum and has m.p. 193–194°.[22] Two structural formulae have been proposed for the substance:

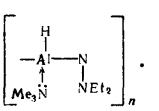


but have not been confirmed by direct experimental data, however.

When 1,1-dimethylhydrazine and trimethylaminealane in the molar ratio $Me_2NNH_2 : AlH_3.NMe_3 = 2 : 1$ react in pentane a substance with the empirical formula $C_2H_7N_2Al$ is obtained[22]. The infrared spectrum agrees best with the polymeric formula:



This structural formula is also supported by the fact that 1,2-diethylhydrazine also reacts with trimethylaminealane[22] only here the trimethylamine molecule is associated with the aluminium atom. As a result of the reaction a viscous substance is formed, the structural formula of which may be:

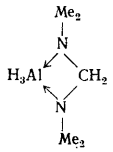


When the reagent ratio is $AlH_3.NMe_3 : Et_2NNH_2 = 1 : 1$, a white, involatile solid is formed, 1,1-diethylhydrazidoalane $AlH_2.NHNEt_2$.[22]

Trimethylhydrazine with trimethylamine–alane forms dimethylaminoalane $AlH_2–NMe_2$.[22]

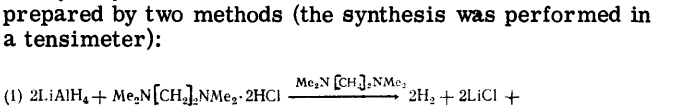
It must be pointed out that freshly prepared aluminium hydride–ether does not react with tetramethylhydrazine[22], although earlier it was thought that it has the same basicity as trimethylamine.

Trimethylamine–alane forms with *NNN'N'*-tetramethylmethylenediamine a cyclic complex which has a sharp melting point (25–26°) and is readily distilled in a vacuum at room temperature[22]. Starting from the NMR spectra and ultimate analysis the following structural formula was advanced for it:

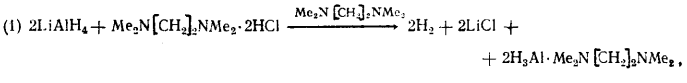


(this complex is evidently partly dimerised in benzene, where its molecular weight is 164–167, against the calculated 132).

A complex of aluminium hydride with *NNN'N'*-tetramethylethylenediamine has also been obtained[23]. It was prepared by two methods (the synthesis was performed in a tensimeter):

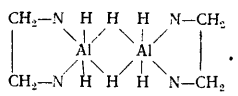


(1) $2LiAlH_4 + Me_2N[CH_2]_2NMe_2 \cdot 2HCl \xrightarrow{Me_2N[CH_2]_2NMe_2} 2H_2 + 2LiCl + 2H_3Al \cdot Me_2N[CH_2]_2NMe_2$,

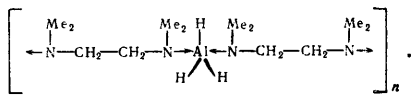


(2) $AlH_3 \cdot 2NMe_3 + Me_2N[CH_2]_2NMe_2 \longrightarrow 2NMe_3 + AlH_3 \cdot Me_2N[CH_2]_2NMe_2$.

The complex is a white solid which does not decompose on heating to 133° for 24 h. Its vapour pressure at 99.3° and 119.2° is 1.5 and 10.6 mmHg respectively. In measuring the vapour pressure it was found that the product is apparently dimeric and the probable structural formula for it with six-coordinated aluminium atoms was proposed:



However, later investigations[2,3] established the existence of associates with a linear N–Al–N bond:



The same structural formula can be proposed also for the complexes of aluminium hydride with *NNN'N'*-tetramethyl--1,3-propanediamine and 1,4-bis(dimethylamino)but-2-ene[24], since with them aluminium hydride also gives complexes of 1 : 1 composition. *NNN'N'*-tetramethyl-1,3-propanediamine–alane is a white solid with m.p. 136–140°; it distils in a vacuum at 80°/0.05 mmHg. It is obtained by the reaction of trimethylamine–alane with *NNN'N'*-tetramethyl-1,3-propanediamine[24].

The complex with 1,4-bis(dimethylamino)but-2-ene

$$[H_3Al \cdot (Me_2N) \cdot CH_2CH=CHCH_2(NMe_2)],$$

is obtained by reaction with trimethylamine–alane in n-octane[24]. Its m.p. is 150–155° and it distils at 105°/0.05 mmHg. It should be noted that the investigation of these complexes has been qualitative in nature.

Fetter and Moore[24] investigated the reaction of trimethylamine–alane with tetrakisdimethylaminoethylene $[(CH_3)_2N]_2C=C[N(CH_3)_2]_2$ and hexamethylenetetramine. However, here the investigation was purely qualitative: there is no distinct chemical analysis of the product. The authors suggest that the tetrakisdimethylaminoethylene is bonded in a complex with two molecules of aluminium hydride, after which decomposition of the complex occurs (the decomposition products were not determined). The sublimation temperature of the compound is 75°.

With hexamethylenetetramine a stable complex is formed, presumably $AlH_3.(CH_2)_6H_4$, which does not sublime up to 120° and does not melt up to 200°, but above that temperature it decomposes with formation of an aluminium mirror.

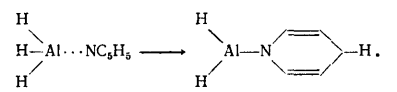
The mechanism of the reaction and the end product of the reaction of trimethylamine–alane with tetramethyltetrazene has been established sufficiently accurately[25]. Tetramethyltetrazene heated in an inert solvent decomposes with formation of tetramethylhydrazine and liberation of hydrogen; however, in the presence of trimethylaminealane the dimethylamino-group does not add to the tetramethylhydrazine but reacts to form dimethylaminoalane:

$$2H_3Al \cdot NMe_3 + Me_2NN=NNMe_2 \rightarrow 2H_2Al–NMe_2 + H_2 + N_2 + 2NMe_3.$$

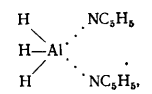
The substance was sublimed at 60°/0.005 mmHg, and then identified by melting point, ultimate analysis and infrared spectra (see above for the physical constants).

3. Compounds of Aluminium Hydride with Pyridine

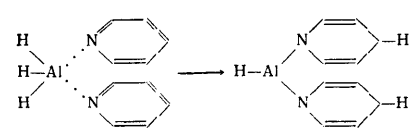
Aluminium hydride reacts in ethereal solution with pyridine in the molar ratio $AlH_3 : NC_5H_5 = 1 : 1$ at -30° with the formation of a white crystalline addition product, $AlH_3.NC_5H_5$.[19] When the latter is heated to room temperature its colour changes from white to yellow. This behaviour is explained by intramolecular rearrangements in which one atom of hydrogen connected with aluminium is introduced into the pyridine ring with formation of a compound with a quinonoid structure:



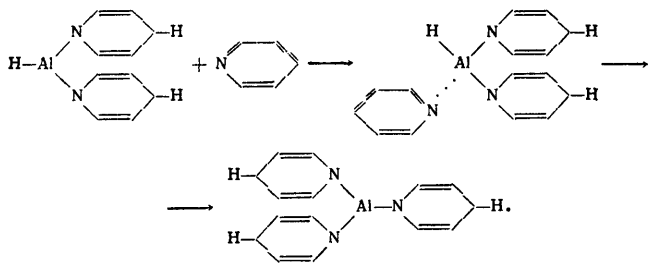
When an excess of pyridine is taken, then aluminium hydride–bis-pyridine is formed under analogous conditions:



which when slowly heated to room temperature gradually changes colour from white to dark red. During this there is considerable heat liberated and the residue melts (60–70°). This change in colour is due to the same intramolecular rearrangement:



Bis(dihydropyridyl)alane is insoluble in benzene, petroleum ether, tetrahydrofuran, chloroform, and does not dissolve in an excess of pyridine. After distilling off the excess of solvent a brownish-red solid of composition $AlH_3.3NC_5H_5$ remains[19]. Hydrolytic decomposition of this compound showed that it does not contain active hydrogen bound to the aluminium atom. Hence bis(dihydropyridyl)-alane and pyridine give tris(dihydropyridyl)alane:



The completeness of the conversion of bis(dihydropyridyl)-alane into tris(dihydropyridyl)alane depends on the reaction time. Both products are sensitive to oxygen.

4. Alkyl-Substituted Complexes of Aluminium Hydride with Tertiary Amines

In addition to the amine complexes of aluminium hydride, a series of complexes is known in which the hydrogen in AlH_3 is partly replaced by alkyl. Such compounds can be prepared as follows:

1. By the reduction of alkylhalides of aluminium with lithium hydride[43,44]:

$$R_2AlHal\cdot NMe_3 + LiH \longrightarrow R_2AlH\cdot NMe_3 + LiCl,$$
$$RAlHal_2\cdot NMe_3 + 2LiH \longrightarrow RAlH_2\cdot NMe_3 + 2LiCl.$$

2. By the alkylation of trimethylamine–alane with dialkylmercury compounds[43,44]:

$$AlH_3\cdot NMe_3 + R_2Hg \longrightarrow R_2AlH\cdot NMe_3 + H_2 + Hg,$$
$$AlH_3\cdot NMe_3 + {}^1/_2R_2Hg \longrightarrow RAlH_2\cdot NMe_3 + {}^1/_2H_2 + {}^1/_2Hg.$$

3. By disproportionations[43,44]:

$$AlH_3\cdot NMe_3 + 2R_2Al\cdot NMe_3 \longrightarrow 3R_2AlH\cdot NMe_3,$$
$$2AlH_3NMe_3 + R_3Al\cdot NMe_3 \longrightarrow 3RAlH_2\cdot NMe_3.$$

4. By alkylation of trimethylamine–alane and dimethylaminoalane with butyl-lithium[44]:

$$AlH_3\cdot NMe_3 + LiC_4H_9 \longrightarrow LiH + C_4H_9AlH_3\cdot NMe_3.$$

The reaction is complicated by a side-reaction:

$$LiH + AlH_3\cdot NMe_3 \longrightarrow LiAlH_4 + NMe_3,$$

which makes control over the stoichiometry of the reaction difficult.

The amine complexes of the alkyl hydrides are extremely sensitive to moisture and oxygen. From the little information which is available about these compounds it can be concluded that the introduction of alkyl groups into the molecule of an amine complex of the hydride stabilises the compound (Table 3).

TABLE 3.

Compound	M.p., °C	B.p., °C	Degree of association
$MeAlH_2\cdot NMe_3$	−35	25–26	1.95
$Me_2AlH\cdot NMe_3$	33–35	42–43	1.34
$EtAlH_2\cdot NMe_3$	—	35–40	1.60
$Et_2AlH\cdot NMe_3$	−28	63–65	1.18

5. Quaternary Ammonium Salts of Aluminium Hydride [Quaternary Ammonium Tetrahydroaluminates]

A paper recently appeared[45] on a new method of stabilising aluminium hydride by the formation of quaternary ammonium salts of tetrahydroaluminates.

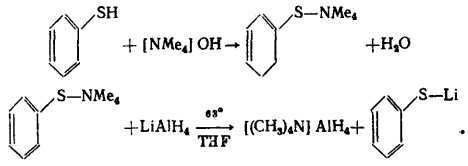
Two salts of this type have been obtained, tri-n-octyl--n-propylammonium tetrahydroaluminate, $[(C_8H_{17})_3(C_3H_7)N].AlH_4$ (I) and tetramethylammonium tetrahydroaluminate $[(CH_3)_4N]AlH_4$ (II).

They are crystalline. (I) melts at 61–63° with decomposition, and is readily soluble in benzene, toluene, and diethyl ether and poorly soluble in pentane and hexane; (II) decomposes at 173° and is not soluble in any of the organic solvents.

Both the compounds, unlike the amine complexes of aluminium hydride, exhibit great stability against hydrolysis: to complete their hydrolysis heating in 6 *N* HCl in sealed tubes for two weeks is necessary. The infrared spectra of these compounds suggest an ionic structure for their molecules. This is also confirmed for (I) by the measurements of electrical conductivity in tetrahydrofuran, which showed that the electrical conductivity of (I) is greater than (approximately twice) that of lithium tetrahydroaluminate.

The ionic character of (II) is confirmed by its insolubility in all organic solvents and by its relatively high decomposition temperature.

Compound (I) is obtained by the reaction of $[(C_8H_{17})_3.(C_3H_7)N]Br$ with lithium tetrahydroaluminate at room temperature in benzene for three days. The pure substance was isolated by treating the filtered solution with pentane. $[(CH_3)_4N]AlH_4$ was obtained by the scheme:



The substance was filtered off, washed with tetrahydrofuran and dried in a vacuum for five hours at room temperature.

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The above review shows that attention has so far been mainly directed to problems on the preparation of various derivatives of aluminium hydride. However, insufficient attention has been paid to systematic physicochemical investigation of the substances obtained.

Only two substances have been investigated by X-ray diffraction: bistrimethylamine–alane and *NNN'N'*-tetramethylethylenediaminealane; the structural formulae proposed for the other compounds are based on indirect data and are therefore not very trustworthy.

Most of the complex molecules in solution are either dimeric or trimeric, but the nature of the bonds brought about by dimerisation has been little studied; the data are contradictory and are not based on any reliable experimental evidence; there is hardly any information on the

thermodynamic characteristics of the phase transformations of the various complexes of aluminium hydride, etc.

We therefore consider that future work in the field of the complexes of aluminium hydride will be successful only if physical and physicochemical methods are widely employed.

1. N.C.Baenziger, Acta Cryst., 4, 216 (1951).
2. C.W.Heitsch, C.E.Nordman, and R.W.Parry, Inorg.Chem., 2, 508 (1963).
3. G.J.Palenik, Acta Cryst., 17, 1573 (1964).
4. D.F.Shriver and C.E.Nordman, Inorg.Chem., 2, 1298 (1963).
5. B.Siegel, J.Amer.Chem.Soc., 82, 1535 (1960).
6. P.Breisacher and B.Siegel, J.Amer.Chem.Soc., 86, 5053 (1964).
7. V.I.Mikheeva, Z.K.Sterlyadkina, and A.A.Chertkov, Zhur. Neorg.Khim., 8, 1710 (1963) [Russ.J.Inorg.Chem., 888 (1963)].
8. O.Stecker and E.Wiberg, Chem.Ber., 75, 2003 (1942).
9. E.Wiberg, Chem.Ber., 77A, 75 (1944).
10. A.E.Finholt, A.C.Bond,Jnr., and H.J.Schlesinger, J.Amer. Chem.Soc., 73, 4585 (1951).
11. U.S.P. 2 567 972 (18th September 1951); Chem.Abs., 46, 2762e (1952).
12. E.Wiberg, H.Graf, M.Schmidt, and R.Uson, Z.Naturforsch., 76, 578 (1952).
13. E.Wiberg, H.Graf, and R.Uson, Z.anorg.Chem., 272, 221 (1953).
14. German P. 1 005 935 (12th July 1954); Chem.Zentr., 2, 530 (1958).
15. German P. 1 024 062 (9th February 1956); Chem.Zentr., 43, 13 912 (1959).
16. German P. 1 141 623 (1st January 1960); Ref.Zhur.Khim., 12L184 (1964).
17. G.Chizinsky, G.G.Evans, T.K.P.Gibb, Jnr., and M.J.Rice, Jnr., J.Amer.Chem.Soc., 77, 3164 (1955).
18. E.Wiberg and A.May, Z.Naturforsch., 10B, 229 (1955).
19. E.Wiberg and W.Gösele, Z.Naturforsch., 10B, 236 (1955).
20. E.Wiberg, A.May, and H.Noth, Z.Naturforsch., 10B, 239 (1955).
21. E.Wiberg, Angew.Chem., 65, 16 (1953).
22. N.R.Fetter, B.Bartocha, F.E.Brinckman, Jnr., and D.W.Moore, Canad.J.Chem., 41, 1359 (1963).
23. J.M.Davidson and T.Wartik, J.Amer.Chem.Soc., 82, 5506 (1960).
24. N.R.Fetter and D.W.Moore, Canad.J.Chem., 42, 885 (1964).
25. N.R.Fetter and B.Bartocha, Canad.J.Chem., 40, 342 (1962).
26. J.K.Ruff and M.F.Hawthorne, J.Amer.Chem.Soc., 82, 2141 (1960).
27. F.M.Peters, Canad.J.Chem., 42, 1755 (1964).
28. A.C.Ashby, J.Amer.Chem.Soc., 86, 1882 (1964).
29. E.Wiberg, K.Hertwig, and U.Bolz, Z.anorg.Chem., 256, 177 (1948).
30. E.Wiberg and A.Bolz, Chem.Ber., 73, 209 (1940).
31. L.M.Trefonas and W.N.Lipscomb, J.Amer.Chem.Soc., 81, 4435 (1959).
32. J.K.Ruff, J.Amer.Chem.Soc., 83, 2835 (1961).
33. J.K.Ruff and M.F.Hawthorne, J.Amer.Chem.Soc., 83, 535 (1961).
34. U.Longi, G.Mazzanti, and F.Bernardini, Gazzetta, 90, 180 (1960).
35. H.Rosinski, A.Doutel, and W.Zeil, Z.phys.Chem.(Frankfurt), 36, 26 (1963).
36. F.M.Peters, B.Bartocha, and A.J.Bilbo, Canad.J.Chem. 41, 1051 (1963).
37. J.K.Ruff, J.Amer.Chem.Soc., 83, 1798 (1961).
38. G.Schomburg and E.G.Hoffman, Z.Elektrochem., 61, 1110 (1957).
39. H.Ulich and W.Nespital, Angew.Chem., 44, 750 (1931).
40. G.W.Fraser, N.N.Greenwood, and B.P.Straughan, J.Chem. Soc., 3742 (1963).
41. H.Bock, Z.Naturforsch., 176, 429 (1962).
42. E.Wiberg and H.Nöth, Z.Naturforsch., 10B, 237 (1955).
43. F.M.Peters and B.Bartocha, Chem.and Ind., 1271 (1961).
44. B.Bartocha, A.J.Bilbo, and M.J.Gray, Angew.Chem., 72, 36 (1960).
45. R.Ehrlich, A.R.Young, and D.D.Perry, Inorg.Chem., 4, 758 (1965).

Faculty of Chemistry, Lomonosov
Moscow State University,
Moscow

U. D. C. 546.668 : 546.174

PARAMAGNETIC DERIVATIVES OF NITROGEN MONOXIDE

E. G. Rozantsev

CONTENTS

1. Introduction 658
2. Paramagnetic nitrogen oxides 659
3. Fremy's salt 660
4. Nitroxides 661
5. Iminoxyls 664
6. Individual polyradicals 667

1. INTRODUCTION

Just as half a century ago, stable radicals continue to play an important part in the development of the theoretical concepts of contemporary chemical science.

The discovery and the wide use of the electron paramagnetic resonance (EPR) method was a powerful tool in the development of this field of chemistry[1-3].

Stable radicals are quite useful in solving many specific problems arising during the course of chemical, physical, and biological experiments.

This class of substances is successfully used in studying the rates of initiation of chain reactions, in catalysis, and in photochemical and quantum-chemical investigations.

After the discovery and study of the phenomenon of dynamic nuclear polarisation, stable radicals with a simple hyperfine spectral structure became used in the construction of high-sensitivity magnetometers and "Maser" type devices.

In recent years several reviews and monographs devoted to free radicals have appeared[4-12], in which little mention has been made of an important class, the paramagnetic derivatives of nitrogen monoxide.