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Structure and properties of the aluminium and gallium halide complexes with water

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Abstract—The molecular complexes of aluminium and gallium halides (chlorides and bromides) with water in benzene solutions have been investigated by calorimetry, cryoscopy, dielectrometry and IR spectroscopy. The existence of complexes $H_2O \cdot MX_3$ (I), $H_2O \cdot M_2X_6$ (II) and $2H_2O \cdot MX_3$ (III) has been established. Complexes (I) are formed by the donor–acceptor bond between a lone electron pair of the oxygen atom and a vacant orbital of a metal atom. The six-membered ring are formed by the hydrogen bonds O—H···X in complexes (II) and O—H···O, O—H···X in complexes (III). The experimental values of the dipole moments and the formation enthalpies of the water complexes compare fairly well with the corresponding parameters of the alcohol's complexes and the aliphatic ether complexes. Semi-empirical quantum chemical calculations were carried out for these systems by the PM3 method. © 1997 Elsevier Science Ltd

Keywords: Lewis acids; water; complexes; calorimetry; dielectrometry; quantum chemical calculations.

Halides and organometallic compounds of aluminum and other metals, which constitute acids of the Lewis type, are widely used as catalysts for various reactions in chemistry. However their catalytic properties are realized in the presence of co-catalysts only. Thus the isomerization of cyclohexane (catalyst $AlCl_3$ [1]), the polymerization of ethylene ($AlCl_3$ [1]), styrene ($SnCl_4$ [2]) and 3,3′-bis-(chloromethyl)oxetane (Al(iso-$C_4H_9)_3$ [3,4]), the alkylation of benzene ($AlCl_3$ [5]) are realized in the presence of water only. It is necessary to have more detailed information about interaction in the water–Lewis acid system, in particular, about the possibility of the molecular complex formation, in order to establish the nature of the promoting influence of water. At this time there is no information because studies of complex formation in these systems are hampered by the ease of hydrolysis of the III and IV group metal halides. Nevertheless in this work, using original methods we have studied successfully the interaction of aluminium and gallium halides with water by calorimetry dielectrometry, cryoscopy and IR spectroscopy. Also semi-empirical quantum chemical calculations were carried out for the systems studied.

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EXPERIMENTAL

Dipole moments of the complexes were determined by the dielectrometric titration. This method involves the measurement of the dielectric constant (ε) and density of solutions in the cell of the heterodyne-beat apparatus on addition of small portions of one component to the solution of the other one [6]. The electric conductivity of the studied solutions should be less than 10^{-7}–10^{-8} (ohm cm)$^{-1}$. This precludes measurements of solutions containing free ions.

The heats of complex formation were obtained by the calorimetric titration A calorimeter with a piezo-quartz resonator as a temperature data-unit was used (accuracy of determination is ± 2 kJ/mol) [7]. IR spectra were measured in the 2000–4000 cm^{-1} range with a UR-20 spectrometer. All the experiments were carried out under dry argon at 25°C. Quantum chemical calculations of the aluminium halides complexes with water were carried out by the SCF MO LCAO method using the PM3 approximation program MOPAC 6.0.

We have shown that an addition of even small portions of water into benzene or cyclohexane solutions of aluminium bromide (concentration 0.03–0.05 mol/l calculated in regard to $AlBr_3$) is followed by hydrolysis of bromide. Injection of water as a complex with another acceptor, successfully used to delay ethylaluminium dichloride hydrolysis [8], was shown to be not effective in this case. However, it was found that hydrolysis does not take place on addition of water in a wet benzene or cyclohexane state into $AlBr_3$ solution. The aluminium and gallium halide complexes with water are slightly soluble in cyclohexane, and the solubility of water in benzene is considerably more than it is in cyclohexane (0.06% at 22.5°C for benzene and 0.015% at 28.5°C for cyclohexane [9]). Therefore, benzene was used as a solvent for all types of measurements.

In case of the direct calorimetric and dielectrometric titrations, a benzene solution of water (0.02 mol/l, 0.05%) was added into the measuring cell containing the benzene solution of the halide using a thermostated feeder.

In the case of the $GaCl_3$–H_2O–C_6H_6 and $GaBr_3$–H_2O–C_6H_6 systems, a small portion of water was added into the measuring unit (direct titration), because gallium halides do not hydrolyze in benzene solution. In the case of the reverse titration small portions of gallium halides were added into benzene solution of water. This method also allows the determination of the content of water in the solvents which are not n-donors towards gallium halides (cyclohexane, benzene etc.).

In the case of the IR spectroscopy titration the heavy water was used because of the O—D stretching vibrations are resolved better than O—H ones.

RESULTS AND DISCUSSION

Figure 1 shows the calorimetric titration by water of aluminium bromide solution in benzene which shows a distinct bend of the curve at the equimolar ratio of the components ($m_2/m_1 = 1.0$). Thus, the curve is approximated by two straight-line segments (both correlation factors are 0.998). This fact comes as evidence of the formation of the non-dissociated 1 : 1 complex (reaction 1).

$$1/2M_2X_6(sol)+H_2O(sol) = H_2O \cdot MX_3(sol)\ldots\Delta H_1 \quad (1)$$

Similar curves of calorimetric titration were obtained for water complexes with gallium halides.

It should be noted that aluminium and gallium halides in benzene solution exist as dimers [6], and water in aliphatic and aromatic hydrocarbon solutions is a monomer [10]. The thermal effects of reaction (1) of aluminium and gallium halide complexes with aliphatic ethers, amines, and other n-donors may be as large as 70–150 kJ/mol. These complexes do not dissociate in benzene solutions [6].

Addition of the second water molecule to the $H_2O \cdot AlBr_3$ complex (region $m_2/m_1 > 1.0$) is followed by a considerable thermal effect (reaction 2).

$$H_2O \cdot MX_3(sol)+H_2O(sol) = 2H_2O \cdot MX_3(sol)\ldots\Delta H_2 \quad (2)$$

Figure 2 shows a curve of the dielectrometric titration by water of gallium chloride solution in benzene. There exists a distinct bend of the curve at the equimolar ratio of the components ($m_1/m_2 = 1.0$) similar to the one of the calorimetric titration curves. This fact also points to the 1 : 1 complex formation. Moreover, it is assumed that there exists a weakly pronounced bend of the curve at the $m_2/m_1 = 0.5$ ratio. In other words the curve (Fig. 2) can be approximated by three straight-line segments. The correlation factors are equal to 0.999 ($m_2/m_1 < 0.5$), 0.999 ($0.5 < m_2/m_1 < 1.0$), and 0.994 ($m_2/m_1 > 1.0$), respectively.

Since the calorimetry data give strong evidence that

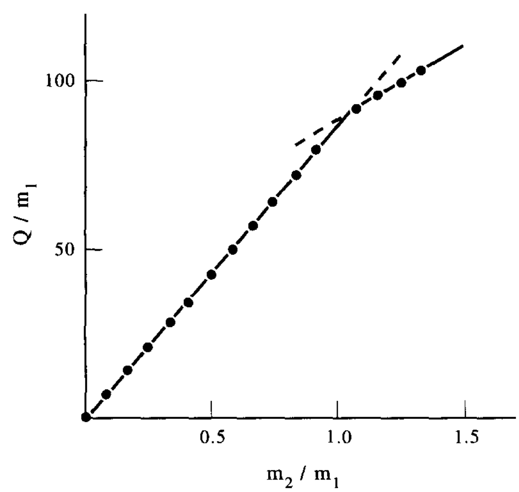


Fig. 1. Curve of calorimetric titration by water of aluminium bromide solution in benzene. Q—the quantity of heat liberated (kJ/mol); m_1 and m_2—the mole numbers of $AlBr_3$ and H_2O, respectively (direct titration).

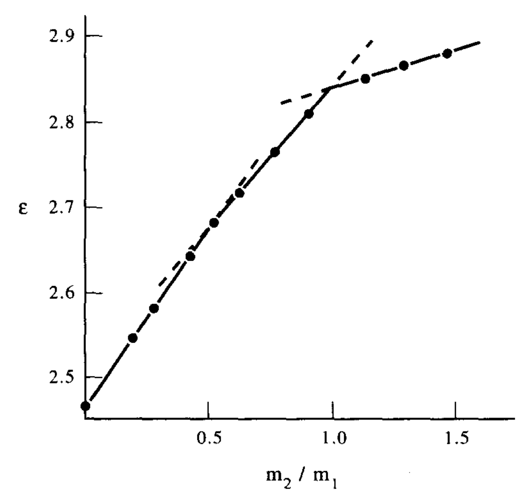


Fig. 2. Curve of dielectrometric titration by water of gallium chloride solution in benzene. Δε—the increase of dielectric constant; m_1 and m_2—the mole numbers of $GaCl_3$ and H_2O, respectively (direct titration).

1 : 1 complexes do not dissociate in benzene solutions, the appearance of the second bend at $m_2/m_1 = 0.5$ ratio may be attributed to: (1) the dipole–dipole association of 1 : 1 complex; (2) the formation of the $H_2O \cdot Ga_2Cl_6$ (1 : 2) complex at the components ratio $m_2/m_1 < 0.5$. The dipole–dipole association really takes place in the studied systems because of molecular masses of the $H_2O \cdot GaX_3$ complexes in benzene solutions are equal to 239 and 445 (X = Cl and Br, respectively) according to the cryoscopy data. These values are larger than the calculated ones (194 and 327 for X = Cl and Br, respectively). However, the fact that the $0.5 < m_2/m_1 < 1.0$ region of the dielectrometric titration curve (Fig. 2) is approximated by a straight-line segments contradicts this interpretation. Therefore we believe that the bend at the ratio $m_2/m_1 = 0.5$ should be connected with formation of a $H_2O \cdot Ga_2Cl_6$ (1 : 2) complex at the ratios of the components $0 < m_2/m_1 < 0.5$. The IR-spectroscopy data and the quantum chemical calculations results also provide evidence for the formation of the 1 : 2 complexes (see below).

The formation of 2 : 1, 1 : 1 and 1 : 2 complexes in the systems studied is supported by the reverse titration data. Figure 3 shows a curve of the dieletrometric titration by gallium bromide of water solution in benzene. There exist three bends on the curve at the ratios $m_2/m_1 = 0.5$, 1.0, and 2.0. Thus, the curve is approximated by four straight-line segments (all correlation factors are equal to 0.999). This provides evidence for the formation of a $2H_2O \cdot GaBr_3$ (2 : 1) complex at the ratios of the components $0 < m_2/m_1 < 0.5$, $H_2O \cdot GaBr_3$ (1 : 1) at $0.5 < m_2/m_1 < 1.0$, and $H_2O \cdot Ga_2Br_6$ (1 : 2) at $1.0 < m_2/m_1 < 2.0$, respectively. The dipole moment of Ga_2Br_6 in benzene solution ($\cong 1$ D) was calculated from the slope of the last region ($m_2/m_1 > 2.0$).

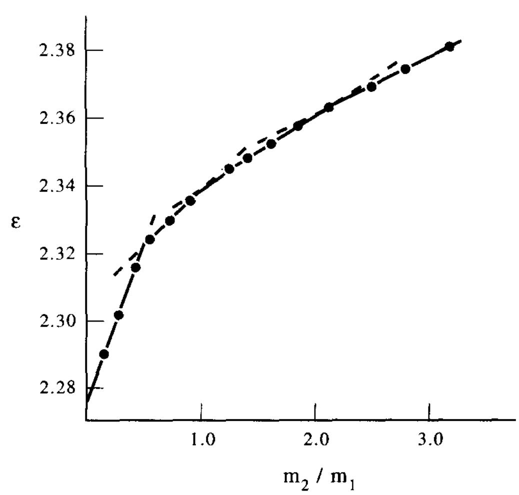


Fig. 3. Curve of dielectrometric titration by gallium bromide of water solution in benzene. Δε—the increase of dielectric constant; m_1 and m_2—the moles number of H_2O and $GaBr_3$, respectively (reverse titration).

Formation enthalpies of molecular complexes in nonpolar solvents are close to formation enthalpies in the gas phase and to energies of donor–acceptor bonds [6,11,12]. The formation enthalpies of complexes $H_2O \cdot MX_3$ (ΔH_3, reaction 3) can be calculated from $-\Delta H_1$ with correction made for the dimerization energies of halides ($-\Delta H_{dim} = 55.6$, 43.9 and 38.9 kJ/mol for $AlBr_3$, $GaCl_3$ and $GaBr_3$, respectively [6].

$$H_2O(sol) + MX_3(sol) = H_2O \cdot MX_3(sol) \ldots \Delta H_3 \quad (3)$$

As aluminium chloride is insoluble in benzene, the thermal effect of the reaction (4) (substitution of diphenylsulfide by water in complex $Ph_2S \cdot AlCl_3$) was measured in order to determine the value ΔH_3 of complex $H_2O \cdot AlCl_3$.

$$Ph_2S \cdot AlCl_3(sol) + H_2O(sol) = H_2O \cdot AlCl_3(sol) + Ph_2S(sol) \ldots \Delta H_4 \quad (4)$$

Complex $Ph_2S \cdot AlCl_3$ was chosen, in the first place, for its comparatively low formation enthalpy ($-\Delta H_3 = 81.2$ kJ/mol [13]) which results in the considerable value of the heat evolution ($-\Delta H_4 = 53.1$ kJ/mol) for the reaction (4). Secondly, diphenylsulfide isolated by reaction (4) does not form any hydrogen bonds with the complex $H_2O \cdot AlCl_3$. Thus, by summing $-\Delta H_4$ and the formation enthalpy of complex $Ph_2S \cdot AlCl_3$, we have obtained the formation enthalpy ($-\Delta H_3$) of $H_2O \cdot AlCl_3$ to be equal to 134.3 kJ/mol.

All experimental and calculated results are summarized in Table 1. It illustrates the experimentally determined thermal effects of reactions (1), (2), (4) ($-\Delta H$) and the calculated formation enthalpies of the complexes ($-\Delta H_3$). Other experimental data: molar polarizations at infinite dilution obtained by Hedestrand's extrapolation (P_∞), molar refractions calculated in accordance with the additive scheme (R_D), dipole moments of complexes calculated according to the formula $\mu_c = (P_\infty - 1.05\ R_D)^{1/2}$ are also presented in the Table 1.

The formation enthalpies and dipole moments of water complexes with aluminium and gallium halides and those for some alcohol and ether complexes taken from the literature are given in the Table 2.

The formation enthalpies and dipole moments of the 1 : 1 aluminium and gallium halide complexes with water are similar to those for the molecular complexes with alcohols and ethers. This strongly suggests that the 1 : 1 water complexes have the same molecular nature as the complexes with alcohols and ethers. The donor–acceptor bonds are formed due to a lone electron pair of the oxygen atom and a vacant orbital of the metal atom.

The results of semi-empirical quantum chemical calculations for $H_2O \cdot AlX_3$ complexes (Fig. 4, structure I) correlate rather well with the obtained experimental data. Thus, for $H_2O \cdot AlX_3$ complex the calculated values of formation enthalpies are equal to 129 and

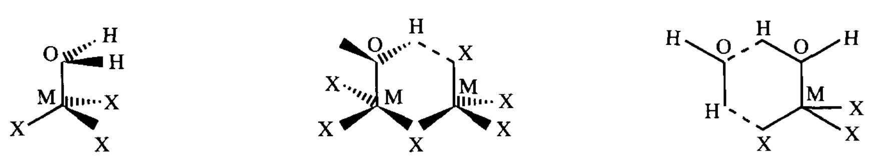
Table 1. Molar polarizations (P_∞, cm^3), molar refractions (R_D, cm^3), dipole moments (μ_c, D), thermal effects of reactions ($-\Delta H_3$, kJ/mol) and formation enthalpies ($-\Delta H_3$, kJ/mol) of the aluminium and gallium halide complexes with water

					Thermal effect of reaction		Formation enthalpy of complex	
Complex	Titration	P_∞	R_D	μ_c	$-\Delta H$	Reaction equation	$-\Delta H_3$	Reaction equation
$H_2O \cdot AlCl_3$	direct				53.1	(4)	134.3	(3)
$H_2O \cdot AlBr_3$	direct	996.9	48.7	6.77	93.3	(1)	149.0	(3)
$2H_2O \cdot AlBr_3$	direct				47.7	(2)		
$H_2O \cdot GaCl_3$	direct	777.4	41.8	5.96	66.9	(1)	110.9	(3)
	reverse	733.0	41.8	5.78	66.1	(1)	110.0	(3)
$2H_2O \cdot GaCl_3$	direct	850.6	45.5	6.23	21.3	(2)		
	reverse	917.8	45.5	6.50	25.5	(2)		
$H_2O \cdot Ga_2Cl_6$	direct	1049.1	77.9	6.84				
	reverse	1089.7	77.9	6.99				
$H_2O \cdot GaBr_3$	reverse	650.1	52.2	5.38	72.4	(1)	111.3	(3)
$2H_2O \cdot GaBr_3$	reverse	866.7	56.1	6.26	28.5	(2)		
$H_2O \cdot Ga_2Br_6$	reverse	846.2	100.5	6.01				

Table 2. Formation enthalpies ($-\Delta H_3$, kJ/mol) and dipole moments (μ_c, D) of the water, alcohols and ethers complexes with aluminium and gallium halides

Complex	$-\Delta H_3$	References	μ_c	References
$H_2O \cdot AlCl_3$	134.3	this work		
$R_2O \cdot AlCl_3$	141.4[a]	13		
$H_2O \cdot AlBr_3$	149.0	this work	6.77	this work
$C_2H_5OH \cdot AlBr_3$	156.9	14	6.1	16
$C_9H_{19}OH \cdot AlBr_3$	160.7	14		
$R_2O \cdot AlBr_3$	153.1[a]	6	7.2[a]	6
$H_2O \cdot GaCl_3$	110.9	this work	5.96	this work
$ROH \cdot GaCl_3$	118.0[a]	16	6.5[a]	16
$R_2O \cdot GaCl_3$	113.0[a]	6	6.5[a]	6
$H_2O \cdot GaBr_3$	111.3	this work	6.26	this work
$ROH \cdot GaBr_3$	105.3[a]	16	6.2[a]	16
$(C_4H_9)_2O \cdot GaBr_3$	110.0	15	6.7	15

[a] Average value



I II III

Fig. 4. The schematic structures of the aluminum and gallium halogenides complexes with water 1 : 1 (I), 1 : 2 (II), 2 : 1 (III) (M = Al, Ga ; X = Cl, Br).

180 kJ/mol (X = Cl and Br, respectively), and calculated dipole moment of $H_2O \cdot AlBr_3$ complex is equal to 6.39 D. The corresponding experimental values (134.3 kJ/mol, 149.0 kJ/mol and 6.77 D) are given in the Table 1. The O—Al interatomic distances in $H_2O \cdot AlX_3$ complex were calculated to be equal 1.884 and 1.845 Å (X = Cl and Br, respectively). These values are less than the sum of Pauling's coval-

ent radii of oxygen and aluminium atoms (1.92 Å). There is no information about the O—Al bond length in these water complexes in the literature, but our data were compared with the X-ray diffraction analysis data for the O—Al coordination bonds in the similar aluminium-containing compounds (1.736 Å for $(C_6H_5)_3PO \cdot AlCl_3$ [17], 1.819 Å for $C_6H_5COCl \cdot AlCl_3$ [18], 1.901 Å for $(C_2H_5)_2O \cdot Al(CH_2C_6H_5)_3$ [19]).

For 1 : 1 complexes the geometry optimization indicated that the eclipsed configuration (Fig. 4, structure I) are more preferable than the staggered one. A certain decrease of the electron density on hydrogen atoms of water by complexation was indicated: from +0.179 e for the free H_2O molecule to +0.252 e and +0.258 e for the $H_2O \cdot AlCl_3$ and $H_2O \cdot AlBr_3$ complexes, respectively.

Complexes 1 : 1 that are more traditional for such type of compounds have been examined above. However, the possibility of complex formation with another stoichiometry besides 1 : 1 in the studied systems is of principal importance. First of all it is corresponded to $H_2O \cdot M_2X_6$ complexes (1 : 2) which are supposed [4] to be active in catalysis. The illegible bend of the curve of Fig. 2 at the ratio $m_2/m_1 = 0.5$ and of the curve of Fig. 3 at the ratio $m_2/m_1 = 2.0$ can be considered as the evidence of $H_2O \cdot M_2X_6$ complex formation. On the other hand the results of quantum chemical calculations indicate the possibility of the 1 : 2 complexes existence too. The six-membered ring in the chair-conformation (Fig. 4, structure II) with the intramolecular hydrogen bond O—H···X characterized by the parameters typical for the strong H-bonds (interatomic distances O···X 2.716 Å, H···X 1.696 Å, O—H 1.025 Å; angle OHX 172.8°C for X = Cl; and the same for X = Br: 3.358 Å, 2.551 Å, 0.969 Å, 140.8°) is the stable form for AlX_3 complexes.

According to the IR spectroscopy data obtained by us, there are three types of $GaBr_3$ complexes with D_2O in benzene solution (Fig. 5). The contour of the band in the range of stretching vibrations ν_{OD} 2500 cm^{-1} substantially depends on the ratio m_2/m_1, the moles

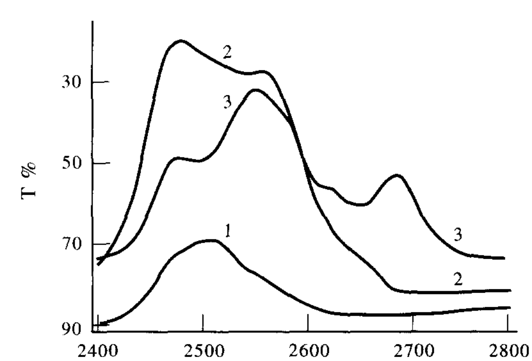


Fig. 5. IR spectra of D_2O complexes with gallium bromide in benzene solution at different ratios m_2/m_1, m_1 and m_2—the moles number of $GaBr_3$ and D_2O, respectively. m_2/m_1: 1–0.5, 2–1.0, 3–2.0.

number of D_2O (m_2) and ones of $GaBr_3$ (m_1) in solution. The only evident band at the low D_2O concentration ($m_2/m_1 < 0.3$–0.5) is at 2515 cm^{-1}. Intense bands at 2480 and 2560 cm^{-1} appear being dominant at the ratio $m_2/m_1 = 1.0$, when the 1 : 1 complexes only exist in the solution according to the data given in Fig. 1. According to data described above, the 2515 cm^{-1} band observed at the low water content can be attributed to the $D_2O \cdot Ga_2Br_6$ (1 : 2) complex. The existence of a whole series of bands: 2480, 2560, 2630 (sh) and 2690 cm^{-1} in spectra of solutions containing D_2O and $GaBr_3$ in the ratio $m_2/m_1 = 2.0$ can be attributed to joining the second D_2O molecule to the $D_2O \cdot GaBr_3$ and to the formation of a $2D_2O \cdot GaBr_3$ (2 : 1) complex (Fig. 4, structure III). Thus the IR spectra point to the existence of the 1 : 2, 1 : 1 and 2 : 1 gallium bromide complexes with D_2O in benzene solutions.

As stated above for 1 : 1 complexes the electron density on the hydrogen atoms of the water molecule decreases on the formation of the O—Al donor–acceptor bond. The proton donor ability of hydroxyl group increases in this case, so as it takes place in the aluminium and gallium halides complexes with alcohols [16].

The addition of the second water molecule to the $H_2O \cdot MX_3$ complex is followed by a considerable thermal effect, noticeably more for aluminium bromide than for gallium halides (compare the $-\Delta H_2$ values, Table 1). This difference can be caused by the more high proton donor ability of $H_2O \cdot AlBr_3$ complex in comparison with the analogous complexes of gallium halides owing to the higher extent of the charge transfer from H_2O molecule to $AlBr_3$.

The supposed structure for complexes 2 : 1 is shown by structure III (Fig. 4). However it is known that a number of aluminium complexes with such composition, for instance $2(CH_3)_3N \cdot AlH_3$ [20], $2C_4H_8O \cdot AlCl_3$ [21] etc., have the form of a trigonal bipyramid with axial arrangement of two electron donor molecules. These complexes are characterized by small values of μ_c owing to compensation of dipole moments for two donor–acceptor bonds. Thus, $2(CH_3)_3N \cdot AlH_3$ (2 : 1) complex has μ_c only about 1 D, while the μ_c value of $(CH_3)_3N \cdot AlH_3$ (1 : 1) one is up to 4 D [20]. But our values of dipole moments (Table 1) for $2H_2O \cdot GaCl_3$ and $2H_2O \cdot GaBr_3$ complexes (6.23 D and 6.26 D, respectively) not only are considerably high but even exceed the dipole moments of corresponding 1 : 1 complexes (5.96 and 5.38 D, respectively). This is the forcible argument against the realization of the symmetric structure with axial arrangement of two H_2O molecules in $2H_2O \cdot GaX_3$ complexes. The six-membered ring with H-bonds and four-coordinated aluminium and gallium atoms appears to be formed in the case of the 2 : 1 aluminium and gallium halides complexes with water (Fig. 4, structure III). The absence of five-coordinated aluminium atom in 2 : 1 aluminum halides complexes with alcohols has been proved by [27] Al NMR [16].

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