ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2016, Vol. 42, No. 1, pp. 19–26. © Pleiades Publishing, Ltd., 2016.
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Gallium Isopropoxide: Synthesis, Properties, “Coordination Polymerism”. New Pentanuclear Gallium Oxoisopropoxochloride

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Received March 10, 2015

Abstract—Conditions for the synthesis of gallium isopropoxide (**I**) by anodic dissolution of the metal in *i*-PrOH (in the presence of Bu_4NBr supporting electrolyte) and by exchange reaction of $GaCl_3$ with *i*-PrONa were studied. In the latter case, the crude product was a waxy substance (**II**) infinitely soluble in the alcohol and hydrocarbons and containing 12–30% Cl, which cannot be removed by adding an excess of *i*-PrONa due to the formation of insoluble $NaGa(OPr\text{-}i)_4$. During 1.5–2 months, **II** is solidified to give non-melting non-volatile amorphous product (**III**) poorly soluble in the alcohol. Upon heat treatment of **II** in vacuum, compound **I** is distilled off as an oily liquid consisting, according to mass spectrometry, of $[Ga(OPr\text{-}i)_3]_2$ dimer molecules. It can be retained for a long period of time in the presence of the $[Ga(OPr\text{-}i)_3]_4$ tetramer crystals. The existence of oligomeric molecules of different size up to polymers (“coordination polymerism”) in the materials is related to the possibility of tetrahedral or octahedral coordination of the metal atom. From concentrated solutions of components, the oxoalkoxochloride $[Ga_5(\mu_5\text{-}O)(\mu\text{-}OPr\text{-}i)_8Cl_5]$ (**IV**) is crystallized. Its molecule is a flattened tetragonal pyramid. The equatorial plane formed by four gallium atoms has the μ_5-O group at the center. The axial Ga atom has an octahedral coordination. All eight sides of the pyramid are drawn together by the μ-OPr-*i* groups, and the chlorine atoms occupy the terminal positions. (CIF file CCDC no. 693282.)

DOI: 10.1134/S1070328416010061

INTRODUCTION

Gallium isopropoxide is of interest in relation to the possible use in the sol–gel process, which is due to its high solubility in organic solvents, and as a CVD precursor owing to the volatility [1, 2].

The first studies of gallium alkoxides date back to the mid-1960s, when $Ga(OR)_3$ (R = Et, *i*-Pr) were prepared by exchange reactions between $GaCl_3$ and NaOR [3–8]. Other known synthetic routes to $Ga(OR)_3$ are the tranesterification of $Ga(OEt)_3$ with isopropyl alcohol [5, 6, 8] and alcoholysis of $[Ga(NMe_2)_3]_2$ [1, 9] or $Ga[N(SiMe_3)_2]_3$ [10]. The structure of the tetrameric gallium isopropoxide molecule with the central octahedrally coordinated and three peripheral tetrahedrally coordinated metal atoms, $Ga[(\mu\text{-}OPr\text{-}i)_2Ga(OPr\text{-}i)_2]_3$, was proposed based on ^1H NMR spectra [11] and later confirmed by X-ray diffraction of the $[Ga(OPr\text{-}i)_3]_4$ crystals grown in dichloromethane [1]. The dimer $\rightleftarrows$ tetramer equilibrium of $Ga(OPr\text{-}i)_3$ in hydrocarbons was studied by ^1H NMR spectroscopy [11] and thermodynamic parameters of the process were determined [1].

In the description of the syntheses of $Ga(OPr\text{-}i)_3$, no synthetic details or the yields of the intermediate and target product were indicated, most often, and the question of available methods for the synthesis of this compound remained open. This communication proposes the first direct electrochemical synthesis: anodic dissolution of the metal in anhydrous isopropyl alcohol in the presence of electrically conducting $[Bu_4N]Br$ additive. The conditions of synthesis of gallium isopropoxide by exchange reaction of gallium chloride with sodium isopropoxide were studied. The intermediate and side reaction products were isolated and characterized, and the structure of the new oxoalkoxochloride was determined. The formation and interconversion conditions of various $Ga(OPr\text{-}i)_3$ species were elucidated.

EXPERIMENTAL

All operations related to the synthesis, analysis, and study of the properties of alkoxides were performed in a dry box in an N_2 or Ar atmosphere. Anhydrous organic solvents were used: *i*-PrOH was dehydrated by refluxing with $Al(OPr\text{-}i)_3$, while toluene and diethyl ether were kept over P_2O_5 for several days and then refluxed with sodium metal. $GaCl_3$ was prepared by direct chlorination of the metal followed by vacuum distillation, and commercials chemicals (Merck) were used. For some operations, commercial Ga(OPr-*i*)$_3$ (Aldrich) was used.

Analysis for Ga was performed by complexometric titration with a $Pb(NO_3)_2$ solution with the Xylenol orange indicator at pH 5, while chlorine was quantified by argentometric titration against K_2CrO_4 at pH 7. The IR spectra of mineral oil and hexachlorobutadiene mulls were measured on a PE 1600 FTIR or PE Spectrum One Fourier Transform spectrometer. The X-ray diffraction patterns for powders pressed between X-ray amorphous films were obtained on an Image Plate Guinier Camera G670, and mass spectra were run on JEOL JMS-SX/SX-102ADSQ-2 or Trace JC Ultra DSQ 2 instrument with direct injection with dynamic heating from 20 to 300°C at a rate of 10°C/min (calculation for the ^{69}Ga isotope).

Electrochemical synthesis of Ga(OPr-*i*)$_3$ (I). The synthesis was performed by a standard procedure [2] at a constant current in an undivided cell equipped with a reflux condenser and a shell for external cooling. A 10 cm^2 platinum plate served as the cathode and a ~6 cm^3 cylindrical piece of gallium (99.999% of the major component) was the anode. The electrolyte contained $[Bu_4N]Br$ in a concentration of 1.2%. The applied voltage was 60 V and the current was ~150 mA. The synthesis was continued for 15–30 h. No metal refining took place. The residue after vacuum evaporation of the solvent was distilled at 75–80°C/10^{-2} mm Hg. This was a yellowish oily liquid, Ga(OPr-*i*)$_3$, in which separate well-formed crystals of **I** were present.

For $C_9H_{21}O_3Ga$

anal. calcd., %:	C, 43.72;	H, 8.50;	Ga, 28.34.
Found, %:	C, 43.81;	H, 8.34;	Ga, 28.54.

IR (ν, cm^{-1}): 1165 vs, 1115 vs, 995 s, 941 s, 834 w, 827 s, 692 m, 641 m, 601 s, 490 m, 462 w, 415 w (which coincides with published data [1]).

The mass spectra of **I** (crystals and liquid) differed by the presence of peaks corresponding, most probably, to tetramer molecules (in the case of crystals). The spectrum of the liquid (marked by italic) corresponds to dimers.

Mass spectrum of **I** (*m*/*z* (%)): 925 (2), 866 (2), 679 (5), 621 (1), 577 (0.3), [477 (2), 433 (35), 418 (1), 374 (64), 331 (10), 316 (9), 303 (11), 288(19), 275 (10), 272 (8), 257 (20), 244 (17), 229 (17), 214 (24), 200(9), 170 (5)] (Fig. 1).

The reaction of $GaCl_3$ with NaOPr-*i* in 1 : 3 ratio. The standard procedure for the synthesis was as follows. $GaCl_3$ was introduced into the reaction in the solid state or as toluene or diethyl ether solution. Sodium metal was dissolved in a mixture of *i*-PrOH and PhMe (~1 : 1). The reactants were added at vigorous stirring, using different order of addition and different temperatures. In all cases, the reaction mixture was appreciably warmed up and a white solid precipitated. Then the mixture was refluxed for 2–3 h, the solution was centrifuged, decanted from the precipitate, and distilled in vacuum. Below some examples are given.

(1) A solution of $GaCl_3$ (0.80 g, 4.5 mmol) in 15 mL of toluene (6%) was added at 0°C to sodium metal (0.31 g, 13.5 mmol) dissolved in 17 mL of *i*-PrOH (8% of NaOPr-*i*).

A precipitate containing NaCl and NaGa(OPr-*i*)$_4$ was formed from the solution.[1]

(2) A solution of Na (2.94 g, 128 mmol) in 100 mL of *i*-PrOH and 25 mL of toluene (11% of NaOPr-*i*) was added to a solution of $GaCl_3$ (7.52 g, 42 mmol) in 30 mL of toluene (22%). Upon storage of the solution for 2 weeks, prismatic crystals of Ga_5O(OPr-*i*)$_8Cl_5$ (**IV**) were formed. Yield 4.26 g (50%). m.p. (dec.) = 165–170°C.

For $C_{24}H_{56}O_9Cl_5Ga_5$

anal. calcd., %:	C, 28.36;	H, 5.51;	Cl, 17.48;	Ga, 34.46.
Found, %:	C, 27.80;	H, 5.25;	Cl, 17.52;	Ga, 33.25.

IR (ν, cm^{-1}): 1279 w, 1265 w, 1159 s, 1121 s, 1101 vs, 1039 m, 959 br.s, 917 s, 817 s, 628 sh.m, 580 m, 355 vs.

MS (*m*/*z* (%)): 973 (30), 949 (25), 942 (27), 910 (20), 847 (10), 786 (8), 777 (10), 727 (8), 643 (40), 629 (10), 625 (20), 598 (20), 539 (25) (Fig. 2).

The powder X-ray diffraction pattern of the crystals of **IV** corresponds to the theoretically calculated one and is presented in Fig. 3.

(3a) Solid $GaCl_3$ (7.23 g, 40.9 mmol) was added at –50°C to sodium metal (2.91 g, 126.5 mmol) dissolved in 80 mL of *i*-PrOH and 20 mL of toluene (5%). A yellow waxy product **II** (7.47 g) containing considerable amount of chlorine was isolated from the reaction mixture.

(3b) Sodium metal (8.53 g, 371 mmol) dissolved in a mixture of 54 mL of *i*-PrOH and 80 mL of toluene (25%) was added to $GaCl_3$ (21.82 g, 123 mmol) in 75 mL of toluene (20%) at 0°C. Product **II** (8.08 g) was isolated from the reaction mixture.

(4) Sodium metal (1.14 g, 49.5 mmol) dissolved in a mixture of 20 mL of *i*-PrOH and 80 mL of toluene (5%) was added to $GaCl_3$ (2.91 g, 16.5 mmol) in 50 mL of Et_2O (10%) at 0°C. Product **II** (4.07 g) was isolated from the solution.

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[1] The set of interplanar spacings of NaGa(OPr-*i*)$_4$ was obtained for the product resulting from direct reaction of Ga(OPr-*i*)$_3$ with NaOPr-*i*. The bimetallic complex, like its Al analog [12], was insoluble in the alcohol and hydrocarbons.

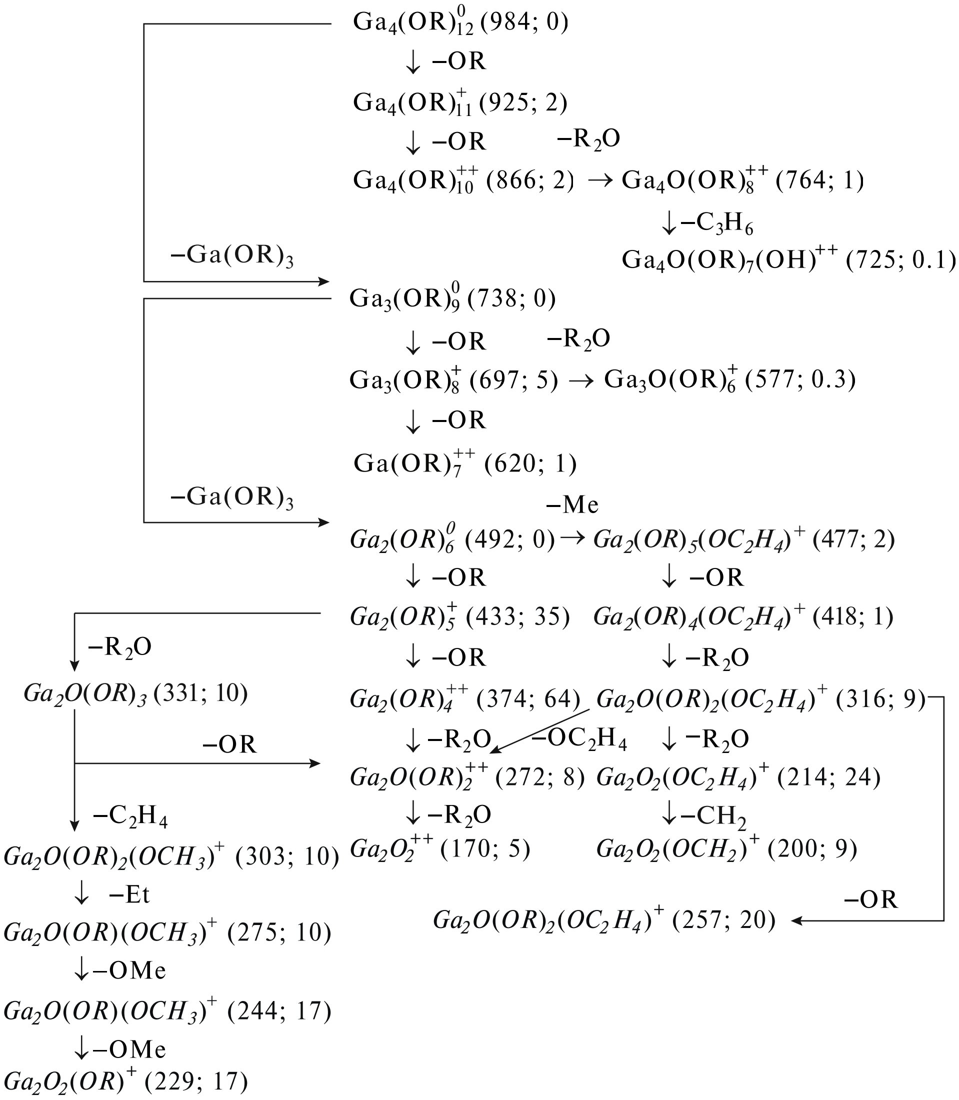

Fig. 1. Mass spectral fragmentation of compounds **I** and **II** (italic).

The freshly prepared compounds **II** are infinitely soluble in *i*-PrOH and toluene; however, storage of the compounds or solutions for several weeks affords nonvolatile white solids **III** amorphous to X-rays, which do not differ from **II** in the composition. The solubility of **III** in the alcohol at 20°C does not excess 3–5%.

Chemical analysis of products **II** from syntheses 3a, 3b, and 4 and products **III**:

Found, %: Cl, 12–32; Ga, 24–32.

IR spectra of **II** and **III** (ν, cm^{-1}): 2960 s, 2920 m, 2848 m, 2650 vw, 1460 vs, 1376 vs, 1366 s, 1342 m, 1258 m, 1144 m, 1128 vs, 986 vs, 844 br.w, 834 vs, 792 m, 646 m, 628 vs, 536 sh.w, 488 br.w, 414 m.

The mass spectrum of **II** does not differ from the mass spectrum of liquid **I**.

In some cases, by heating **II** at 160–170°C/10^{-2} mm Hg, it was possible to distill off Ga(OPr-*i*)$_3$ (**I**) as an oily liquid with a boiling point of 75–80°C/10^{-2} mm Hg, the properties of which were the same as those of the product obtained by electrochemical synthesis.

X-ray Diffraction. The crystal structure of **IV** was determined on a Bruker APEX2 CCD diffractometer (MoK_α radiation, $\lambda = 0.71073$ Å, $2\theta < 60°$) at 100 K. The structure was solved by the direct methods and refined by full-matrix least-squares method on F^2_{hkl} in the anisotropic approximation for all non-hydrogen atoms. The hydrogen atom coordinates calculated geometrically were included in the refinement in the isotropic approximation with the U_{iso}(H) parameter equal to 1.5 $U_{\rm eq}(C_i)$ for Me groups. The latter are dis-

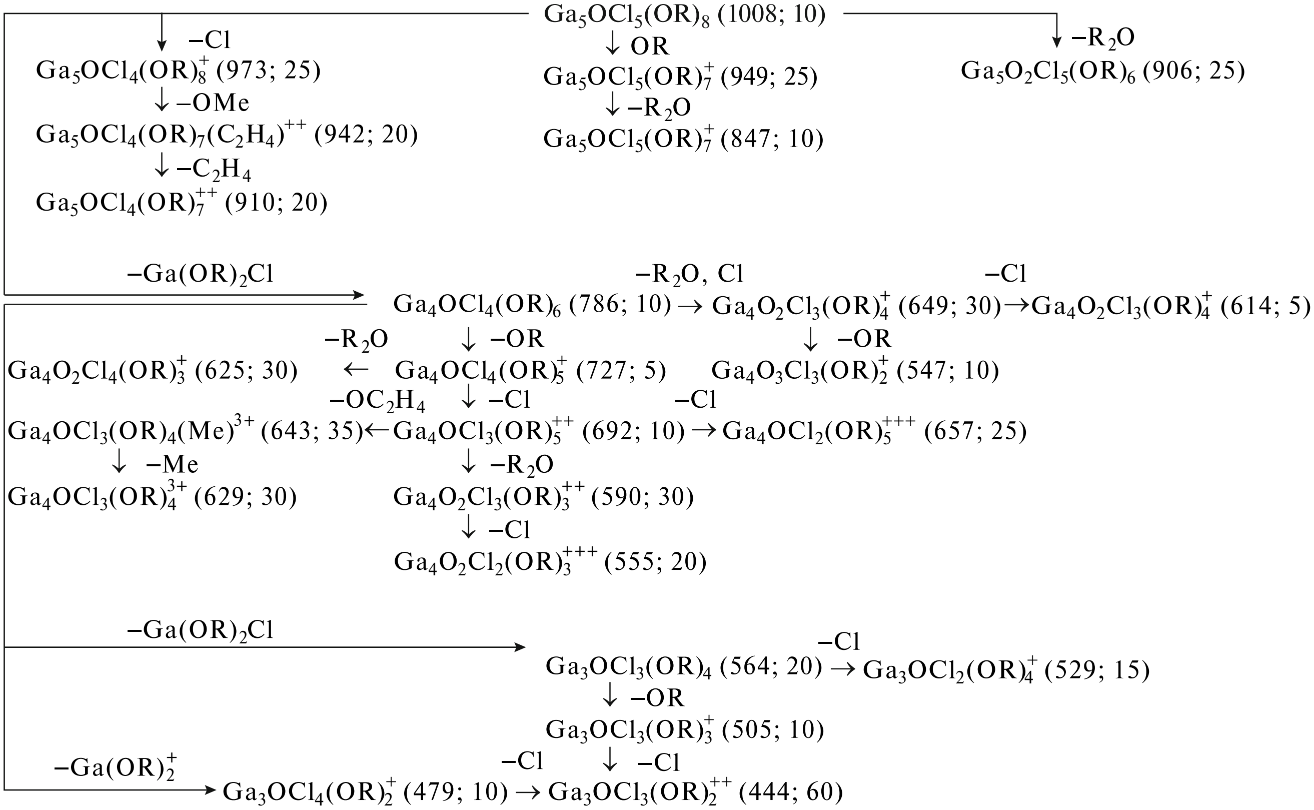

Fig. 2. Mass spectral fragmentation of complex **IV**.

ordered over two positions with occupancy factors of 0.70 and 0.30. All calculations were performed using SHELXTL software [13]. Selected bond lengths and angles of structure **IV** are summarized in the table.

The full set of crystallographic parameters for structure **IV** was deposited with the Cambridge Crystallographic Data Centre (CCDC no. 693282; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

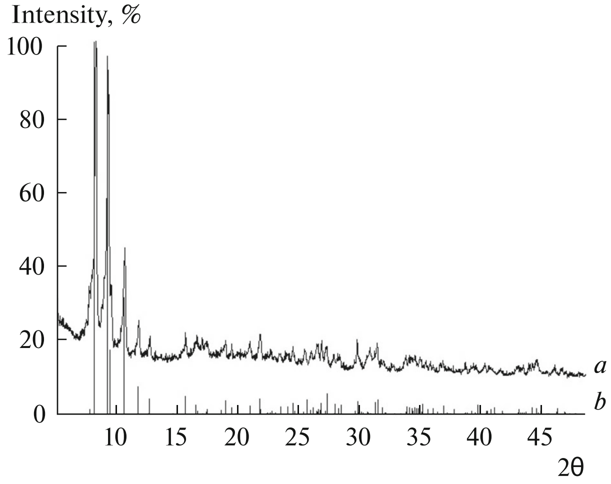

Fig. 3. (*a*) Experimental and (*b*) simulated single crystal X-ray diffraction patterns for $Ga_5O(OPr\text{-}i)_8Cl_5$ (**IV**).

RESULTS AND DISCUSSION

This communication describes the development of an electrochemical synthesis of gallium isopropoxide by anodic dissolution of gallium metal in isopropyl alcohol. The exchange reaction between gallium chloride and sodium isopropoxide, which has been repeatedly described in the literature and is a traditional method for alkoxide synthesis for a broad range of metals, is also studied in detail [14]. Alternative synthetic routes to **I** are faced with considerable drawbacks. The transesterification of $Ga(OEt)_3$ with isopropyl alcohol [4, 7] is difficult due to low solubility of gallium ethoxide [2], while alcoholysis of alkyl- or silylamides [1] is complicated by their low accessibility and the need for purification and low process rate.

Previously, we studied in detail the electrochemical synthesis of many Group III–VIII metal alkoxide derivatives [14], which were accumulated in the electrolyte solution or precipitated in the cathode space. A drawback of this process is the difficulty of separation of the target product from the supporting electrolyte (R_4NBr or LiCl often form stable bimetallic alkoxo chlorides). This drawback was overcome in the synthesis of **I**, and the final product formed in an almost quantitative yield can be purified by vacuum distillation.

In a detailed discussion of the exchange reaction between $GaCl_3$ and a solution of NaOPr-*i*, the attention is first attracted by the possibility of HCl formation upon alcoholysis of $GaCl_3$ (strong Lewis acid). The reaction of HCl with *i*-PrOH is known to afford water, which may lead to formation of oxogroups in the products. Thus, the reaction should be carried out on cooling and the contact between gallium chloride and isopropyl alcohol should be avoided until alkali metal alkoxide is added [14, 15].

All of the syntheses in which we varied the solvent (toluene, diethyl ether, isopropyl alcohol), the reactant concentrations, and the order and the way of reactant involvement into the reaction, as well as the temperature resulted in the formation of alkoxochlorides of variable composition $GaO_x(OPr\text{-}i)_{3-2x-y}Cl_y$, where $y = 1–2.7$ (these complexes were not mentioned in [3–8].)[2] These complexes are present both in solutions and in the precipitate together with NaCl, their ratio varying over rather wide limits. As a result, the yields of crude **II** (yellow waxy compound remaining after solvent evaporation) were substantially different. The attempts to bind chloride by a slight excess of NaOPr-*i* failed due to the formation of insoluble $NaGa(OPr\text{-}i)_4$; the addition of a solution of $GaCl_3$ to a solution of NaOPr-*i* proved inefficient for the same reason. Product **II** is converted on storage to insoluble polymeric **III**. The same product is precipitated with time from solutions of **II**.

It should be noted that the products of the described reactions differ considerably from those of the synthesis of alkoxides of other polyvalent metals under similar conditions. Sodium alkoxo metallates $Na_xM(OR)_y$ are, most often, soluble and their formation does not prevent the exchange reaction. In particular, irrespective of the way and the order of reactant addition, the reaction between the solutions of chlorides and NaOR gives rise to $Ga(OEt)_3$ [2], $In_5O(OPr\text{-}i)_{13}$ [17], $Fe_5O(OEt)_{13}$ [18, 19], $Bi(OEt)_3$ [20], $VO(OR)_3$ [21], $MoO(OR)_4$ [22], $WO(OR)_4$ [23], and so on. For example, $NaGa(OEt)_4$ is readily soluble in organic solvents, while in the $NaOR–Fe(OR)_3–ROH$ system, solid alkoxoferrates do not exist [24]. There are only a few examples of alkoxochlorides, obtained by the reaction of MCl_n with sodium alkoxides, that do not decompose upon the addition of excess sodium alkoxide or upon refluxing of $Y_3(OBu\text{-}t)_8Cl \cdot 2THF$ [25] and $Nd_6(OPr\text{-}i)_{17}Cl$ [26].

Selectede bond lengths (*d*, Å) and bond angles (ω, deg) in $[Ga_5(\mu^5\text{-}O)(\mu\text{-}OPr\text{-}i)_8(OPr\text{-}i)_5]$ (**IV**) (Ga^6 are octahedrally coordinated and Ga^5 are trigonal bipyramidal coordinated atoms)

Parameters	Value
$Ga(3)^6–(\mu^5\text{-}O)$	1.9312
$Ga(1,2)^5–(\mu^5\text{-}O)$	2.2483; 2.0865
$Ga(3)^6–(\mu\text{-}OR)^{5–6}$	2.0109; 2.0294
$Ga(1,2)^5–(\mu\text{-}OR)^{5–6}$	1.8729; 1.8894
$Ga(1,2)^5–(\mu\text{-}OR)^{5–5}$	1.8865; 1.9218; 1.8891; 1.8979
$Ga(3)^6–Cl(3)$	2.2076
$Ga(1,2)^5–Cl(1,2)$	2.2028; 2.2164
$(\mu^5\text{-}O)Ga(3)^6(\mu\text{-}OR)^{5–6}$	79.26; 79.49; 80.30; 160.61
$(\mu^5\text{-}O)Ga(1,2)^5\mu\text{-}OR)^{5–5}$	75.56; 75.94; 79.64; 79.26 ....
$(\mu\text{-}RO)^{5–6}Ga(3)^6(\mu\text{-}OR)^{5–6}$	88.82; 158.98
$(\mu\text{-}RO)Ga(1,2)^5(\mu\text{-}OR)^{5–6}$	107.11; 107.67; 120.08; 120.91
$(\mu\text{-}RO)Ga(1,2)^5(\mu\text{-}OR)^{5–5}$	114.44; 121.77
$(\mu^5\text{-}O)Ga(3)^6Cl(3)$	180
$(\mu^5\text{-}O)Ga(1,2)^5Cl\ (1,2)$	173.431; 176.118
$(\mu\text{-}RO)^{5–6}Ga(3)^6Cl(3)$	100.51–99.70
$(\mu\text{-}RO)^{5–6}Ga(1,2)^5Cl(1,2)$	102.49; 105.37
$Ga(3)^6(\mu^5\text{-}O)Ga(1,2)^5$	98.47; 96.45
$Ga(1,2)^5(\mu^5\text{-}O)Ga(1,2)^5$	88.702; 89.401; 163.06; 167.09
$Ga(3)^6(\mu\text{-}OR)^{5–6}Ga(1,2)^5$	102.60; 106.31
$Ga(1,2)^5(\mu\text{-}OR)^{5–5}Ga(1,2)^5$	106.49; 106.00

On heating of freshly prepared waxy product **II** in vacuum above 160°C/10^{-2} mm Hg (unlike aged polymers **III**), it is possible to distil liquid **I**. The amount of **I** obtained upon distillation of product **II** varies over a broad range and also depends on the content of chlorine in **II**. This result is consistent with the substantial difference of the product yield described in the litera-

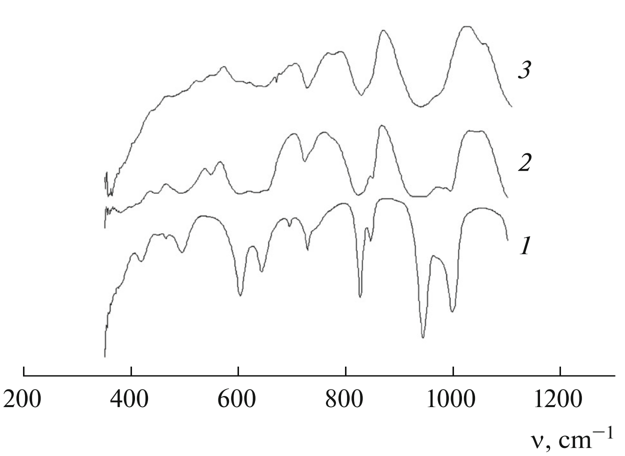

Fig. 4. IR spectra of complexes (*1*) **I**, (*2*) **II**, **III**, and (*3*) **IV**.

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[2] Nevertheless, the formation of volatile $Ga(OPr\text{-}i)_2Cl$ was implied under the described conditions in patent [16].

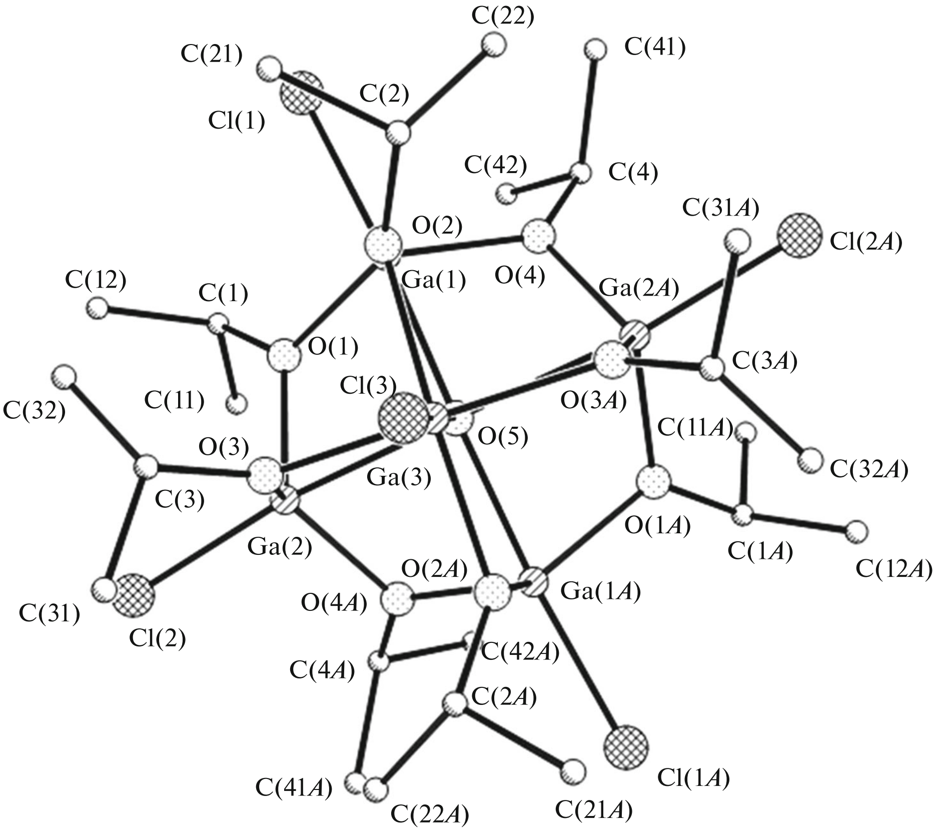

Fig. 5. Molecular structure of **IV**.

ture: in [7], the yield of **I** was 75%. Nevertheless, it was noted [11] that only a slight amount of liquid **I** can be obtained by distillation of the intermediate.

The IR spectrum of **I** differs substantially from the spectra of chlorine-containing products **II**, **III**, and **IV**, which are very similar in the regions typical of ν(Ga–O) and ν(Ga–Cl) stretching vibrations (Fig. 4).

The existence of oligomeric molecules of different size and structure in the alkoxide samples, possible interconversions, and the dependence of the physicochemical properties on the molecular composition were repeatedly described in the literature. We called this phenomenon the "coordination polymerism" [14, 27]. A typical example of this phenomenon is aluminum isoproxide $Al(OPr\text{-}i)_3$ containing two types of associates. The liquid distillate contains trimeric molecules with a five-coordinate central atom and two tetrahedral terminal atoms: $(RO)Al[(\mu\text{-}OR)_2Al(OR)_2]_2$. The liquid crystallizes for ~40 days with the formation of $Al[(\mu\text{-}OR)_2Al(OR)_2]_3$ tetramers, each consisting of the central octahedrally coordinated aluminum atom and three terminal tetrahedrally coordinated atoms (Mitsubishi type). In the presence of alcohol, this transition occurs instantaneously. Aromatic hydrocarbons can induce the reverse tetramer to trimer transition [25].

For **I**, the closest analog of $Al(OPr\text{-}i)_3$, two types of associates are known: dimers $[(RO)_2Ga(\mu\text{-}OR)_2Ga(OR)_2]$ (two tetrahedrally coordinated gallium atoms sharing an edge) and tetramers (structural analog of $[Al(OPr\text{-}i)_3]_4$) [1]. Freshly distilled samples can remain without changes for a long period of time (in some cases, even in the presence of some well-faceted crystals), and isopropyl alcohol does not induce crystallization. Partial crystallization can be induced mechanically; however, the crystals are again rapidly dissolved. The crystals of **I** are formed in minor amounts in a dichloromethane solution at –30°C [1].

The mass spectra indicate that the liquid samples of compound **I** consist of dimeric molecules. The mass spectrum of crystalline **I** exhibits, apart from the masses corresponding to dimers, fragments with large m/z values formed from tetramers (Fig. 1). The mass spectral fragmentation of the tetramer is similar to that observed in the spectrum of $[Al(OPr\text{-}i)_3]_4$ [25].

The considerable stability of the low-molecular-mass associates (dimers) compared with more associated molecules (tetramers) distinguishes **I** not only from $Al(OPr\text{-}i)_3$ but also from other alkoxides prone to coordination polymerism. Tetramers exist in very dilute solutions of **I** in toluene [28]. Meanwhile, the oligomerizing role of aromatic hydrocarbons was established for many akoxides [14]. The proneness of **I** to association can be attributed to stable tetrahedral configuration of the gallium atoms in dimeric molecules, unlike "incomplete" coordination polyhedra in less associated samples (in particular, in aluminum isopropoxide trimers, C.N. 5).

The samples of crude **II**, unlike **I**, are subject to aging: their solubility and volatility appreciably decrease with time, apparently, due to polymerization of their amorphous structures. The accurate determination of the melting point of $Ga(OPr\text{-}i)_3$ is impossible. All gallium isopropoxide samples both commercial (Aldrich) and synthesized were crystalline and contained a minor amount of the melt. This fact obviously attests to the equilibrium between dimer and tetramer molecules, which was described for the $[Al(OPr\text{-}i)_3]_3$–$[Al(OPr\text{-}i)_3]_4$ system [29].

Oxoalkoxochloride **IV** was crystallized in ~50% yield from the solution obtained upon the reaction between concentrated solutions of $GaCl_3$ and NaOPr-*i* and studied by X-ray diffraction (Fig. 5). The molecule of **IV** is a flattened Ga_5 pyramid with the octahedrally coordinated axial gallium atom $[Ga(\mu_5\text{-}O)(\mu\text{-}OPr\text{-}i)_4Cl]$ and trigonal bipyramidally coordinated equatorial gallium atom $[Ga(\mu_5\text{-}O)(\mu\text{-}OPr\text{-}i)_3Cl]$. The pentadentate oxogroup is located at the center of the pyramid in which all sides are drawn together by eight μ-OPr-*i* groups. Four short bridges are located between the apical six-coordinate Ga atom and the equatorial Ga atoms (designated as 5–6 in the table), while the other four long bridges connect the trigonal-bipyramidal Ga atoms to the equatorial plane (designated as 5–5, Fig. 5). The bond lengths in molecule **IV** are almost identical to those in analogs: $Ga_5O(OEt)_8Cl_5$ [30], $Fe_5O(OR)_8X_5$ (R = Et, *i*-Pr, X = Cl, OEt, OPr-*i*, OPr^n, OBu-*i*, OCH_2CF_3, $OSiEt_3$) [18, 31], and $Al_5O(OBu\text{-}i)$ [32]. Indeed, the same type of μ_5-O ligand arrangement was observed in the case of tetragonal pyramidal complexes $M_5(\mu_5\text{-}O)(\mu_3\text{-}OR)_4(\mu\text{-}OR)_4(OR)_5$ (M = In, Sc, Y, Ln) in which all metal atoms are octahedrally coordinated by alkoxo groups, which connect the axial and equatorial metal atoms at the faces.

The mass spectral fragmentations of the crystal of **IV** and $Ga_5O(OEt)_8Cl_5$ are very similar (Fig. 2).

In conclusion, note that **I** is the most well known homolog. This compound has been repeatedly described in the literature and is used in technology practice. This communication gives the first discussion of the importance of the stability of alkoxo chlorides formed upon exchange reactions and their effect on the yield and purity of the final product, which always contains some chlorine. However, industrial implementation of electrochemical synthesis (using R_4NBr) or alcoholysis of gallium alkylamide or silylamide is apparently difficult due to the high cost of the starting compounds.

ACKNOWLEDGMENTS

The authors are grateful to Yu.A. Velikodnyi and A.S. Mityaev for powder X-ray diffraction studies of the products.

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Translated by Z. Svitanko