

## SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

# Gallium Alkoxides: Synthesis and Properties

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**Abstract**—Compounds Ga(OR)<sub>3</sub> (R = Me, Et, Pr<sup>i</sup>, Bu<sup>n</sup>, C<sub>2</sub>H<sub>4</sub>OMe) were synthesized by exchange reactions between gallium chloride and alkali metal alkoxides, the reetherification of Ga(OPr<sup>i</sup>)<sub>3</sub> and Ga(OC<sub>2</sub>H<sub>4</sub>OMe)<sub>3</sub> by other ROH (R = Me, Et), and anodic dissolution of metallic gallium in the presence of a electroconductive additive (LiCl, Bu<sub>4</sub>NBr). When solid GaCl<sub>3</sub> is introduced into an alcoholic solution of NaOEt, stable soluble gallium oxoalkoxyhalides are formed. The same reaction with a GaCl<sub>3</sub> solution in toluene or electrochemical synthesis produces nonvolatile Ga(OEt)<sub>3</sub> samples, which have the polymer zigzag configuration [Ga(OR)<sub>4/2</sub>(OR)]<sub>∞</sub>. Mass spectrometry shows that only Ga(OPr<sup>i</sup>)<sub>3</sub> and freshly prepared X-ray amorphous Ga(OEt)<sub>3</sub> samples (produced by reetherification) are transferred to the gas phase. The spectra of the latter contain ions generated by penta- and hexanuclear oxoalkoxide molecules, along with fragments of orthospecies [Ga(OEt)<sub>3</sub>]<sub>2–4</sub>. IR spectra are described for all compounds synthesized.

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Current interest to organogallium derivatives is due to their utility as precursors for some oxide composites in the manufacturing of gas sensors [1], luminophores [2], solid electrolytes (above all, LaGaO doped with some metals [3]), and zeolite catalytic systems [4].

The pioneering studies of gallium alkoxides date to the middle 1960s [5–8]; at that time, Ga(OR)<sub>3</sub> was synthesized via exchange reactions between GaCl<sub>3</sub> and NaOR (R = Et, Pr<sup>i</sup>). Another synthesis method is the transesterification of Ga(OEt)<sub>3</sub> with isopropanol [7], Ga(OPh)<sub>3</sub> with methanol or ethanol [9], and Ga(OPr<sup>i</sup>)<sub>3</sub> with several ROH alcohols (R = Me, Et, <sup>n</sup>Pr, <sup>n</sup>Bu, <sup>s</sup>Bu, <sup>t</sup>Bu) [10]. The third described synthesis Ga(OR)<sub>3</sub> is alcoholysis of Ga[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> [2] or [Ga(NMe<sub>2</sub>)<sub>3</sub>]<sub>2</sub> [11, 12]. 2-methoxyethoxides Ga(OC<sub>2</sub>H<sub>4</sub>OMe)<sub>3</sub> and Ga(OCMe<sub>2</sub>CH<sub>2</sub>OMe)<sub>3</sub>, aminoalkoxides, and volatile Ga(OR)<sub>3</sub> (R = Pr<sup>i</sup>, Bu<sup>i</sup>, Bu<sup>t</sup>, C<sub>5</sub>H<sub>11</sub><sup>t</sup>, C<sub>8</sub>H<sub>17</sub><sup>t</sup>, C<sub>6</sub>H<sub>13</sub><sup>t</sup>) were prepared in this way [11].

The configuration of a tetrameric gallium isopropoxide molecule proposed on the basis of <sup>1</sup>H NMR data as an analogue of [Al(OPr<sup>i</sup>)<sub>3</sub>]<sub>4</sub> [13] was verified by single-crystal X-ray diffraction data for Ga[(μ-OPr<sup>i</sup>)<sub>2</sub>Ga(OPr<sup>i</sup>)<sub>2</sub>]<sub>3</sub> [11]. Dimeric molecules [Ga(μ-OR)(OR)<sub>2</sub>]<sub>2</sub> are found in the structure of *tert*-amoxide; monomers [Ga(OBu<sup>t</sup>)<sub>3</sub>(HNMe<sub>2</sub>)] are found in the *tert*-butoxide complex with amine [11]. <sup>1</sup>H NMR was used to study dimer ↔ tetramer equilibrium for Ga(OPr<sup>i</sup>)<sub>3</sub> in hydrocarbon solutions [14], and the thermodynamic parameters of the process were determined [11].

Alkoxides have recently been used in CVD and sol-gel processes for the manufacture of Ga<sub>2</sub>O<sub>3</sub> films and ZnGa<sub>2</sub>O<sub>4</sub> ceramics [2, 11, 12].

As a rule, product yields were not indicated in the description of Ga(OR)<sub>3</sub> syntheses; accessible preparation methods remained to be developed. Property data for alkoxides are quite controversy. Here, we attempted to repeat the Ga(OR)<sub>3</sub> syntheses described in the literature via exchange reactions between GaCl<sub>3</sub> and alkali alkoxides and transesterification reactions Ga(OR)<sub>3</sub> + R'OH; we also developed a new electrochemical synthesis. Products were characterized by elemental analysis, IR spectroscopy, mass spectrometry, and X-ray powder diffraction. The most accessible homologues are proposed for use in sol-gel processes.

## EXPERIMENTAL

### Methods

All manipulations associated with the synthesis, analysis, and characterization of alkoxides were carried out in a dry box under an N<sub>2</sub> or Ar atmosphere. Absolute organic solvents were used: MeOH was absolutized by long boiling over Mg(OMe)<sub>2</sub>; EtOH, over Ca(OEt)<sub>2</sub>; and <sup>i</sup>PrOH, over Al(OPr<sup>i</sup>)<sub>3</sub>. Methylcellosolve from Merck was distilled under atmospheric pressure (124.6°C). Toluene and hexane were stored over P<sub>2</sub>O<sub>5</sub> for several days; then, they were boiled over metallic sodium. GaCl<sub>3</sub> was prepared by direct chlorination of metallic gallium followed by vacuum distillation [15],

**Table 1.** Parameters of the reaction  $\text{GaCl}_3 + 3\text{MOR}$  and characteristics of the product

No.	Precursors		Observations	For $\text{Ga}(\text{OR})_3$ found (calcd.), %		
	$\text{GaCl}_3$	MOR		Ga	C	H
1	Sln of $\text{GaCl}_3$ (0.84 g, 4.76 mmol) in PhMe (10 mL)	LiOMe (0.54 g, 14.3 mmol) in MeOH (10 mL)	No precipitate. After boiling and evacuation of sln $\rightarrow$ precipitate insoluble in MeOH and PhMe	–	–	–
2	»	NaOMe (0.77 g, 14.3 mmol) in MeOH (10 mL)	Precipitate NaCl + $\text{Ga}(\text{OMe})_3$	–	–	–
3	Sln of $\text{GaCl}_3$ (1.91 g, 10.8 mmol) in PhMe (20 mL)	NaOEt (2.31 g, 34 mmol) in EtOH (50 mL)	Precipitate NaCl + $\text{Ga}(\text{OEt})_3$ ; after sln was evacuated $\rightarrow$ $\text{Ga}(\text{OEt})_3$ microcrystals (yield, ~20%)	35.86 (34.14)	–	–
4	Solid $\text{GaCl}_3$ (2.85 g, 16.0 mmol)	NaOEt (3.60 g, 53 mmol) in EtOH (80 mL)	Precipitate NaCl (2.39 g, 41 mmol); after sln was evacuated $\rightarrow$ product (2.65 g)	38.86 (34.14)	29.09 (35.12)	6.29 (7.30)
5	Solid $\text{GaCl}_3$ (6.61 g, 37.5 mmol) in ester (50 mL)	NaOPr <sup>1</sup> (8.47 g, 124.6 mmol) in <sup>i</sup> PrOH (150 mL) and PhMe (50 mL)	Precipitate NaCl; from sln, $\text{Ga}(\text{OPr}^i)_3$ * (7.04 g, 28.5 mmol; yield, 76%)	31.68 (32.73)	40.20 (43.72)	6.31 (8.50)

\* IR spectrum of  $\text{Ga}(\text{OPr}^i)_3$  is described in Table 3. Mass spectrum: 925 (2), 866 (2), 764 (1), 725 (0.1), 679 (5), 620 (1), 577 (0.3), 433 (35), 418 (1), 374 (64), 331 (10), 316 (9), 272 (8), 214 (24), 200 (9), 170 (5) (Fig. 1).

or a  $\text{GaCl}_3$  sample purchased from Merck was used.  $\text{Ga}(\text{OPr}^i)_3$  from Aldrich was used in several syntheses.

Another precursor was liquid solvate  $\text{GaCl}_3 \cdot \text{EtOH}$  prepared by a new method: metallic gallium was dissolved in a 6 M HCl solution in absolute ethanol. This solvate with  $T_m = 10^\circ\text{C}$  was earlier synthesized by the direct reaction between stoichiometric amounts of the components [16].

Gallium was determined by back complexometric titration with a  $\text{CuSO}_4$  solution (PAN indicator) at pH 4.

IR spectra were recorded as Nujol and hexachlorobutadiene mulls on a PE 1600 FTIR spectrometer. X-ray diffraction patterns were recorded from powders sealed between X-ray amorphous films on an Image Plate Guinier Camera G670 instrument. Mass spectra were recorded on a Jeol JMS-SX/SX-102A DSQ-2 or Trace JC Ultra DSQ-2 instrument with direct injection and dynamic heating from 2 to  $180^\circ\text{C}$  at 10 K/min (based on  $^{69}\text{Ga}$ ).

The onset decomposition temperature was determined in a tensimeter in vacuum in an isothermal

mode. The temperature at which the dissociation pressure reached 10 mm Hg (for a sample size of 0.5 g) was believed equal to the decomposition onset.

To determine solubilities, solid  $\text{Ga}(\text{OEt})_3$  and EtOH were placed into an ampoule with a finger and thermostated; then, the saturated solution was poured into the finger.

*Exchange Reactions of  $\text{GaCl}_3$  with Alkali Alkoxides:*  
 $\text{GaCl}_3 + 3\text{MOR} \rightarrow \text{Ga}(\text{OR})_3 + 3\text{MCl} \downarrow$

$\text{GaCl}_3$  entered the reaction as a solid product, a solution in alcohol, ether, or toluene, or  $\text{GaCl}_3 \cdot \text{EtOH}$  in ethanol. A solution of NaOR in EtOH or <sup>i</sup>PrOH–toluene was accurately added to a solution of  $\text{CaCl}_2$  with vigorous stirring at  $0^\circ\text{C}$ . The reaction mass strongly heated, and a white precipitate appeared. The reaction mixture was refluxed for 2–3 h; the solution was centrifuged and decanted from the precipitate, which was twice washed with hot toluene or alcohol and evacuated. The results of the synthesis are compiled in Table 1.

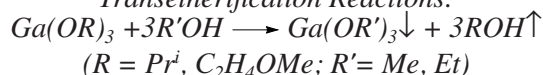
**Table 2.** Parameters of reetherification reactions and characteristics of the products\*

No.	Precursors		Product composition, % Ga found (calcd.),	
1	Ga(OPr <sup>i</sup> ) <sub>3</sub> (0.33 g, 1.34 mmol)	MeOH (2 mL, 50 mmol)	Ga(OMe) <sub>3</sub>	41.39 (42.94)
2	»	EtOH (2 mL, 35 mmol)	Ga(OEt) <sub>3</sub>	32.00 (34.14)
3	Ga(OC <sub>2</sub> H <sub>4</sub> OMe) <sub>3</sub> (0.33 g, 1.12 mmol)	MeOH (2 mL, 50 mmol)	Ga(OMe) <sub>2.5</sub> (OC <sub>2</sub> H <sub>4</sub> OMe) <sub>0.5</sub>	37.40 (37.83)
4	»	EtOH (2 mL, 35 mmol)	Ga(OEt)(OC <sub>2</sub> H <sub>4</sub> OMe) <sub>2</sub>	25.05 (26.41)

\* IR spectra for all products are described in Table 3.

Ga(OEt)<sub>3</sub> mass spectrum: 1031 (6), 986 (4), 957 (1), 943 (1), 901 (7), 897 (20), 883 (40), 856 (1), 838 (30), 827 (100), 771 (8), 764 (4), 726 (6), 697 (50), 652 (2), 567 (11), 522 (6), 493 (21), 478 (16), 448 (15), 363 (28), 318 (55), 274 (89), 229 (90), 200 (10) (Fig. 2).

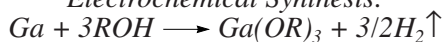
#### Transetherification Reactions:



Synthesis was carried out as follows: to a solution of Ga(OPr<sup>i</sup>)<sub>3</sub> or Ga(OC<sub>2</sub>H<sub>4</sub>OMe)<sub>3</sub> in toluene (8 mL) at room temperature, a considerable excess of MeOH or EtOH was added. A white jel precipitated instantaneously. Solid products remaining after evacuation had the compositions specified in Table 2. Ga(OEt)<sub>3</sub> samples prepared as described above (they contained trace unreacted Ga(OPr<sup>i</sup>)<sub>3</sub>) were volatile. The product of the same composition after the reaction mixture was refluxed for 1 h was, however, nonvolatile.

The treatment of 2-methoxyethanol with MeOH or EtOH induced only partial replacement of MeOC<sub>2</sub>H<sub>4</sub>O groups and the formation of Ga(OMe)<sub>2.5</sub>(OC<sub>2</sub>H<sub>4</sub>OMe)<sub>0.5</sub> and Ga(OEt)(OC<sub>2</sub>H<sub>4</sub>OMe)<sub>2</sub>.

#### Electrochemical Synthesis:



Synthesis was performed in a cell with unseparated cathodic and anodic spaces equipped with a cooling jacket and a refluxer. The anode was a metallic gallium pool into which a platinum wire was dipped. The cathode was a platinized platinum plate ~10 cm<sup>2</sup> in surface area. The electroconductive additive was Bu<sub>4</sub>NBr, Et<sub>3</sub>BzNCl, or LiCl in appropriate alcohols (80–100 mL) in the form of ~0.05 M solutions (in MeOH, 0.01 M solutions). All electroconductive additives were recrystallized from MeOH and dried in vacuo. The process was performed at a direct current (current, 0.0017–0.10 A; voltage, 50–110 V; for MeOH, 20 V); vigorous hydrogen evolution on the cathode was observed, and white solids precipitated from MeOH, EtOH, and <sup>t</sup>BuOH. The products of electrochemical synthesis from <sup>i</sup>PrOH

and methylcellosolve were colorless liquids. Electrolysis lasted 4–15 h. Solid products were separated from the electrolyte, washed with absolute alcohol two times (to remove electroconducting additives), and dried in vacuo. In the case of Ga(OC<sub>2</sub>H<sub>4</sub>OMe)<sub>3</sub>, the residue after the solvent was evacuated was separated from LiCl by extraction to toluene.

For Ga(OMe)<sub>3</sub> anal. calcd., %: Ga, 42.94; C, 20.11; H 4.37.

Found, %: Ga, 42.07; C, 22.09; H, 5.52.

For Ga(OEt)<sub>3</sub> anal. calcd., %: Ga, 34.14; C, 35.12; H, 7.30.

Found, %: Ga, 36.80; C, 33.95; H, 6.93.

For Ga(OBu<sup>n</sup>)<sub>3</sub> anal. calcd., %: Ga, 24.22; C, 49.83; H, 6.23.

For GaO<sub>0.75</sub>(OBu<sup>n</sup>)<sub>1.5</sub> anal. calcd., %: Ga, 36.55; C, 37.60; H, 7.05.

Found, %: Ga, 36.67; C, 35.73; H, 6.95.

For Ga(OC<sub>2</sub>H<sub>4</sub>OMe)<sub>3</sub> anal. calcd., %: Ga, 22.73; C, 36.61; H, 7.12.

Found, %: Ga, 22.33; C, 35.29; H, 6.31.

The product obtained from butanol was likely an oxo complex.

Electrolysis was accompanied by metal refining, which generated metallic gallium microparticles in Ga(OR)<sub>3</sub> samples; the proportion of the particles increased with time. To illustrate this phenomenon, we list below the analyses of Ga(OEt)<sub>3</sub> samples depending on the electrolysis time.

For Ga(OEt)<sub>3</sub> anal. calcd., %: Ga, 34.14; C, 35.12; H, 7.30.

Found, %: Ga, 36.80 (4 h); C, 30.60; H, 5.61.

Found, %: Ga, 44.81 (10 h); C, 19.95; H, 4.93.

Found, %: Ga, 50.29 (15 h); C, 13.78; H, 3.43.

IR spectra are described in Table 3.

**Table 3.** IR spectra for gallium alkoxides. The synthesis method is indicated in parentheses: I, exchange reaction; II, transesterification ; III, anodic dissolution of metal

Ga(OMe) <sub>3</sub> (II, III)	Ga(OEt) <sub>3</sub> (II, III)	Ga(OPr <sup>i</sup> ) <sub>3</sub> (I)	“Ga(OBu <sup>n</sup> ) <sub>3</sub> ” (III)	Ga(OC <sub>2</sub> H <sub>4</sub> OMe) <sub>3</sub> (III)	Ga(OMe) <sub>2.5</sub> (OR) <sub>0.5</sub> R = C <sub>2</sub> H <sub>4</sub> OMe (II)	Ga(OEt)(OR) <sub>2</sub> R = C <sub>2</sub> H <sub>4</sub> OMe (II)
2992–2846 –s br	2964 vs 2902 vs	2960 s 2920 m	2956 vs 2930 vs	2920 vs 2878 vs	2922 vs 2848 s	2922 vs 2850 m sh
2826 s	2844 vs	2848 m	2872 vs	2632 vw		
1460 vs	2720 m	2650 vw	1204 w	2724 sh		
1376 s	2710 m	1558 vw	1096 m sh	1942 w		1626 vs
1308 w	2604 w	1460 vs	1066 m	1696 vw	1612 s	
1260 m	1288 w	1376 vs	1026 m	1618 vs		
1178 m	1156 s	1366 s sh	888 vw	1452 vs		
1078 vs	1108 vs	1342 m	842 w	1382 w sh		
1044 vs	1068 vs	1258 m	716 w	1366 s		
978 w	1038 vs	1144 m	652 w	1306 vw		
938 w	912 m	1128 vs	590 w	1260 w	1240 w	
852 m	888 vs 782 m	986 vs 844 vs	564–414 m br	1240 s	1194 m	
792 w		834 vs		1196 s	1086 vs	1098 m sh
720 m		792 m		1106 vs	1044 vs	1050 vs
				1058 vs	966 msh	
				1018 vs	894 msh	964 w
				976 m sh	834 m	880 w
				898 s		824 w
				836 s		714 s
682 w sh				710 m sh	600–500 vs br	600 s
660 w sh	622 s sh	646 w sh		624 m		480 vs br
654 m	570 vs	628 vs		456 m		
524 m sh		536 w br				
490 m br		488 w br				
		414 m				

### Crystallography

X-ray diffraction patterns for Ga(OEt)<sub>3</sub> powders prepared electrochemically and by the exchange reaction are displayed in Fig. 1. The sample prepared by the second method (Table 1; sample 3) contains trace NaCl. The details of the structure experiment are listed in Table 4.

TREOR90 software [17] was used to determine unit cell parameters; the STOE WinXPow program package was used in the final indexing (Table 5). The crystal structure was solved ab initio proceeding from powder data. Suggested space group  $P\bar{4}2_1c$  was chosen proceeding from systematic extinctions. The primary model was found using FOX software [18]. Isolated Ga atoms and Et groups as rigid fragments are randomly distributed over the unit cell. Jana2000 software was used for the Rietveld refinement of the calculated model [19]. Thermal parameters were fixed at  $U_{\text{iso}} = 0.05$  for all atoms. Mild constraints were imposed on the geometry of ethoxy groups during the refinement:  $d_{\text{C-C}} = 1.40(6)$  Å,  $d_{\text{C-O}} = 1.40(6)$  Å, and  $\angle\text{OCC} = 113(2)^\circ$ . Figure 2 displays the measured, simulated, and difference X-ray diffraction patterns. Atom coordi-

nates, interatomic distances, and bond angles in the Ga(OEt)<sub>3</sub> structure are compiled in Tables 6 and 7.

### RESULTS AND DISCUSSION

In attempted to repeat Ga(OR)<sub>3</sub> two syntheses described in the literature: (1) an exchange reaction between GaCl<sub>3</sub> and alkali alkoxides and (2) reetherification of gallium isopropoxide by other alcohols. In addition, we pioneered the use of anodic oxidation of metals in absolute alcohol to prepare Ga(OR)<sub>3</sub>. LiOR was used to prepare methoxide and ethoxide (because LiCl is soluble in the relevant alcohols). As a result of the reaction, however, Ga(OR)<sub>3</sub> did not precipitate, likely because of the formation of stable lithium alkoxochlorogallates.

Repeating many times the exchange reaction of alcoholic solutions of GaCl<sub>3</sub> with sodium ethoxide in the proportion 1 : 3 or using solid gallium chloride (which was described as a method for Ga(OEt)<sub>3</sub> synthesis [6–8]), we obtained soluble oxoethoxochlorides of variable composition, which did not degrade during long boiling (the yield of an NaCl precipitate was ~80% of the theory). The products formed after the solutions

were evacuated ranged in color from white yellow; their solubility in alcohol or toluene also varied widely. Complexes  $[\text{Ga}_5(\mu_5\text{-O})(\mu\text{-OEt})_8\text{Cl}_5]$  and  $[\text{Ga}_{12}(\mu_4\text{-O})_2(\mu_3\text{-O})_5(\mu\text{-OEt})_{10}\text{Cl}_{12}\text{Py}_4]\text{Py}$  crystallized in insignificant yields from reaction solution upon addition of solid MeCN and Py, respectively [20]. The appearance of oxo groups in the above-described compounds was likely due to alcoholysis of solid  $\text{GaCl}_3$  (a strong Lewis acid) and partial HCl evolution. HCl reacts with alcohol, yielding water (this reaction is catalyzed by  $\text{MCl}_n$ ) [13].

When the reaction was carried out with  $\text{GaCl}_3$  dissolved in toluene or with  $\text{GaCl}_3 \cdot \text{EtOH}$  in alcohol (i.e., under the conditions maximally excluding alcoholysis [21]), the product was microcrystalline  $\text{Ga}(\text{OEt})_3$ , which is sparingly soluble in alcohol or toluene. Electrochemical synthesis gave the same result.

The exchange reaction of  $\text{GaCl}_3$  with  $\text{NaOPr}^i$  is the only method for preparing  $\text{Ga}(\text{OPr}^i)_3$ ; the product yield is high (anodic dissolution of gallium is inefficient in this case because of the impossibility of separating the desired product from the electroconductive additive).

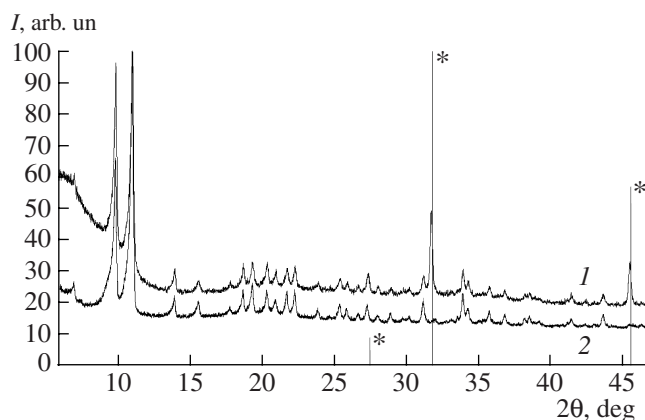
$\text{Ga}(\text{OEt})_3$ ,  $\text{Ga}(\text{OPh})_3$ , and  $\text{Ga}(\text{OPr}^i)_3$  were earlier proposed as precursors for reetherification [7, 9, 10]. In view of their solubility in toluene, it is pertinent to use  $\text{Ga}(\text{OPr}^i)_3$  or  $\text{Ga}(\text{OC}_2\text{H}_4\text{OMe})_3$  in this reaction. Elemental analysis showed that methoxide and ethoxide were prepared in this way. However, mass spectrometry showed residual isopropoxide groups in  $\text{Ga}(\text{OEt})_3$  prepared from  $\text{Ga}(\text{OPr}^i)_3$  (Fig. 3).

Anodic gallium dissolution yielded  $\text{Ga}(\text{OR})_3$  with  $\text{R} = \text{Me, Et, C}_2\text{H}_4\text{OMe, or GaO}(\text{OEt})_3$ . Metal microparticles were piled up in solid samples during long electrolysis (which was verified by X-ray powder diffraction); as a result, the metal prevalence decreased and that of carbon and hydrogen decreased. However, liquid  $\text{Ga}(\text{OC}_2\text{H}_4\text{OMe})_3$  was readily separated from impurity metallic gallium.

All  $\text{Ga}(\text{OR})_3$ —derivatives of aliphatic alcohols—are white solids. A freshly prepared  $\text{Ga}(\text{OPr}^i)_3$  sample is a yellow waxy substance, which cures in 3–5 weeks, in accordance with [6, 7].  $\text{Ga}(\text{OC}_2\text{H}_4\text{OMe})_3$  is a colorless vitrifying liquid.

Gallium ethoxide and gallium oxobutoxide decompose without melting at 195 and 174°C, respectively.  $\text{Ga}(\text{OEt})_3$  decomposes under solution at 135°C. The melting temperature of  $\text{Ga}(\text{OPr}^i)_3$  is 75–80°C/10<sup>-3</sup> mmHg.

$\text{Ga}(\text{OMe})_3$  and  $\text{Ga}(\text{OEt})_3$  are insoluble in alcohols and aromatic hydrocarbons.  $\text{Ga}(\text{OEt})_3$  is sparingly soluble in alcohol and hot toluene.  $\text{Ga}(\text{OPr}^i)_3$  and  $\text{Ga}(\text{OC}_2\text{H}_4\text{OMe})_3$  are well soluble in alcohols and hydrocarbons. The solubility of  $\text{Ga}(\text{OEt})_3$  samples prepared electrochemically or by exchange reaction increases from 3 to 6 wt % in the range 20–100°C (Table 8).



**Fig. 1.** Powder X-ray diffraction pattern for  $\text{Ga}(\text{OEt})_3$  samples prepared by (1) exchange reaction or (2) anodic dissolution of metal (\*NaCl lines).

All  $\text{Ga}(\text{OR})_3$  samples were studied by IR spectroscopy. The spectra measured in the range of the vibrations of OR groups were close to the spectra of individ-

**Table 4.** Details of the X-ray diffraction experiment and structure parameters for  $\text{Ga}(\text{OEt})_3$

$T, \text{K}$	293
Formula weight	189.78
Crystal system	Tetragonal
Space group	$P\bar{4}2_1c$ (114)
$a, \text{\AA}$	18.0047(3)
$c, \text{\AA}$	5.5957(2)
$V, \text{\AA}^3$	1813.96(5)
$Z$	8
$d_{\text{calc}}, \text{g/cm}^3$	1.3894
Radiation, $\lambda, \text{\AA}$	$\text{CuK}\alpha_1, 1.54051,$ Ge-monochromator, Image Plate Detector
$\mu, \text{cm}^{-1}$	3.770
Diffractometer	G670 Huber
$2\theta$ range, deg	3–85
$h, k, l$ range	$0 \rightarrow h \rightarrow 15$ $-10 \rightarrow k \rightarrow 10$ $0 \rightarrow l \rightarrow 4$
Refinement technique	Full profile
Software	Jana2000
$R_p/R_{wp}$	1.41/1.86
$\text{GOOF}/\chi^2$	0.97/0.95
Number of refined parameters	73
Weighting scheme $(\Delta/\sigma)_{\text{max}}$	Single
Orientation parameter (direction)	March-Dollase 0.860(4), (001)

**Table 5.** Indexing of powder X-ray diffraction patterns for Ga(OEt)<sub>3</sub>

<i>I</i> , %	2θ <sub>obs</sub> , deg	2θ <sub>calc</sub> , deg	Δ2θ, deg	<i>d</i> <sub>obs</sub> , Å	<i>d</i> <sub>calc</sub> , Å	<i>hkl</i>
5.2	6.937	6.933	0.0039	12.7321	12.7393	110
62.9	9.821	9.811	0.0095	8.9993	9.0081	200
100	10.992	10.972	0.0200	8.0425	8.0571	210
7.6	13.901	13.892	0.0087	6.3657	6.3697	220
6.5	15.566	15.541	0.0252	5.6880	5.6972	310
3	17.764	17.736	0.0284	4.9888	4.9968	320
9	18.660	18.658	0.0029	4.7513	4.7520	201
12.2	19.309	19.302	0.0068	4.5933	4.5949	211
8.9	20.322	20.307	0.0148	4.3664	4.3696	410
5.2	20.894	20.902	-0.0084	4.2481	4.2464	330
8.7	21.701	21.695	0.0066	4.0919	4.0931	301
9.5	22.257	22.255	0.0027	3.9909	3.9914	311
2.6	23.860	23.859	0.0009	3.7263	3.7265	321
5.8	25.364	25.368	-0.0045	3.5087	3.5081	401
3.7	25.857	25.853	0.0038	3.4430	3.4435	411
2.1	26.654	26.623	0.0303	3.3418	3.3455	520
5.9	27.273	27.259	0.0142	3.2673	3.2690	421
2.1	28.016	27.993	0.0229	3.1823	3.1848	440
3.3	28.903	28.873	0.0298	3.0866	3.0897	530
1.8	29.759	29.729	0.0295	2.9998	3.0027	600
2.5	30.171	30.149	0.0220	2.9597	2.9618	610
8.5	31.150	31.125	0.0257	2.8689	2.8712	521
1.3	31.341	31.378	-0.0367	2.8519	2.8486	620
2.1	31.972	31.974	-0.0023	2.7970	2.7968	002
1.1	32.750	32.757	-0.0067	2.7323	2.7318	112
1.9	33.123	33.095	0.0278	2.7024	2.7046	531
2.2	33.525	33.523	0.0019	2.6709	2.6710	202
11.9	33.904	33.855	0.0486	2.6419	2.6456	601*
6.2	34.240	34.229	0.0110	2.6167	2.6175	611
1.4	35.022	35.011	0.0107	2.5601	2.5608	222
1.7	35.348	35.331	0.0168	2.5372	2.5384	621*
4.9	35.714	35.692	0.0222	2.5121	2.5136	541*
1	35.960	35.916	0.0442	2.4954	2.4984	640
3.8	36.808	36.797	0.0108	2.4398	2.4405	322
2.3	38.183	38.174	0.0087	2.3551	2.3556	412
3.1	38.521	38.471	0.0494	2.3352	2.3381	701*
0.9	38.831	38.807	0.0241	2.3173	2.3187	711
1.4	39.165	39.180	-0.0150	2.2983	2.2974	422
0.7	41.169	41.129	0.0396	2.1909	2.1929	512
2.5	41.425	41.408	0.0169	2.1779	2.1788	731
0.7	42.375	42.350	0.0251	2.1313	2.1325	651
1	43.003	43.005	-0.0018	2.1016	2.1015	442
5.1	43.618	43.579	0.0383	2.0734	2.0752	811*
0.3	44.212	44.220	-0.0082	2.0469	2.0466	602
1.4	45.434	45.409	0.0253	1.9947	1.9957	622
1.2	45.736	45.702	0.0332	1.9822	1.9836	542
1.5	46.283	46.250	0.0329	1.9600	1.9614	751

\* Reflections to which more than one set of indices can be assigned (within an error of 0.05 in Δ2θ).

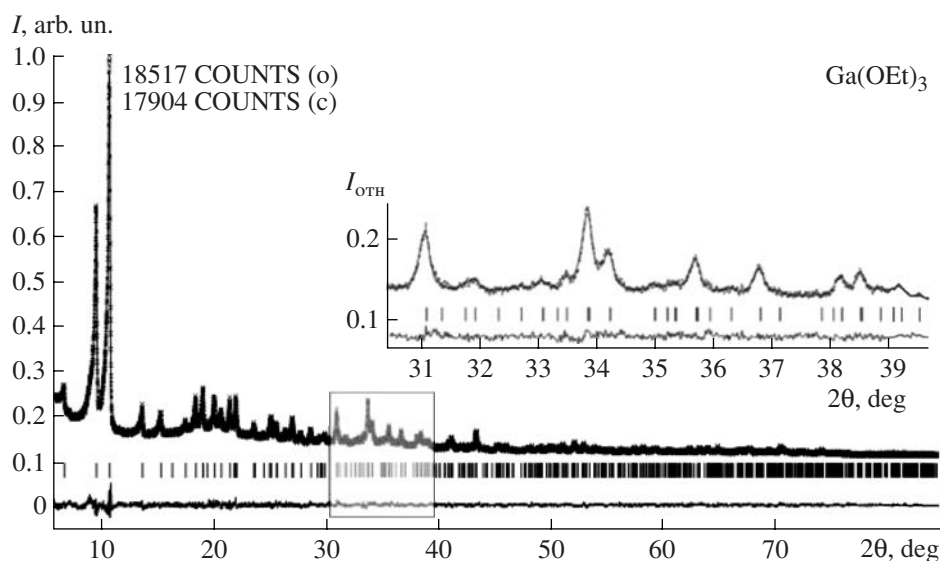


Fig. 2. Measured, simulated, and difference X-ray diffraction powder patterns for an electrochemically prepared  $\text{Ga}(\text{OEt})_2$  sample.

ual homologues of other metals, which verifies the individuality of our  $\text{Ga}(\text{OR})_3$  samples (Table 3). Mass spectra showed that  $\text{Ga}(\text{OR})_3$  with  $\text{R} = \text{Me}$  or  $\text{Bu}^n$  and crystalline  $\text{Ga}(\text{OEt})_3$  samples prepared by anodic stripping, exchange reaction, or transesterification during boiling are not volatile, as opposed to [8]. However, amorphous gallium ethoxide samples prepared by transesterification at room temperature (they are loose, unlike microcrystalline powders) are volatile. In the mass spectrum of this product (Table 2, Fig. 4), there are ions whose compositions indicate an incomplete substitution of ethoxy for isopropoxy groups ( $\text{Ga}_4(\text{OEt})_n(\text{OPr}^i)_{12-n}^+$ ,  $n = 2, 3$ ); the other mass numbers correspond to  $\text{Ga}(\text{OEt})_3$  and are similar to those reported in [8]. High-mass ions were interpreted in [8] as resulting from the fragmentation of ortho species [ $\text{Ga}(\text{OEt})_3$ ]<sub>5-6</sub>. Comparing  $\text{Ga}(\text{OEt})_3$  spectra and the

$\text{Al}(\text{OEt})_3$  spectra in [22], we can infer that these polynuclear ions refer to oxo species  $\text{Ga}_6\text{O}_2(\text{OEt})_{13}^+$  and  $\text{Ga}_5\text{O}(\text{OEt})_{12}^+$ . The adequacy of this interpretation is validated by the nature of the fragmentation species (OR,  $\text{R}_2\text{O}$ , R), which are typical of mass spectra of metal alkoxides [13, 22–24].

Table 7. Bond lengths ( $\alpha$ ) and bond angles ( $\omega$ ) in the structure of  $\text{Ga}(\text{OEt})_3$

Bond	$d, \text{\AA}$	Bond	$d, \text{\AA}$
$\text{Ga}(1)^1\text{--O}(1)^4$	1.74(1)	$\text{Ga}(1)^1\text{--O}(2)^2$	2.00(2)
$\text{Ga}(1)^1\text{--O}(2)^1$	1.89(2)	$\text{Ga}(1)^1\text{--O}(3)^6$	2.01(2)
$\text{Ga}(1)^1\text{--O}(3)^5$	1.98(2)		
Angle	$\omega, \text{deg}$	Angle	$\omega, \text{deg}$
$\text{O}(3)^6\text{Ga}(1)^1\text{O}(2)^2$	176.8(9)	$\text{Ga}(1)^7\text{O}(1)^1\text{C}(2)^1$	134.8(15)
$\text{O}(3)^6\text{Ga}(1)^1\text{O}(3)^5$	101.4(8)	$\text{Ga}(1)^1\text{O}(2)^1\text{C}(4)^1$	126.6(15)
$\text{O}(3)^6\text{Ga}(1)^1\text{O}(2)^1$	79.7(9)	$\text{Ga}(1)^8\text{O}(3)^1\text{C}(6)^1$	123.8(14)
$\text{O}(3)^6\text{Ga}(1)^1\text{O}(1)^4$	94.5(8)	$\text{Ga}(1)^3\text{O}(2)^1\text{C}(4)^1$	120.3(15)
$\text{O}(2)^2\text{Ga}(1)^1\text{O}(3)^5$	77.7(8)	$\text{Ga}(1)^9\text{O}(3)^1\text{C}(6)^1$	136.0(14)
$\text{O}(2)^1\text{Ga}(1)^1\text{O}(2)^2$	97.6(9)	$\text{Ga}(1)^9\text{O}(3)^1\text{Ga}(1)^8$	99.3(8)
$\text{O}(2)^2\text{Ga}(1)^1\text{O}(1)^3$	88.4(9)	$\text{Ga}(1)^1\text{O}(2)^1\text{Ga}(1)^3$	102.7(9)
$\text{O}(3)^5\text{Ga}(1)^1\text{O}(2)^1$	108.7(9)	$\text{C}(1)^1\text{C}(2)^1\text{O}(1)^1$	114.4(16)
$\text{O}(3)^5\text{Ga}(1)^1\text{O}(1)^4$	125.7(9)	$\text{C}(3)^1\text{C}(4)^1\text{O}(2)^1$	111.1(17)
$\text{O}(2)^1\text{Ga}(1)^1\text{O}(1)^4$	125.2(9)	$\text{C}(5)^1\text{C}(6)^1\text{O}(3)^1$	111.2(17)

<sup>1</sup>  $x, y, z$ ; <sup>2</sup>  $1/2 + y, -1/2 + x, m - 1/2 + z$ ; <sup>3</sup>  $1/2 + y, -1/2 + x, 1/2 + z$ ; <sup>4</sup>  $3/2 - x, -1/2 + y, 3/2 - z$ ; <sup>5</sup>  $1 - y, x, 1 - z$ ; <sup>6</sup>  $1/2 + x, 1/2 - y, 3/2 - z$ ; <sup>7</sup>  $3/2 - x, 1/2 + y, 3/2 - z$ ; <sup>8</sup>  $y, 1 - x, 1 - z$ ; <sup>9</sup>  $-1/2 + x, 1/2 - y, 3/2 - z$ .

Table 6. Atomic coordinates in the structure of  $\text{Ga}(\text{OEt})_3$

Atom	$x$	$y$	$z$
Ga(1)	0.7055(2)	0.1593(2)	0.760(1)
O(1)	0.724(1)	0.594(1)	0.772(4)
O(2)	0.709(1)	0.243(1)	0.964(4)
O(3)	0.166(1)	0.385(1)	0.437(3)
C(1)	0.614(1)	0.527(1)	0.707(4)
C(2)	0.673(1)	0.555(2)	0.606(3)
C(3)	0.755(1)	0.373(1)	1.045(3)
C(4)	0.702(1)	0.322(2)	0.893(3)
C(5)	0.118(1)	0.497(1)	0.508(3)
C(6)	0.156(1)	0.454(2)	0.351(3)

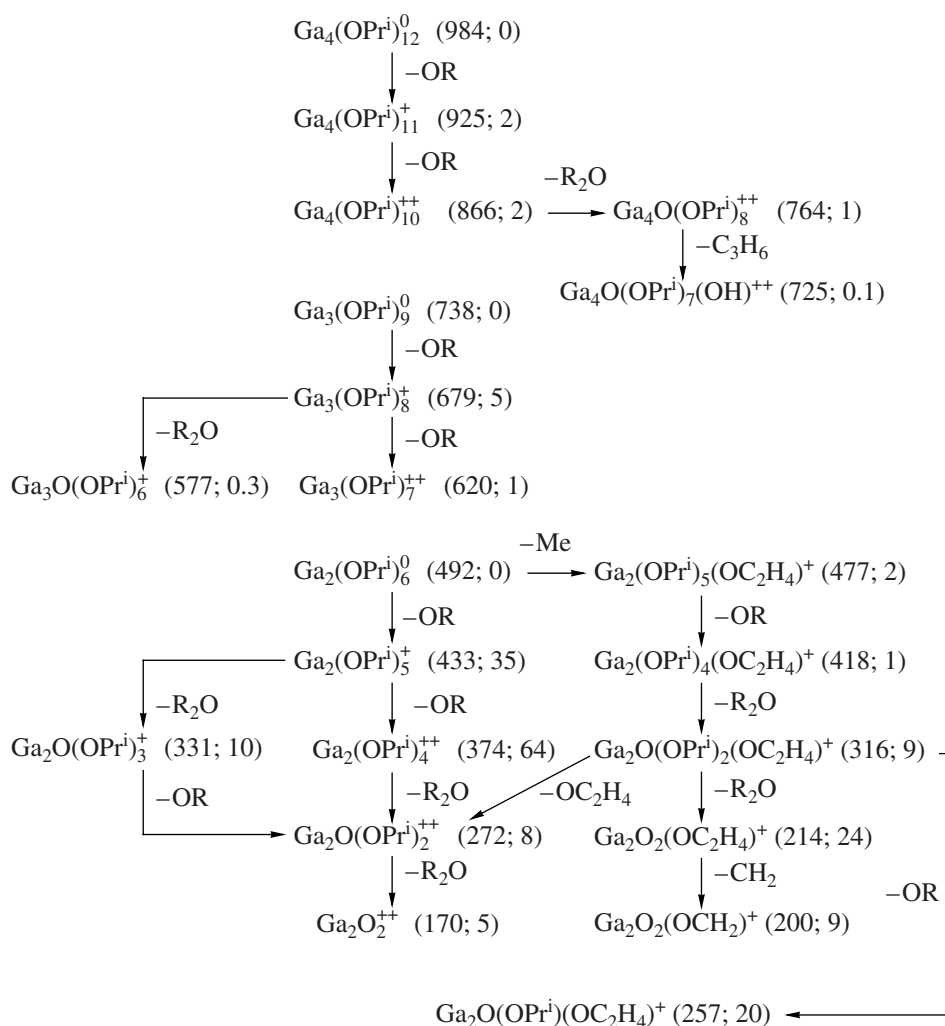


Fig. 3. Fragmentation in the mass spectrum of  $\text{Ga}(\text{OPr}^i)_3$ .

Freshly prepared  $\text{Ga}(\text{OPr}^i)_3$  enters the gas phase in the dimer form. Tetramer fragments appear in the spectrum of an aged sample (Fig. 3); this spectrum resembles that reported in [8]. The fragmentation character does not differ from that observed in the  $[\text{Al}(\text{OPr}^i)_3]_4$  spectrum [25].

Table 8.  $\text{Ga}(\text{OEt})_3$  solubility in EtOH

Point no.	$t$ , °C	$\text{Ga}(\text{OEt})_3$ concentration in solution, wt %
1	22	3.51
2	40	4.90
3	70	5.79
4	100	6.02
5	130	7.05
6	135	Decomposes

$\text{Ga}(\text{OMe})_3$ ,  $\text{Ga}(\text{OEt})_3$  (a freshly prepared transesterification product),  $\text{Ga}(\text{OPr}^i)_3$ , and  $\text{Ga}(\text{O}^n\text{Bu})_3$  samples were X-ray amorphous. The X-ray diffraction patterns for nonvolatile  $\text{Ga}(\text{OEt})_3$  powders (produced by either the exchange reaction of electrochemical synthesis) contain well-resolved peaks. The solution of this structure showed that it is built of polymer zigzag chains of trigonal bipyramids  $[\text{Ga}(\mu\text{-OEt})_{4/2}(\text{OEt})]_\infty$ . Axial atoms are  $\text{O}(3)^6$  and  $\text{O}(2)^2$ ; equatorial atoms are  $\text{O}(1)^4$ ,  $\text{O}(2)^1$ , and  $\text{O}(3)^5$  (Figs. 5, 6). Pentacoordinate gallium atoms are linked to one another via two pairs of  $(\mu\text{-OEt})_2$  bridges, each being formed by one axial group and one equatorial group; the fifth equatorial group  $\text{O}(1)^4$  is terminal. The latter forms the shortest bond with the metal atom (1.74(1) Å). The bridges lying in the equatorial plane (1.89(2) and 1.98(2) Å) are slightly shorter than the axial ones (2.00(2) and 2.01(2) Å). On the whole, the lengths of the terminal and bridging bonds in the  $\text{Ga}(\text{OEt})_3$  structure do not differ from those found in  $[\text{Ga}_5\text{O}(\text{OEt})_8\text{Cl}_5]$  and  $[\text{Ga}_{12}\text{O}_7(\mu\text{-OEt})_{10}\text{Cl}_{12}\text{Py}_4]\text{Py}$ ,



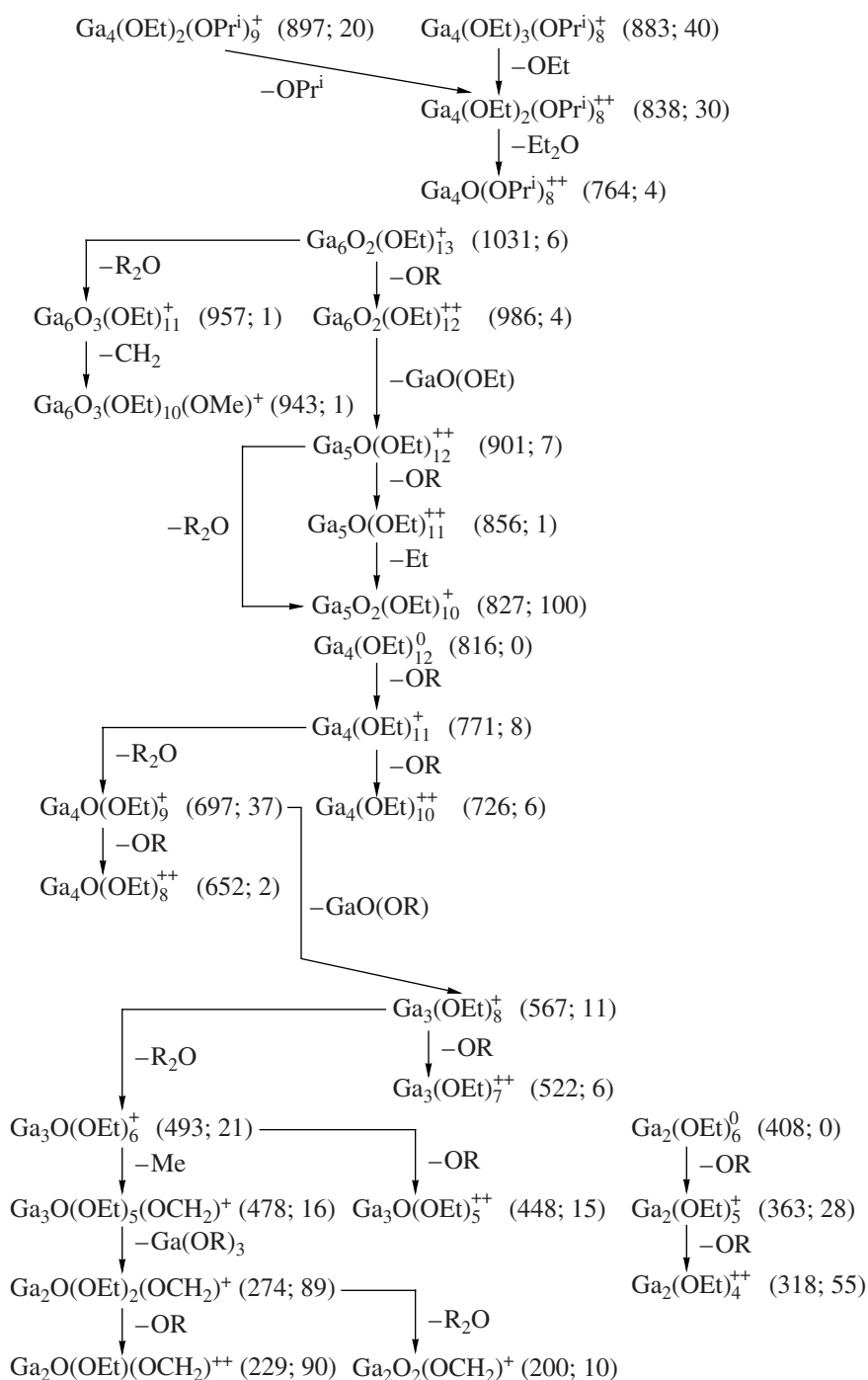


Fig. 4. Fragmentation in the mass spectra of  $\text{Ga}(\text{OEt})_3$  and the product of incomplete substitution of  $\text{EtOH}$  for  $\text{Ga}(\text{OPr}^i)_3$ .

which also contain trigonal bipyramids  $[\text{GaO}_5]$  [20]. A similar structure motif is known in the structure of 2-methoxyethanol, a zigzag polymer:  $[\text{Bi}_2(\mu, \eta^1\text{-OC}_2\text{H}_4\text{OMe})_4(\eta^1\text{-OC}_2\text{H}_4\text{OMe})_2]_\infty$  [26, 27]; however, metal coordination in this case is tetragonal-pyramidal.

Methoxides are virtually the only studied alkoxide structures with  $n$ -radicals described. The exceptions are

$[\text{Ti}(\text{OEt})_4]_4$  [28], cluster  $[\text{W}(\text{OEt})_4]_4$  [29], and poorly structured polymers  $[\text{M}(\text{OEt})_n]_\infty$  with  $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Pb},$  or  $\text{Ni}$  [30–32]. Ethoxy groups are mainly encountered in oxoalkoxides, in which they reside on the surface of  $[\text{M}_n\text{O}_m]$  aggregates [33].

Most of the structures studied are derivatives with branched and sterically crowded radicals, whose con-

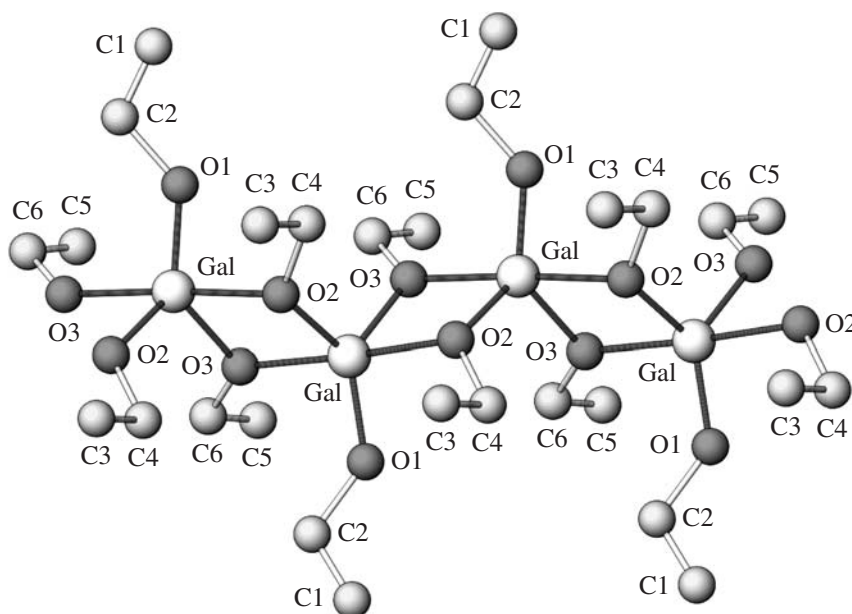


Fig. 5. Configuration of a fragment of a polymeric  $[\text{Ga}(\text{OEt})_{4/2}(\text{OEt})]_{\infty}$  structure.

figuration makes it possible to overcome the effect of hydrocarbon chain entangling. Most metal ethoxides are amorphous polymers. The presence of ortho- and oxoalkoxides species of various nuclearity in  $\text{Ga}(\text{OEt})_3$  samples is another example of what we call coordina-

tion polymerism [13]. This phenomenon, in particular known for aluminum alkoxides and manifested as wide variations in the physical state, melting point, gas-transition temperature, solubility, and other physicochemical parameters, is associated with the history of the sample: synthesis temperature, the solvent from which it was separated, aging time, and other parameters.

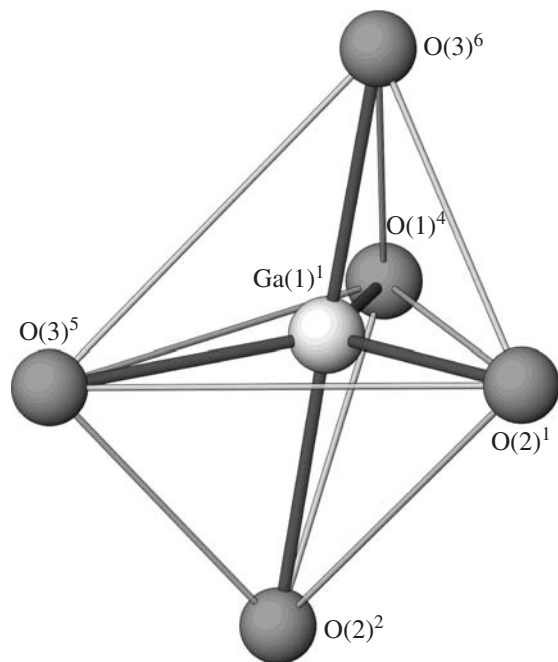


Fig. 6. Coordination polyhedron about a Ga atom in the  $[\text{Ga}(\text{OEt})_3]_{\infty}$  structure.

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