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Structure and Properties of Dibutylamine Complexes with Aluminum and Gallium Halides: The Role of Hydrogen Bonds

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Abstract — Reactions of aluminum and gallium halides MX_3 (M = Al, Ga; X = Cl, Br) with dibutylamine in benzene solutions were studied by calorimetry, dielectrometry, and cryoscopy. The formation of molecular complexes $Bu_2NH \cdot MX_3$ (1 : 1), $2Bu_2NH \cdot MX_3$ (2 : 1) and $6Bu_2NH \cdot MX_3$ (6 : 1) was established. In the 1 : 1 complexes, the donor–acceptor bond is formed by the lone electron pair of the nitrogen atom and a vacant orbital of the metal. Hydrogen bonds strongly affect the structure and properties of the 2 : 1 and 6 : 1 complexes. Complexes of the composition $2Bu_2NH \cdot MX_3$ are present in solution as six-membered metallacycle with a four-coordinate metal atom, and the second amine molecule linked with the complex $Bu_2NH \cdot MX_3$ with N–H···N and N–H···X hydrogen bonds.
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Aluminum and gallium halides and organometallic compounds (MX_3) are widely used as catalysts of various chemical reactions (alkylation, hydrochlorination, etc.). However, it has been shown in [1–3] that in fact catalysts are not halides, but their molecular complexes with water. The formation of such complexes in benzene solutions has been proved by calorimetry, dielectrometry, and IR spectroscopy [1, 3, 4]. The structure and properties of these complexes in many respects are determined by the presence of intramolecular H-bonds. Apparently, complexes of aluminum and gallium halides with alcohols and primary and secondary amines as electron donors can also exhibit catalytic activity in the above-mentioned reactions. These compounds can form not only donor–acceptor bonds with halide metal atoms [via the lone electron pair of the donor heteroatom (D)], but also H bonds due to the hydrogen atom directly bound to the donor heteroatom.

The $D \cdot MX_3$ (1 : 1) complexes of aluminum and gallium halides with ethers and tertiary amines have been much studied [5], in particular, the enthalpies of complex formation and their dipole moments have been measured. Complexes of aluminum and gallium halides with water [1, 3, 4] and alcohols [6] have been systematically investigated. In these systems, in addition to 1 : 1 complexes, more complicated complexes exist: $D \cdot M_2X_6$ (1 : 2), $2D \cdot MX_3$ (2 : 1), and $6D \cdot MX_3$ (6 : 1), which is connected with the capacity of water and alcohols to form H bonds. Complexes of aluminum and gallium halides with primary and secondary amines have been much less studied.

The purpose of the present work was to continue the systematic study [7] of complexes of aluminum and gallium halides with dibutylamine (Bu_2NH). Special attention was given to the influence of H bonds bonds on the composition, structure, and properties of the complexes. Dipole moments and enthalpies of formation of Bu_2NH complexes with gallium tribromide have been determined. Furthermore, parameters of certain Bu_2NH complexes with aluminum bromide and gallium trichloride, which were studied in [7], were refined

In the Bu_2NH-MX systems (M = Al, Ga; X = Cl, Br), we performed calorimetric, dielectrometric, and cryoscopic titration in benzene. The curve of calorimetric titration a benzene solution of gallium tribromide with dibutylamine (direct titration) is given in Fig. 1 as an example. The curve of calorimetric titration of a Bu_2NH solution with gallium trichloride (back titration) is shown in Fig. 2. The curve of dielectrometric back titration of a Bu_2NH solution with gallium tribromide is presented in Fig. 3. Analogous curves were also obtained for the other systems.

The obtained titration curves point to a stepwise nature of the complex formation. The composition of the complexes is determined by the component ratio (m_2/m_1) in inflection points of the curves. The first section ($0 < m_2/m_1 < 1$) of the direct calorimetric titra-

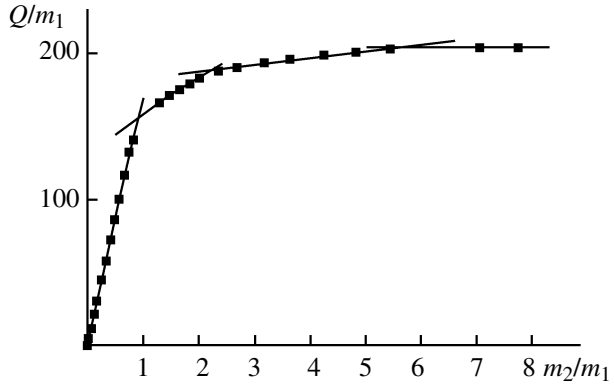


Fig. 1. Calorimetric titration curve of a benzene solution of $GaBr_3$ with dibutylamine. Q is the amount of evolved heat (kJ) and m_1 and m_2, numbers of moles of $GaBr_3$ and Bu_2NH in the solution, respectively.

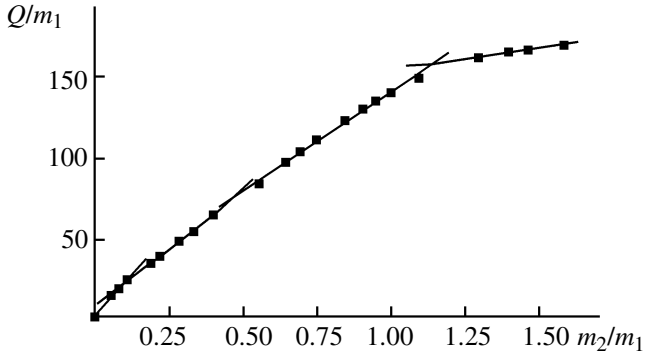


Fig. 2. Calorimetric titration curve of a benzene solution of Bu_2NH with gallium trichloride. Q is the amount of evolved heat (kJ) and m_1 and m_2, numbers of moles of Bu_2NH and $GaCl_3$ in the solution, respectively.

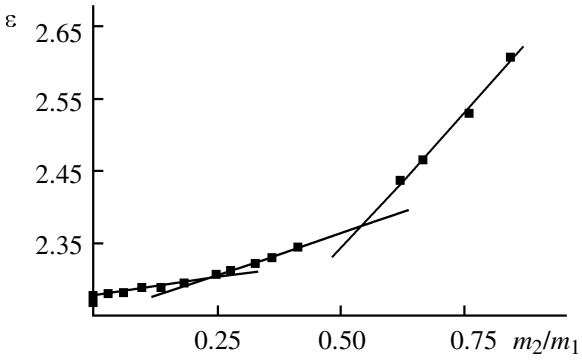


Fig. 3. Dielectrometric titration curve of a benzene solution of Bu_2NH with gallium tribromide. ε is permittivity and m_1 and m_2, numbers of moles of Bu_2NH and $GaBr_3$ in the solution, respectively.

tion curve (Fig. 1) corresponds to reaction (1) and the second ($1 < m_2/m_1 < 2$), to reaction (2). Note that aluminum and gallium halides are dimeric in benzene solutions [5].

$$Bu_2NH(sol.) + 1/2M_2X_6(sol.) = Bu_2NH \cdot MX_3(sol.) \qquad \Delta H_1, \qquad (1)$$

$$Bu_2NH(sol.) + Bu_2NH \cdot MX_3(sol.) = 2Bu_2NH \cdot MX_3(sol.) \qquad \Delta H_2. \qquad (2)$$

The heat of solution of Bu_2NH in benzene, measured in an independent experiment, is 0.8 kJ mol^{-1}, i.e. the solution in benzene occurs with heat absorption. As seen from Fig. 1, on the titration with dibutylamine heat absorption occurs only at $m_2/m_1 > 6$. This fact suggests that, along with $Bu_2NH \cdot MX_3$ (1 : 1) and $2Bu_2NH \cdot MX_3$ (2 : 1), complexes of more complicated composition, apparently, octahedral complexes $6Bu_2NH \cdot MX_3$ (6 : 1), are formed by reaction (3).

$$4Bu_2NH(sol.) + 2Bu_2NH \cdot MX_3(sol.) = 6Bu_2NH \cdot MX_3(sol.) \qquad \Delta H_3. \qquad (3)$$

The inflections in the calorimetric back titration curve (Fig. 2) point to the formation of 2 : 1 and 1 : 1 complexes in the solution. The appreciable heat evolution on addition of first portions of gallium trichloride and the inflection in the region of $m_2/m_1 \approx 0.15$–0.20 suggest the formation of a 6 : 1 complex with excess Bu_2NH.

Dielectrometric titration of a benzene solution of Bu_2NH with gallium tribromide (Fig. 3) proved possible only up $m_2/m_1 \approx 0.8$. Further addition of the bromide resulted in quenching of beatings. The inflections in the titration curve point to the formation of 6 : 1 and 2 : 1 complexes.

Previously [1, 3, 4] we detected 1 : 2 complexes ($H_2O \cdot M_2X_6$) on complex formation of water with aluminum and gallium halides (with excess halide). These complexes are of special interest as catalysts of olefin hydrochlorination reactions. To find out whether analogous $Bu_2NH \cdot M_2X_6$ complexes exist, we studied in detail the direct dielectrometric titration curve of a benzene solution of gallium trichloride with butylamine in the range $0 < m_2/m_1 < 1$. The presence of an ill-defined inflection in this part of the curve at $m_2/m_1 = 0.5$ points to the formation of the complex $Bu_2NH \cdot Ga_2Cl_6$.

In the reaction of aluminum tribromide with butyl alcohol, the complex $4BuOH \cdot AlBr_3$ (4 : 1) [6] can be formed, along with 1 : 1, 2 : 1, and 6 : 1 complexes. The

Table 1. Molar polarizations at infinite dilution (P_∞), molar refractions (R_D), dipole moments (μ_c), heat effects of reactions (ΔH), and enthalpies of formation (ΔH_c^0) of complexes of aluminum and gallium halides with dibutylamine (benzene, 298 K)

Complex	P_∞	R_D	μ_c, D	$-\Delta H$, kJ mol^{-1} (reaction)	$-H_c^0$, kJ mol^{-1}
$Bu_2NH \cdot AlBr_3$ [a]	1544.3	87.8	8.38	171 (1)	227
$2Bu_2NH \cdot AlBr_3$	727.9	130.5	5.35	54 (2)	281
$6Bu_2NH \cdot AlBr_3$	590.3	301.6	3.64	17 (3)	298
$Bu_2NH \cdot GaCl_3$ [a]	1324.3	80.9	7.75	153 (1)	197
$2Bu_2NH \cdot GaCl_3$	823.2	123.6	5.79	43 (2)	240
$Bu_2NH \cdot GaBr_3$	1410.3	89.5	7.98	154 (1)	193
$2Bu_2NH \cdot GaBr_3$	442.3	132.3	5.30	49 (2)	241
$6Bu_2NH \cdot GaBr_3$	632.7	303.3	3.90	12 (3)	253

[a] Data of [7].

possible formation of 4 : 1 complexes on the titration of solutions of aluminum and gallium halides with dibutylamine has been pointed out in [7]. However, we failed to obtain reliable evidence for the formation of such complexes in repeated studies of these systems.

Table 1 lists the molar polarizations at infinite dilution (P_∞), molar refractions (R_D), dipole moments (μ_c), heat effects of reactions (1)–(3) (ΔH), and enthalpies of complex formation (ΔH_c^0). The ΔH_c^0 values for reaction (4) were obtained from the heat effects of reactions (1)–(3) with account for the enthalpies of dissociation of MX_3 dimers (ΔH_{dim}^0, kJ mol^{-1}): 55.6 ($AlBr_3$), 43.9 ($GaCl_3$), and 38.9 ($GaBr_3$) [5]. In reaction (4), n (number of Bu_2NH molecules in a complex) is 1, 2, or 6. For example, the enthalpy of formation of the complex $2Bu_2NH \cdot AlBr_3$ (281 kJ mol^{-1}) was found as the sum of the heat effects of reactions (1) and (2) (171 + 54 = 225 kJ mol^{-1}) plus ΔH_{dim}^0 $AlBr_3$ (55.6 kJ mol^{-1}).

$$n\mathrm{Bu_2NH(sol.)} + \mathrm{MX_3(sol.)} = (n\mathrm{Bu_2NH}) \cdot \mathrm{MX_3(sol.)} \qquad \Delta H_c^0. \qquad (4)$$

The enthalpies of formation of 1 : 1 complexes of Bu_2NH with aluminum bromide, gallium trichloride, and gallium tribromide are 227, 197, and 193 kJ mol^{-1}, respectively (Table 1). The $-\Delta H_c^0$ for 1 : 1 complexes of trialkylamines with the above halides are 192, 180, and 145 kJ mol^{-1} [8, 9]. Therefore, Bu_2NH is a slightly stronger electron donor than trialkylamines in relation to aluminum and gallium halides. The effect of substituents on the electron–donor power of aliphatic amines is determined by inductive and steric effects. Substitution of hydrogen for an alkyl group should reduce the capacity of the amine nitrogen atom to donate the lone electron pair due to the inductive effect. Taft's inductive constants $\sigma\%$ are +0.490 for H and ~–0.15 for alkyl groups [10]. However, in terms of steric effects, Bu_2NH should be a much stronger electron donor than trialkylamines. The steric constants E_s^0 are +0.25 for H and ~–0.5 for normal alkyl groups [10]. Consequently, the slightly higher $-\Delta H_c^0$ values for complexes of aluminum and gallium halides with Bu_2NH, as compared to $-\Delta H_c^0$ for complexes with trialkylamines, are attributable to the prevailing steric effect.

The 1 : 1 complexes with Bu_2NH, like complexes with trialkylamines and trialkylphosphines, are donor–acceptor in nature. The donor–acceptor bond N→M involves the lone electron pair of the nitrogen atom and a vacant orbital of the metal. According to Mulliken's formalism, such complexes feature a linear correlation between the enthalpy of complex formation and the charge (Δq) transferred from the donor to acceptor [5]. Such correlation (correlation coefficient 0.942) was obtained in [9] for Group III halides and other compounds with various n donors [Eq. (5)].

$$-\Delta H_c^0 = 289.9(\pm 9.67)\Delta q - 6.49(\pm 4.98). \qquad (5)$$

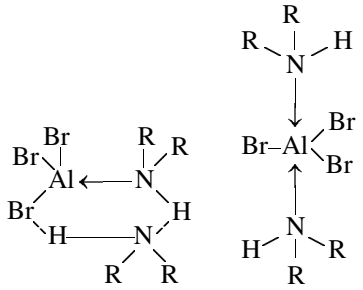
On the basis of the experimental dipole moments of the 1 : 1 complexes (Table 1), using the procedure described in [5, 9], we estimated the degree of charge transfer. For optimal we took an ethane-like geometry of the complexes [5, 11, 12]. The acceptor part of the complexes (MX_3) has a distorted tetrahedral configuration with the XMX angle accepted to be 115° [11]. The CNC and CNH angles of the central fragment Bu_2NH were taken to be 109.5° [12]. The dipole moments of the acceptor parts of the complexes were calculated as a vector sum of the dipole moments of three M–X bonds [5]: $\mu(AlBr_3)$ 1.41, $\mu(GaCl_3)$ 1.82, and $\mu(GaBr_3)$ 1.60 D. The dipole moment of the

donor part of the complexes was accepted to be equal to the dipole moment of Bu_2NH (1.1 D). The length of the donor–acceptor bond (r_{DA}) was accepted to be 1.96 Å for the aluminum tribromide complex and 2.01 Å for the complexes of gallium halides [5, 11]. The calculated dipole moments of the donor–acceptor bonds (μ_{DA}) were 5.87, 4.83, and 5.28 D, and the charge transfer according to Mulliken's formalism ($\Delta q = \mu_{DA}/er_{DA}$) was 0.62, 0.50, and 0.55 for the complexes of Bu_2NH with $AlBr_3$, $GaCl_3$, and $GaBr_3$, respectively. The enthalpies of formation of complexes $Bu_2NH \cdot MX_3$, calculated by Eq. (5) with calculated Δq values, were 176, 145, and 158 kJ mol^{-1}, which is much lower than the $-\Delta H_c^0$ values found by the calorimetric method (227, 197, and 193 kJ mol^{-1}, Table 1). The differences between the $-\Delta H_c^0$ values measured and calculated by Eq. (5) can hardly be related to inaccuracies of the calculation procedure. The most likely reason is that the experimental dipole moments of the complexes are slightly underestimated, which results in underestimation of the μ_{DA} and Δq values, calculated on their basis.

The dipole moments of complexes, measured in solution, are very often underestimated which is accounted for by the molecular association due to dipole–dipole interaction of the highly polar molecules of the complexes [5]. The molecular weights of complexes $Bu_2NH \cdot MX_3$ in benzene solutions, measured by cryoscopy, are strongly overestimated compared to those calculated for monomeric complexes. The differences between the calculated and measured molecular weights depend on experimental conditions and can reach 70–80% for metal halides. It is unlikely that such a strong association of complexes $Bu_2NH \cdot MX_3$ results exclusively from dipole–dipole interaction, and it can also be connected with intermolecular N–H···X hydrogen bonding.

We fulfilled quantum-chemical calculations of the model complexes $Me_2NH \cdot AlCl_3$ and $Me_2NH \cdot AlBr_3$ by the semiempirical PM3 method. The calculations showed that the charge transfer from the donor to acceptor along the N→Al bond decreases the electron density on the hydrogen atom of the amine N–H group, and, as s result, the proton-donor power of the amino group should increase. The charge transferred on the acceptor is not localized completely on the aluminum atom, and passes to halide X atoms to a large extent. The increase of the electron density on the X atoms enhances the capacity of their lone electron pair for H-bond formation. Thus, the association of complexes $Bu_2NH \cdot MX_3$ in benzene solutions, that decreases the μ_c values, seems to be largely connected to intermolecular hydrogen bonding between complexes.

The structure of complexes $2Bu_2NH \cdot MX_3$ is open to question. Two structures are possible (**A** and **B**).

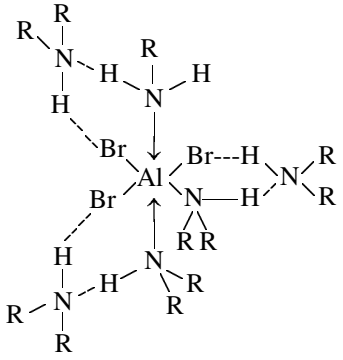


A **B**

In structure **A**, the second Bu_2NH molecule is linked to $Bu_2NH \cdot MX_3$ by the $N^1–H^1\cdots N^2$ and $N^2–H^2\cdots X$ hydrogen bonds to form a six-membered metal cycle with a four-coordinate metal atom. Structure **B** is a trigonal bipyramid with a five-coordinate metal atom and axial amino groups.

As shown in [13, 14], due to the compensation of the dipole moments of two donor–acceptor bonds the dipole moment of the complex $2(CH_3)_3N \cdot AlH_3$ is ~1.5 D, whereas the dipole moment of the complex $(CH_3)_3N \cdot AlH_3$ is 4.2 D. On this basis a conclusion was drawn that the complex $2(CH_3)_3N \cdot AlH_3$ has in solution a trigonal bipyramidal structure with axial arrangement of the two amine molecules. According to X-ray diffraction data, similar structures in crystal are characteristic of complexes with N→Al donor–acceptor bonds {$2(CH_3)_2NH \cdot AlCl_3$ [15] and $2OC_4H_8NH \cdot AlCl_3$ [16]} and complexes with O→Al bonds {$2C_4H_8O \cdot AlCl_3$ [17] and $[(1,4\text{-}C_4H_8O_2) \cdot AlCl_3]_n$ [18]}.

The calculated dipole moments of complexes $2(C_4H_9)_2NH \cdot MX_3$ reach 5.3–5.8 D (Table 1), providing strong evidence against structure **B**. High dipole moments (6–7 D) of complexes of aluminum and gallium halides with alcohols $2ROH \cdot MX_3$ were reported by Dzhulai et al. [6]. The referees used ^{27}Al NMR spectroscopy to show that the hybridization of the aluminum atom in $C_4H_9OH \cdot AlBr_3$ and $2C_4H_9OH \cdot$



C

$AlBr_3$ corresponds to tetrahedral coordination and that no five-coordinate aluminum atom is present [6]. It was also shown in [6] that the $6C_4H_9OH \cdot AlBr_3$ complexes have an octahedral structure, and H-bonds play an important role in their formation. It can be assumed that complexes $6(Bu_2NH) \cdot MX_3$, too, have an octahedral structure (structure **C**).

To assess the structure of complexes $2Bu_2NH \cdot MX_3$, we measured heat effects of reactions (6) between complexes $Bu_2NH \cdot MX_3$ (1 : 1) and *n* donors (D_2) in benzene.

$$Bu_2NH \cdot MX_3(sol.) + D_2(sol.) = (D_2)Bu_2NH \cdot MX_3(sol.) \qquad \Delta H_6. \qquad (6)$$

As D_2 we used compounds meeting the following conditions: (1) capacity for H-bond formation; (2) energetically unfavorable substitution of dibutylamine with D_2 in the complex; (3) various types of heteroatoms (O, N); and (4) substituents with various steric effects. With this in mind we chose the following *n* donors: dibutyl ether, alcohols (CH_3OH, C_2H_5OH, and *t*-C_4H_9OH), pyridine, and triethylamine. The heat effects of reactions (6) for the chosen *n*-donors and also of reactions (2) (D_2 = dibutylamine) are given in Table 2 together with the heats of solution of D_2 in benzene (ΔH_s).

The considered *n* donors can be divided into two groups. The members of the first group (dibutyl ether, pyridine, and triethylamine) can form H bonds only with the N–H groups of complexes $Bu_2NH \cdot MX_3$ via the lone electron pair of the nitrogen or oxygen atom. In addition to this, second group compounds (alcohols and Bu_2NH), having proton-donor OH and NH groups, can form H bonds with halide X atoms.

As seen from Table 2, the first and second groups of compounds have much different heats of formation of the $(D_2)Bu_2NH \cdot MX_3$ complexes. Moderate heat effects of 3–16 kJ mol^{-1} are characteristic for first group compounds. These values were calculated as differences between the heats of solution of D_2 in benzene and in benzene solutions of complexes $Bu_2NH \cdot MX_3$. The order of heat effects seems to be accounted for by the fact that the reactions of complexes $Bu_2NH \cdot MX_3$ with first group compounds involve formation of weak N^1–$H^1 \cdots N^2$ and N^1–$H^1 \cdots N^2$ hydrogen bonds. Note that the first group includes electron donors differing both by heteroatom (O and N) and by steric characteristics [C_5H_5N and $(C_2H_5)_3N$]. Nevertheless, the heat effects of reaction (6) are invariably very small.

The reactions of complexes $Bu_2NH \cdot MX_3$ with second group compounds are accompanied by appreciable heat evolution (50–120 kJ mol^{-1}), which is undoubtedly connected with additional coordination capacity of Bu_2NH and alcohols. The heats of formation of complexes $(D_2)Bu_2NH \cdot AlBr_3$ (D_2 = alcohols) are especially high, and the influence of the steric factor is clearly seen: The heat effects of reactions (6) increase in the series: *t*-C_4H_9OH < C_2H_5OH < CH_3OH (87, 102, and 122 kJ mol^{-1}, respectively; Table 2).

Table 2. Heat effects of reactions (2) and (6) (ΔH) and heats of solution (ΔH_d) of D_2 compounds in benzene (kJ mol^{-1})

Complex	D_2	$-\Delta H$ (reaction)	$-\Delta H_d$
$Bu_2NH \cdot AlBr_3$	$(C_4H_9)_2NH$	54 (2)	–3
$Bu_2NH \cdot AlBr_3$	C_5H_5N	16 (6)	1
$Bu_2NH \cdot AlBr_3$	$(C_2H_5)_3N$	4 (6)	–1
$Bu_2NH \cdot AlBr_3$	$(C_4H_9)_2O$	11 (6)	–3
$Bu_2NH \cdot AlBr_3$	CH_3OH	122 (6)	–15
$Bu_2NH \cdot AlBr_3$	C_2H_5OH	102 (6)	–15
$Bu_2NH \cdot AlBr_3$	*t*-C_4H_9OH	87 (6)	–15
$Bu_2NH \cdot GaCl_3$	$(C_4H_9)_2NH$	43 (2)	–3
$Bu_2NH \cdot GaCl_3$	C_5H_5N	3 (6)	1
$Bu_2NH \cdot GaBr_3$	$(C_4H_9)_2NH$	49 (2)	–3

The calorimetric and cryoscopic data suggest that addition of alcohols to a solution of $Bu_2NH \cdot AlBr_3$, unlike Bu_2NH, results in formation of only one complex $[(ROH)(C_4H_9)_2NH \cdot AlBr_3]$. Further addition of alcohol does not increase the coordination number of aluminum. The endothermic effect observed on addition of an alcohol to a solution of the $(ROH) \cdot (C_4H_9)_2NH \cdot AlBr_3$ complex is equal to the heat of solution of the alcohol in benzene (ΔH_d 15 kJ mol^{-1}).

Figure 4 shows the curves of cryoscopic titration of a benzene solution of the complex $Bu_2NH \cdot AlBr_3$ with dibutylamine (curve *1*) and *tert*-butyl alcohol (curve *2*). It is seen from Fig. 4 that the temperature depression Δt in the initial part of the curve of $Bu_2NH \cdot AlBr_3$ titration with dibutylamine remains invariable according to reaction (2). The shape of curve *1* points to noticeable dissociation of $2Bu_2NH \cdot AlBr_3$. On titration with *tert*-butyl alcohol (curve *2*), the freezing point depression in the region $0 < m_2/m_1 < 1$ sharply decreases, and at $m_2/m_1 = 1$ a well-defined inflection is observed. The molar mass of the added substance calculated for the last part of the curve ($m_2/m_1 > 1$) corresponds to the molar mass of *tert*-butyl alcohol. The molar mass of the complex calculated from the freezing point depression in the point $m_2/m_1 = 1$, M_{exp}, is 930, i.e. double the calculated molar mass of the complex $(C_4H_9OH)Bu_2NH \cdot AlBr_3$ (M_{calc} 470).

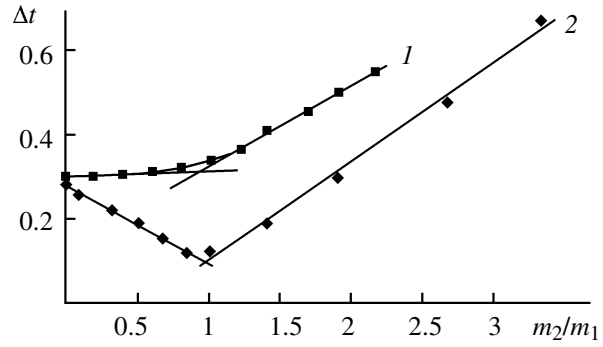
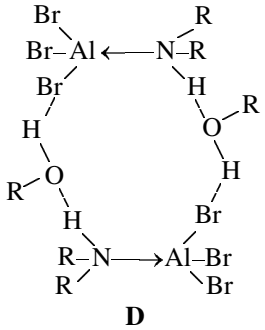


Fig. 4. Cryoscopic titration curves of a solution of the complex $Bu_2NH \cdot AlBr_3$ in benzene with (*1*) dibutylamine and (*2*) *tert*-butyl alcohol. Δt is the freezing point depression, m_1, number of moles of the complex, and m_2, number of moles of Bu_2NH or *tert*-butyl alcohol.

The calorimetric and cryoscopic data testify that the reactions of $Bu_2NH \cdot AlBr_3$ with alcohols give rise to strong, scarcely dissociating complexes $[(ROH)Bu_2NH \cdot AlBr_3]_2$. It can be assumed assume that two alcohol molecules are bridging and bind together two molecules of $Bu_2NH \cdot AlBr_3$ by N–H···O and O–H···Br hydrogen bonds (structure **D**).



D

Thus, H bonds largely determine the composition, properties, and structure of complexes of aluminum and gallium halides with Bu_2NH. We can state with assurance that complexes $2Bu_2NH \cdot MX_3$ in benzene solutions has the structure of a six-membered metal cycle with H bonds and a four-coordinate aluminum atom. At the same time, it is not improbable that in other conditions, for example in crystal, the 2 : 1 complexes can be present as a trigonal bipyramid with a five-coordinate aluminum atom (structure **B**), i.e. to pass from one form to the other does not require essential energy consumption.

EXPERIMENTAL

Complexes were studied by means of calorimetric, dielectrometric, and cryoscopic titration [5]. Small portions of one component were added to a benzene solution of the other component. In the case of direct titration, donor (Bu_2NH, alcohols, butyl ether, or pyridine) was added into the measuring cell charged with a solution of acceptor (MX_3) or a solution of complex $Bu_2NH \cdot MX_3$. In the case of back titration, acceptor was added into the measuring cell charged with a solution of Bu_2NH. The experiments were carried out with 0.03–0.05 M solutions of titrate.

The dipole moments of complexes were determined by dielectrometric titration, measuring the permittivity and density of solutions in the dielcometer cell [5] at 298 K. The values of P_∞ (molar polarization at infinite dilution, extrapolation by the Hedestrand's method), R_D (refraction calculated by the additive scheme), and dipole moment μ found by the equation $\mu = 0.22(P_\infty - R_D)^{1/2}$ are given in Table 1. The accuracy of the determination of dipole moments was 0.1 D.

The heat effects of reactions were determined by calorimetric titration [5], using a liquid calorimeter with a piesoelectric resonator as temperature sensor [19], that allows temperature variations to be measured accurate to $\pm 5 \times 10^{-4}$ K. The accuracy of the determination of heat effects of reactions and heats of solution was 1 kJ mol^{-1}.

Aluminum bromide of chemical grade was purified by vacuum sublimation. Gallium halides were synthesized by passing halogen vapor over a gallium melt [20] and purified by vacuum sublimation. The constants of the electron donors used were consistent with published data. All experiments were carried out under dry argon.

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