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Oxoethoxide Chlorides – Representatives of Oligonuclear Alkoxide Complexes of Gallium: Penta- and Dodecanuclear Molecules

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Metathesis of solid $GaCl_3$ with NaOEt/EtOH (1:3) provided, after separation of the NaCl precipitate, a solution containing oxoalkoxide chloride complexes of gallium. Residues from evacuation of the latter were redissolved in either toluene/MeCN (solution 1) or toluene/pyridine (solution 2). Storage of the first solution provided crystals of $Ga_5(\mu_5\text{-O})(\mu\text{-OEt})_8Cl_5$ (**1**), and of the second solution – $[Ga_{12}(\mu_4\text{-O})_2(\mu_3\text{-O})_5(\mu\text{-OEt})_{10}Cl_{12}Py_4]Py$ (**2**), both at room temperature and in relatively high yields. Compound **1** crystallizes as a vertically contracted tetragonal pyramid with the μ_5-O ligand situated in the center of the equatorial plane defined by four trigonal bipyramidal coordinated gallium atoms. The axial Ga atom has octahedral coordination. All eight edges of the pyramid are capped by μ-OEt groups, and all the chloride ligands are situated in terminal positions. Crystals of $[Ga_{12}(\mu_4\text{-O})_2(\mu_3\text{-O})_5(\mu\text{-OEt})_{10}Cl_{12}Py_4]Py$ (**2**) contain two $[Ga_5(\mu_4\text{-O})(\mu_3\text{-O})_2(\mu\text{-OEt})_5Cl_5Py]$ fragments connected through a cyclic $[Ga_4(\mu_3\text{-O})_5Cl_2Py_2]$ unit with a μ_3-O ligand in its center. Of the metal atoms, three possess tetrahedral, seven trigonal bipyramidal, and two octahedral coordination. The mass spectrum of **1** contains penta- and tetranuclear fragments. The spectrum of **2** contains heptameric fragments in addition to the pentanuclear fragments that are analogous to those in the spectrum of **1**. The factors leading to formation of polymeric $M(OR)_n$ and related oligonuclear oxocomplexes are discussed.

Introduction

The present interest to organic derivatives of gallium is related to the possibilities of their application as precursors of a series of complex oxide materials applied as gas sensors,[1,2] luminophores,[3] and solid electrolytes, on the one hand, and M^{II}-doped $LaGaO_3$[4] and catalysts with zeolyte-type structures on the other hand.[5] The oligonuclear molecular complexes of gallium are also very attractive as close structural analogs, diamagnetic models, and potential reagents for tuning the magnetic moment of the oligonuclear complexes of iron(III) for applications in the field of molecular electronics.[6] It appeared extremely interesting to get closer insight into the chemistry of gallium alkoxide complexes in view of their earlier postulated rendered kinetics (slow reaction rates in ligands exchange and core rearrangements) and polymerism (coexistence of different oligomers with the same chemical composition) in contrast to kinetically unhindered iron(III) alkoxides.[7]

Among the synthetic approaches to gallium alkoxides described in the literature, a considerable emphasis has always been put on the metathesis of gallium chloride with alkali alkoxides.[8–12] Our attempts to reproduce the proposed techniques, in particular those described for the synthesis of $Ga(OEt)_3$, led consequently to rather low yields of the desired products.[13]

In the present work we report the isolation of the products of interaction of solid $GaCl_3$ with a solution of NaOEt in ethanol (taken in the stoichiometric 1:3 ratio) and their structural characterization.

Results and Discussion

Repeated trials of the metathesis of $GaCl_3$ with sodium ethoxide in 1:3 ratio according to the techniques proposed in refs.[10–11] for the synthesis of $Ga(OEt)_3$ resulted in the following observations: (1) Alcoholysis of the solid $GaCl_3$ – a quite strong Lewis acid – resulted, to a certain extent, in the evolution of hydrogen chloride, HCl, which reacted in turn with the alcohol (a process catalyzed by MCl_n) with the release of water; this resulted in the presence of oxo-derivatives in the reaction products.[13] (2) The stability of gallium oxoalkoxide halides is so high that even prolonged heating of the reaction mixture at reflux was unable to achieve their decomposition (the amount of NaCl precipitate constitutes only about 80% of the theoretically calculated yield).

It is important to mention that when a toluene solution of $GaCl_3$ is applied as the reagent in metathesis (i.e., by reducing the extent of the alcoholysis side reaction[13]), the process resulted in the formation of insoluble polymeric *or-*

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tho-ethoxide $Ga(OEt)_3$, which displayed a layered $[Ga(OEt)_{4/2}(OEt)]_\infty$ structure.[14] Oxo complexes are most often more soluble due to their oligonuclear molecular structure.

Preparation of a crystalline sample suitable for single-crystal X-ray studies could be achieved only with the use of polar organic solvents such as acetonitrile or pyridine. Crystals of $Ga_5(\mu_5\text{-}O)(\mu\text{-}OEt)_8Cl_5$ (**1**) were formed from solution after 5 months of storage. Crystals of **1** comprise a flattened tetragonal pyramid of metal atoms, Ga_5, with an octahedrally coordinated metal atom $[Ga(\mu_5\text{-}O)(\mu\text{-}OEt)_4Cl]$ in the axial position and the trigonal bipyramidal coordinated ones $[Ga(\mu_5\text{-}O)(\mu\text{-}OEt)_3Cl]$ in the equatorial plane of the pyramid. A pentadentate oxo group is situated in the center of the pyramid, and all its edges are capped by eight μ-OEt groups. Four shorter bridges are placed between the apical hexacoordinate metal atom and the equatorial metal atoms (designated as $^{(5-6)}$ in Table 1), and the other four longer bridges bind the trigonal bipyramidal coordinated Ga atoms together in the equatorial plane (designated as $^{(5-5)}$ in Table 1), see Figure 1. The bonding parameters for **1** are practically identical to those of its structural analogs – derivatives of aluminium and iron(III),[15–19] see Table 1. The only (minor) difference between the compounds presented in Table 1 lies in the position of the μ_5-O group: in **1** and $Fe_5O(OEt)_8(OEt)_5$[7,16] the oxo atom lies practically within the equatorial plane [the sums of the M^5–(μ_5-O)–M^5 angles are 356.3 and 357.5°, respectively, which corresponds to only ca. 0.02 Å distance from the μ_5-O ligand to the equatorial plane]. The same type of μ_5-O ligand placement can in fact be observed for the tetragonal pyramidal isopropoxide $M_5(\mu_5\text{-}O)(\mu_3\text{-}OR)_4)(\mu\text{-}OR)_4(OR)_5$ (M = In, Sc, Y, Ln) complexes, where all metal atoms are octahedrally coordinated and the alkoxide groups, which are situated between the axial and the equatorial metal atoms, are they cap the faces of the pyramid instead of the edges.[20–25]

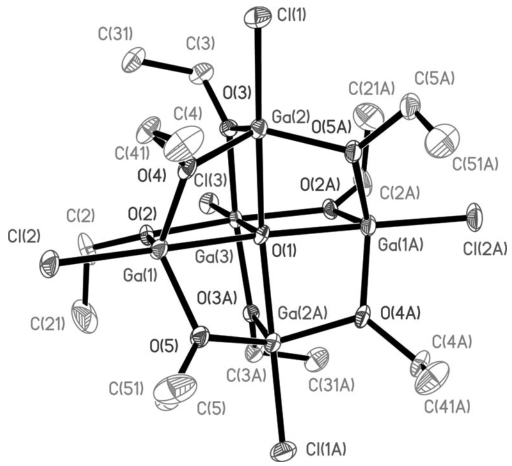

Figure 1. Molecular structure of $Ga_5(\mu_5\text{-}O)(\mu\text{-}OEt)_8Cl_5$ (**1**).

In the other molecules presented in Table 1, the sums of the equatorial angles at the μ_5-O groups are ca. 331°, which corresponds to its distance to the equatorial plane of about 0.22 Å. An interesting peculiarity of all the compared structures is that the length of the bond between the μ_5-O ligand and the axial, hexacoordinate, metal atom is considerably shorter than between this ligand and the pentacoordinate equatorial metal atoms, for gallium – 1.931(11) and 2.162(3) Å, respectively. This fact confirms that the central oxo atom is really involved in five bonds, and it is truly pentacoordinate. The values of the M–(μ-OC) angles in **1** (124.2–129.6°), as well as the corresponding angles for the alkoxide bridging groups in the other molecules in this fam-

Table 1. Comparison of the bonding parameters in the $[M_5(\mu_5\text{-}O)(\mu\text{-}OR)_8X_5]$ molecules (M^6 – octahedral coordinated, M^5 – trigonal bipyramidal coordinated). The molecules with closely related structures have recently been envisaged for a series of other alkoxides of iron(III) – $Fe_5O(OR)_{13}$ (R = *n*Pr, *i*Pr, *i*Bu, CH_2CF_3), and also $Fe_5O(OiPr)_{12}Cl$.[19]

	$Ga_5O(OEt)_8Cl_5$ (**1**)	$Fe_5O(OiPr)_8Cl_5$,[15] $Fe_5O(OEt)_8(OEt)_5$,[7,16] $Fe_5O(OEt)_8(OSiEt)_5$[17]	$Al_5O(OiBu)_{13}$[18]
M^6–(μ_5-O)	1.931	2.194–2.005	1.89
M^5–(μ_5-O)	2.162	2.159–2.205	2.08
M^6–μ-O(R)	1.999–2.010	2.021–2.062	1.96
M^5–μ-O(R) $^{(5-6)}$	1.859–1.862	1.887–1.926	1.80
M^5–μ-O(R) $^{(5-5)}$	1.873- 1.883	1.909–1.957	1.83
M^6–X term	2.198 (Cl)	2.243 (Cl); 1.829 (OR),	1.73 (OR)
M^5–X term	2.182–2.190 (Cl)	2.231 (Cl); 1.756–1.806 (OR)	1.72 (OR)
(μ_5-O)–M^6–μ-O(R)	79.6–80.0	78.4–79.6	79.21
(μ_5-O)–M^5–μ-O(R)	77.0–78.2; 160.1	77.9–79.1; 177.7–178.5	77.6–78.7
μ-(R)O–M^6–μ-O(R)	86.5–89.9; 159.1	87.7–88.0; 157.7–158.1	88.0; 158.4
μ-(R)O–M^5–μ-O(R) $^{(5-6)}$	114.8–109.2	111.2–112.3; 124.43	110.4–115.2
μ-(R)O–M^5–μ-O(R) $^{(5-5)}$	121.3–122.3	118.6–125.1; 117.55	122.6
(μ_5-O)–M^6–X term	180.0 (Cl)	179.0 (OR); 180 (Cl)	180.0
(μ_5-O)–M^5–X term	178.0–180.0 (Cl)	177.7–178.5 (OR); 174.0(Cl)	176.5
μ-(R)O–M^6–X term	100.0–100.4 (Cl)	99.4–101.9 (OR, Cl)	100.8
μ-(R)O–M^5–X term	101.1–104.9 (Cl)	101.5 (OR); 102.40 (Cl)	101.3
M^6–(μ_5-O)–M^5	97.1–97.5	95.6 –96.9	97.3
M^5–(μ_5-O)–M^5	88.60–89.55; 165.0–165.8	89.1–90.5; 164.8–167.2	89.09; 165.5
M^6–(μ-OR)–M^5	105.0–105.8	95.6–96.3; 103.61–106.5	105.6
M^5–(μ-OR)–M^5	108.3	88.8–90.5; 103.07–105.7	105.7
M^6–(μ-O)–C	128.3–129.6	121.3–125.2	128.9
M^5–(μ-O)–C	124.2–126.6	123.7–126.2	124.1–126.3

ily, indicate certain contribution of the d_π–p_π interaction and predominantly sp^2 hybridization for the oxygen atoms according to the well-established structural correlations.[13]

According to the mass spectrometric data, molecules of **1** are present in the gas phase (Figure 2) and are relatively stable to all types of decomposition (by chemical means on evaporation and also by electron impact – the fragmentation series for the pentanuclear species is the most intense in the spectrum). The major alternative in the decomposition of **1** on evaporation is provided by the loss of a Ga(OEt)$_2$Cl molecule, which should lead to a symmetric tetrahedral Ga$_4$O(OEt)$_6$Cl$_4$ molecule, unknown in the condensed phase, but represented by its own fragmentation series in the mass spectrum. The first ion in the series is formed by further loss of a terminal chloride ligand from this molecule, Ga$_4$O(OEt)$_6$Cl$_3^+$. It is interesting to note that the most intense ion in the mass spectrum of iron(III) ethoxide is Fe$_4$O(OEt)$_9^+$ [*m*/*z* (%) = 645 (100)], which possesses most probably a symmetric tetrahedral structure of the same type containing nine ethoxide ligands in addition to the oxo one.[7] Further fragmentation is associated with the loss of two more ethoxide ligands apparently with conservation of the close-packed structure (Figure 3). The formation of the close-packed structures is very characteristic of the molecular alkoxide aggregates even in the solid state and in solution.[26,27] The ionization in a mass-spectrometric experiment occurs by collision of the sample with an electron beam with the energy of 70 eV (about 675 KJ mol^{-1}). This transfers the molecule into a virtual state, where all metal atoms, in a molecule such as **1** that has relatively high symmetry, become equivalent. The energy is then released through ionization and loss of a fragment. The structure of the formed ion corresponds to the energy minimum for the residual fragment, which is achieved by dense packing of the metal cations and residual donor atoms.

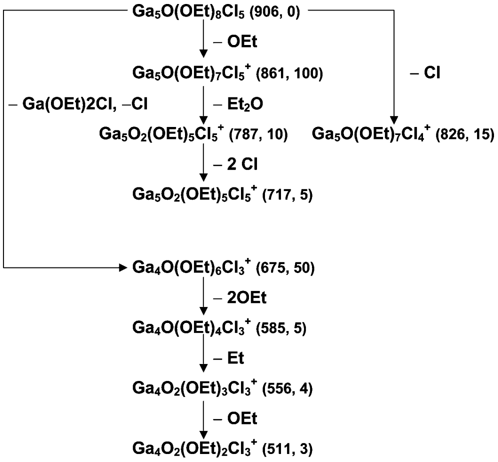

Figure 2. Mass-spectral fragmentation scheme for **1**.

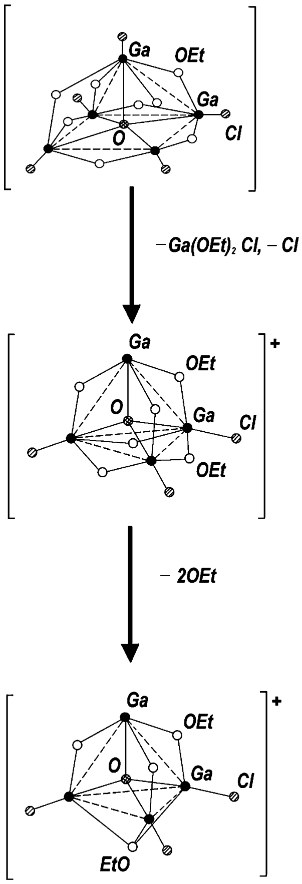

Figure 3. Partial decomposition of **1** in the gas phase.

The crystal structure of compound **2**, obtained from solutions of reaction products in toluene/pyridine, contains noncentrosymmetric dodecanuclear [Ga$_{12}$(μ_4-O)$_2$(μ_3-O)$_5$(μ-OEt)$_{10}$Cl$_{12}$Py$_4$] molecules and additional interstitial pyridine molecules in the cavities of the packing. The dodecanuclear molecules are constituted by two [Ga$_5$(μ_4-O)(μ_3-O)$_2$(μ-OEt)$_5$Cl$_4$Py] fragments connected to each other by a ClGaOpy unit (Figure 4). The molecule contains two octahedrally coordinated metal atoms, Ga8 and Ga9, seven trigonal bipyramidal coordinated Ga atoms – (number 1, 2, 3, 6, 10, 11, and 12), and also three tetrahedral coordinated ones. Two of the latter display a practically regular tetrahedral geometry, Ga4 and Ga7, and the third one is considerably distorted, Ga5, in the center of the molecule. Of the seven oxo groups, the two tetradentate ones, O1 and O7, have distorted tetrahedral coordination, and the four tridentate ones, O4, O6, O2, O8, are practically planar with the sums of the bonding angles of about 358°; the fifth oxo ligand, O5, in the center of the molecule has a pyramidal coordination (valence angle sum 335.6° in the [OGa$_3$] fragment). All OEt groups are bidentate. In the center of each pentanuclear fragment one can find a planar tetragonal fragment, (Ga2–O7–Ga9–O9) and Ga1–O1–Ga8–O3), respectively.

The bond lengths of the Ga–O(oxo) fragments are independent of the coordination number of the metal atom and are determined exclusively by the bonding mode of the oxo groups. Thus, the tetradentate oxygen atoms O1 and O7 form two longer [2.037–2.367(16) Å] and two shorter bonds [1.858–2.007(16) Å]. The length of the latter is of the same order of magnitude as for the tridentate oxygen atoms O4,

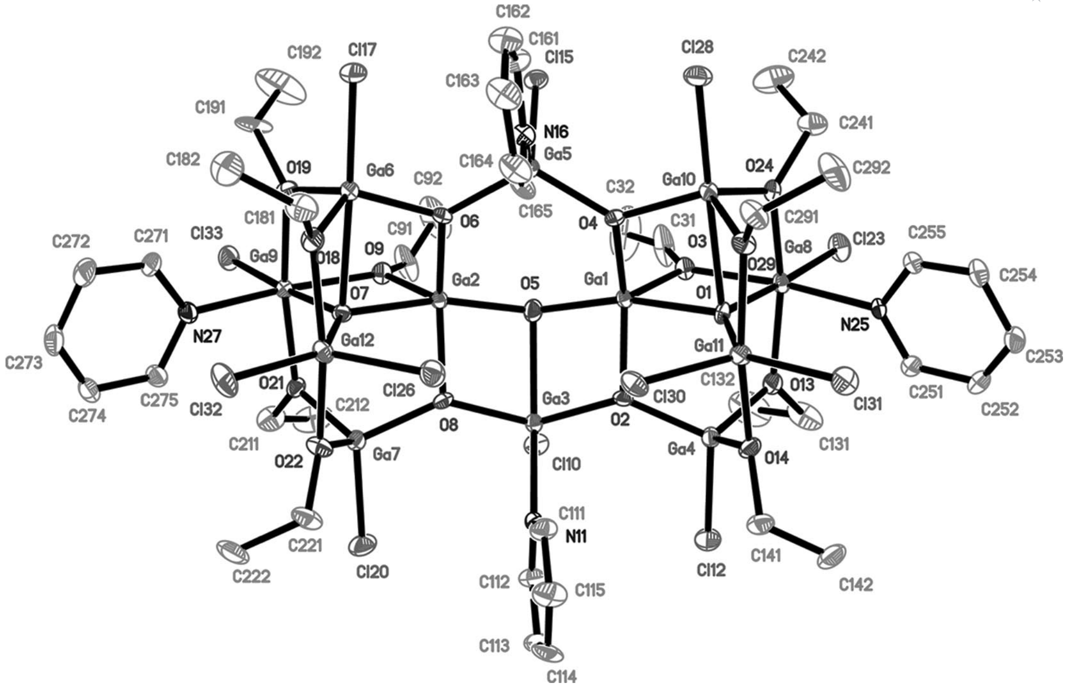

Figure 4. Molecular structure of $Ga_{12}(\mu_4\text{-}O)_2(\mu_3\text{-}O)_5(\mu\text{-}OEt)_{10}Cl_{12}Py_4$ (**2**).

O6, O2, O8–Ga [1.812–1.933(16) Å]. The only exclusion is represented by one of the bonds involving the central tridentate oxygen atom in the molecule, O5–Ga3 [2.161(18) Å]. The lengths of the Ga–(μ-OEt) bridges are within the interval 1.804–2.048(17) Å, and the distances to the terminal chloride ligands Ga–Cl is 2.113–2.236(8) Å, again independently of the coordination number of the metal atom. Only the distance to the terminal nitrogen atoms increases considerably from tetrahedral to octahedral coordination from 2.01(2) to 2.236(9) Å.

The first ions in the mass spectrum of **2** – $Ga_7O_5(OEt)_3Cl_7^+$ $Ga_7O_5(OEt)_2Cl_7^{++}$ – belong to the heptanuclear fragment and correspond to the loss of a pentanuclear core from the original molecule. The light ions correspond to those observed in the spectrum of **1**. It can be explained both by easy fragmentation of **2** into two structural fragments – pentanuclear and heptanuclear – but even possibly by partial decomposition on evaporation with formation of more volatile compound **1**.

The structure of **2** is closely related to the other chemically related oxoalkoxo complexes of aluminium and iron(III) – $[Fe_9O_3(OEt)_{21}]\cdot EtOH$,[28] $[Al_{10}O_4(OEt)_{22}]$,[29] and $[Al_{11}O_6(OnPr)_{10}(OiPr)_{10}(OR)(ROH)_2]$,[30] which have pentanuclear cores connected to each other through a common $[M(\mu_3\text{-}O)(\mu\text{-}OR)]$ edge or through central $[Al_2(\mu_3\text{-}O)_2]$ or $[Al(OR)(\mu\text{-}O)_2(\mu_3\text{-}O)_2]$[31] units (Figure 5). All the abovementioned molecules contain tetrahedral $[(\mu_4\text{-}O)M_4]$ groups, to which an additional fifth metal atom is connected through oxo- or alkoxo bridges. In **2** these additional atoms, Ga4 and Ga7, are attached to the tetrahedral one through two μ-OR groups O13, O14 and O21, O22 and one μ_3-O group O2 and O8, respectively.

Gallium oxoalkoxides were synthesized in this work for the first time, but they definitely show close structural relationship to the derivatives of aluminium and iron. Easy transformations on evaporation trace a closer relationship

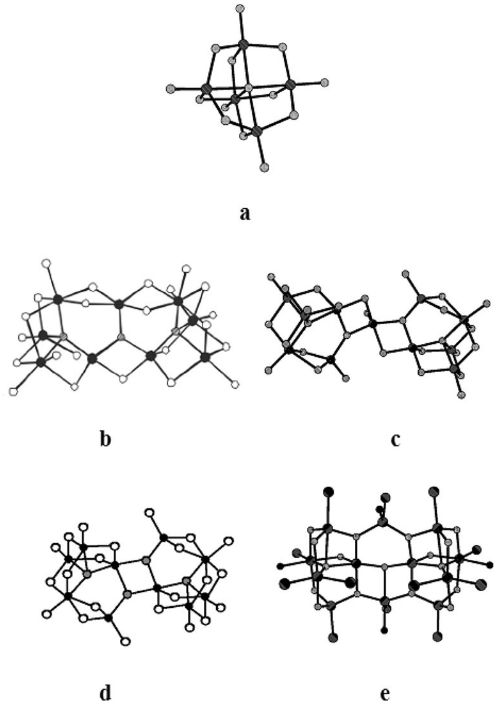

Figure 5. Comparison of the metal–ligand cores in the molecules of the penta-, nona- deca-, undeca-, and dodecanuclear oxoalkoxides: (a) $Fe_5O(OEt)_{13}$[7] or $Ga_5O(OEt)_8Cl_5$ (**1**); (b) $[Fe_9O_3(OEt)_{21}]\cdot EtOH$;[28] (c) $Al_{10}O_4(OEt)_{22}$;[29] (d) $Al_{11}O_6(OnPr)_{10}(OiPr)_{10}(OR)(ROH)_2$;[30] and (e) $Ga_{12}O_7(OEt)_{10}Cl_{12}Py_4$ (**2**).

to the derivatives of iron(III) and thus less kinetically hindered reactivity. The rearrangements of the gallium complexes appear to occur easily and follow the solution equilibria. It opens a way to potential new classes of gallium–iron(III) molecular aggregates, which are attractive for molecular electronic applications.[6]

Experimental Section

All manipulations were carried out under a dry nitrogen atmosphere by using Schlenk techniques or in a glove box. Anhydrous $GaCl_3$ was purchased from Aldrich and used as received. Ethanol was dried by refluxing over $Ca(OEt)_2$ with subsequent distillation, and toluene was distillation from Na and $LiAlH_4$. Mass spectra were recorded with a JEOL JMS-SX/SX-102A mass spectrometer by applying electron beam ionization (U = 70 eV) with direct-probe introduction. The reported masses of the ions were calculated for the ^{71}Ga isotope. IR spectra were registered with a Perkin–Elmer Spectrum 100 instrument (as nujol or hexachlorobutadiene mulls). ^1H NMR spectra were recorded in $CDCl_3$ solutions with a Bruker 400 MHz instrument at room temperature.

Synthetic Procedure: Sodium metal (1.22 g, 53 mmol) was dissolved in EtOH (27 mL) at room temperature. An solid $GaCl_3$ (2.85 g, 16.0 mmol) was then added to the solution. The process was strongly exothermic and accompanied by the evolution of visible amounts of HCl "mist" that was subsequently consumed by redissolution in the reaction mixture. The mixture was then heated at reflux for 5–6 h and then finally left for precipitation of NaCl (2.39 g, 41 mmol) overnight. The clear solution was removed by syringe, and the solvents were evaporated to dryness in vacuo. The residual solid was very sparingly soluble in toluene or alcohol even

Table 2. Crystal data and details of diffraction experiments for compounds **1** and **2**.

	1	**2**
Empirical formula	$C_{16}H_{40}Cl_5Ga_5O_9$	$C_{50}H_{80}Cl_{12}Ga_{12}N_5O_{17}$
M	902.33	2299.24
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/n$
a [Å]	21.758(17)	20.378(11)
b [Å]	9.519(8)	22.127(13)
c [Å]	19.221(16)	20.490(12)
α [°]	90	90
β [°]	121.733(14)	107.176(15)3
γ [°]	90	90
V [Å^3]	3386(5)	8827(9)
Z	4	4
Independent reflections	1696 [R(int) = 0.0417]	8405 [R(int) = 0.0882]
Goodness-of-fit on F^2	0.999	1.019
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0645, wR_2 = 0.1573	R_1 = 0.0691, wR_2 = 0.1488

Table 3. Selected bond lengths [Å] and angles [°] for $Ga_5O(OEt)_8Cl_5$ (**1**).[a]

Ga1–O2	1.859(9)	Ga2–O4	1.883(8)	Ga3–O2	2.010(8)
Ga1–O5	1.873(8)	Ga2–O1	2.161(3)	Ga3–O2#1	2.010(8)
Ga1–O4	1.874(9)	Ga2–Cl1	2.182(4)	Ga3–Cl3	2.198(5)
Ga1–O1	2.162(3)	Ga3–O1	1.931(11)	O1–Ga2#1	2.161(3)
Ga1–Cl2	2.190(4)	Ga3–O3	1.999(7)	O1–Ga1#1	2.162(3)
Ga2–O3	1.862(8)	Ga3–O3#1	1.999(7)	O5–Ga2#1	1.882(8)
Ga2–O5#1	1.882(8)				
O2–Ga1–O5	110.6(4)	O1–Ga2–Cl1	178.0(3)	Ga3–O1–Ga1#1	97.1(3)
O2–Ga1–O4	114.8(4)	O1–Ga3–O3	79.6(2)	Ga2–O1–Ga1#1	89.55(9)
O5–Ga1–O4	121.3(4)	O1–Ga3–O3#1	79.6(2)	Ga2#1–O1–Ga1#1	88.60(9)
O2–Ga1–O1	77.8(4)	O3–Ga3–O3#1	159.1(5)	Ga3–O1–Ga1	97.1(3)
O5–Ga1–O1	77.2(3)	O1–Ga3–O2	80.0(2)	Ga2–O1–Ga1	88.60(9)
O4–Ga1–O1	78.2(3)	O3–Ga3–O2	86.5(3)	Ga2#1–O1–Ga1	89.55(9)
O2–Ga1–Cl2	103.0(3)	O3#1–Ga3–O2	89.9(3)	Ga1#1–O1–Ga1	165.8(6)
O5–Ga1–Cl2	102.8(3)	O1–Ga3–O2#1	80.0(2)	Ga1–O2–Ga3	105.0(4)
O4–Ga1–Cl2	101.1(3)	O3–Ga3–O2#1	89.9(3)	Ga1–O4–Ga2	107.0(4)
O1–Ga1–Cl2	179.1(3)	O3#1–Ga3–O2#1	86.5(3)	Ga1–O5–Ga2#1	108.3(4)
O3–Ga2–O5#1	114.7(4)	O2–Ga3–O2#1	160.1(5)	C2–O2–Ga1	125.3(9)
O3–Ga2–O4	109.2(4)	O1–Ga3–Cl3	180.000(2)	C2–O2–Ga3	128.3(9)
O5#1–Ga2–O4	122.1(4)	O3–Ga3–Cl3	100.4(2)	C3–O3–Ga2	124.2(7)
O3–Ga2–O1	77.0(4)	O3#1–Ga3–Cl3	100.4(2)	C3–O3–Ga3	129.6(8)
O5#1–Ga2–O1	77.0(3)	O2–Ga3–Cl3	100.0(2)	Ga2–O3–Ga3	105.8(4)
O4–Ga2–O1	78.0(3)	O2#1–Ga3–Cl3	100.0(2)	C4–O4–Ga1	126.6(9)
O3–Ga2–Cl1	104.9(3)	Ga3–O1–Ga2	97.5(3)	C4–O4–Ga2	124.9(8)
O5#1–Ga2–Cl1	101.6(3)	Ga3–O1–Ga2#1	97.5(3)	C5–O5–Ga1	125.2(8)
O4–Ga2–Cl1	101.7(3)	Ga2–O1–Ga2#1	165.0(6)	C5–O5–Ga2#1	125.3(7)

[a] Symmetry transformations used to generate equivalent atoms: #1: –x, y, $-z$ + 1/2.

on reflux. Its suspension in 3 mL of toluene was separated into a solution fraction and a sediment.

The sediment was treated with a mixture of MeCN (3 mL) and toluene (3 mL), which provided a dark-red solution that slowly lost its color on storage to produce colorless crystals of **1** with practically quantitative yield after 5 months. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.22 (q, *J* = 6.5 Hz, 16 H, H-CH_2), 1.26 (t, *J* = 6.0 Hz, 24 H, H-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 59.6 (C-CH_2), 16.6 (C-CH_3) ppm. The presence of only one signal for each type of carbon or hydrogen atom indicates rather quick exchange under these conditions. IR (nujol): $\tilde{\nu}$ = 1302 (m), 1166.09 (m), 1093.74 (w), 1034.10 (w), 897.12 (w), 601.19 (w), 467.94 (m), 427.16 (m) cm^{-1}. MS: *m*/*z* (%) = 861(100) $[Ga_5O(OEt)_7Cl_5]^+$, 826 (15) $[Ga_5O(OEt)_7Cl_4]$, 787 (10) $[Ga_5O_2(OEt)_5Cl_5]^+$, 717 (5) $[Ga_5O_2(OEt)_2Cl_3]^+$, 675 (50) $[Ga_4O(OEt)_6Cl_3]^+$, 585 (5) $[Ga_4O(OEt)_4Cl_3]^+$,

Table 4. Selected bond lengths [Å] and angles [°] for $[Ga_{12}O_7(OEt)_{10}Cl_{12}Py_4]2Py$ (**2**).

Ga1–O3	1.82(2)	Ga2–O9	1.897(18)	Ga11–O1	1.878(18)
Ga1–O5	1.861(17)	Ga2–O5	1.861(19)	Ga11–O14	2.021(18)
Ga1–O2	1.891(15)	Ga2–O8	1.916(16)	Ga11–O29	2.041(18)
Ga1–O4	1.929(15)	Ga2–O6	1.940(15)	Ga11–Cl30	2.189(9)
Ga1–O1	2.076(16)	Ga2–O7	2.039(18)	Ga11–Cl31	2.208(9)
Ga4–O2	1.816(17)	Ga7–O8	1.816(17)	Ga3–O2	1.882(16)
Ga4–O13	1.88(2)	Ga7–O21	1.868(18)	Ga3–O5	2.176(19)
Ga4–O14	1.832(19)	Ga7–O22	1.80(2)	Ga3–O8	1.865(17)
Ga4–Cl12	2.170(8)	Ga7–Cl20	2.174(9)	Ga3–N11	2.01(2)
Ga10–O4	1.880(17)	Ga6–O6	1.804(17)	Ga3–Cl10	2.184(8)
Ga10–O1	2.367(17)	Ga6–O7	2.350(16)	Ga12–O7	1.858(18)
Ga10–O29	1.810(19)	Ga6–O18	1.82(2)	Ga12–O22	2.025(19)
Ga10–O24	1.799(19)	Ga6–O19	1.912(19)	Ga12–O18	2.052(19)
Ga10–Cl28	2.192(8)	Ga6–Cl17	2.208(9)	Ga12–Cl26	2.193(9)
Ga8–O1	1.970(18)	Ga9–O7	2.004(18)	Ga12–Cl32	2.172(10)
Ga8–O3	1.992(19)	Ga9–O9	2.041(19)	Ga5–O4	1.797(17)
Ga8–O13	2.032(18)	Ga9–O21	1.980(16)	Ga5–O6	1.860(16)
Ga8–O24	1.988(18)	Ga9–O19	2.044(17)	Ga5–N16	2.01(2)
Ga8–N25	2.13(2)	Ga9–N27	2.10(2)	Ga5–Cl15	2.111(8)
Ga8–Cl23	2.219(9)	Ga9–Cl33	2.237(9)		
O3–Ga1–O1	78.7(8)	N25–Ga8–Cl23	91.1(7)	N27–Ga9–Cl33	92.8 (7)
O5–Ga1–O1	163.5(8)	O9–Ga2–O7	81.3(8)	O1–Ga11–O29	81.5(7)
O3–Ga1–O2	106.0(8)	O5–Ga2–O7	162.5(8)	O14–Ga11–O29	161.9(8)
O2–Ga1–O4	144.6(8)	O9–Ga2–O8	104.5(7)	O1–Ga11–Cl30	112.1(6)
O5–Ga1–O2	81.5(8)	O8–Ga2–O6	146.5(8)	O14–Ga11–Cl30	98.0(6)
O3–Ga1–O4	104.8(8)	O5–Ga2–O8	81.1(8)	O29–Ga11–Cl30	96.5(6)
O3–Ga1–O5	114.4(9)	O9–Ga2–O6	104.6(8)	O1–Ga11–Cl31	134.7(6)
O5–Ga1–O4	101.2(8)	O5–Ga2–O9	113.6(8)	O14–Ga11–Cl31	92.2(6)
O2–Ga4–O14	112.1(8)	O5–Ga2–O6	101.8(7)	O29–Ga11–Cl31	92.0(6)
O2–Ga4–O13	111.8(8)	O22–Ga7–O8	108.6(8)	Cl30–Ga11-Cl31	113.2(4)
O14–Ga4–O13	108.0(9)	O8–Ga7–O21	110.8(8)	O1–Ga11–O14	83.1(8)
O2–Ga4–Cl12	110.5(6)	O22–Ga7–O21	109.8(9)	O8–Ga3–O2	131.9(7)
O14–Ga4–Cl12	108.1(6)	O8–Ga7–Cl20	110.3(6)	O2–Ga3–O5	73.9(7)
O13–Ga4–Cl12	106.1(6)	O22–Ga7–Cl20	108.5(7)	O8–Ga3–O5	74.4(7)
O4–Ga10–O1	77.4(6)	O21–Ga7–Cl20	108.8(6)	O2–Ga3–N11	94.7(8)
O29–Ga10–O4	113.1(8)	O6–Ga6–O7	76.8(6)	N11–Ga3–O5	150.2(9)
O24–Ga10–O4	114.5(8)	O6–Ga6–O18	112.8(9)	O8–Ga3–N11	95.3(8)
O29–Ga10–O1	74.3(7)	O6–Ga6–O19	116.1(8)	O2–Ga3–Cl10	112.1(6)
O24–Ga10–O1	72.8(7)	O18–Ga6–O7	73.9(7)	O5–Ga3–Cl10	107.2(6)
O29–Ga10–O24	112.6(9)	O19–Ga6–O7	77.2(7)	O8–Ga3–Cl10	111.2(6)
O29–Ga10–Cl28	104.6(6)	O18–Ga6–O19	114.2(9)	N11–Ga3–Cl10	102.6(7)
Cl28–Ga10–O1	178.7(5)	O6–Ga6–Cl17	104.9(6)	O7–Ga12–O22	82.5(8)
O24–Ga10–Cl28	107.2(6)	Cl17–Ga6–O7	178.3(5)	O7–Ga12–O18	80.9(8)
O24–Ga10–Cl28	103.7(6)	O18–Ga6–Cl17	105.4(7)	O22–Ga12–O18	160.4(9)
O1–Ga8–O3	77.5(8)	O19–Ga6–Cl17	101.8(6)	O7–Ga12–Cl26	108.1(6)
O1–Ga8–O13	85.2(8)	O7–Ga9–O9	78.7(7)	O22–Ga12–Cl26	95.9(7)
O1–Ga8–O24	78.8(7)	O21–Ga9–O7	85.1(7)	O18–Ga12–Cl26	99.1(6)
O24–Ga8–O3	87.7(7)	O7–Ga9–O19	83.0(7)	O7–Ga12–Cl32	138.7(6)
O3–Ga8–O13	88.1(7)	O9–Ga9–O19	87.8(8)	O22–Ga12–Cl32	94.5(7)
O24–Ga8–O13	164.0(8)	O21–Ga9–O9	87.5(7)	O18–Ga12–Cl32	91.2(6)
O1–Ga8–N25	91.4(8)	O21–Ga9–O19	167.8(8)	Cl32–Ga12-Cl26	113.1(4)
O3–Ga8–N25	168.8(9)	O7–Ga9–N27	90.4(9)	O4–Ga5–O6	120.8(7)
O13–Ga8–N25	89.8(9)	O9–Ga9–N27	169.1(9)	O4–Ga5–N16	99.0(9)
O24–Ga8–N25	91.3(9)	O21–Ga9–N27	91.1(8)	O6–Ga5–N16	97.7(9)
O13–Ga8–Cl23	100.2(6)	O19–Ga9–N27	91.4(9)	O4–Ga5–Cl15	112.4(6)
O1–Ga8–Cl23	177.3(6)	O21–Ga9–Cl33	97.0(6)	O6–Ga5–Cl15	112.4(6)
O24–Ga8–Cl23	99.6(6)	O7–Ga9–Cl33	176.2(6)	N16–Ga5–Cl15	112.5(8)

556 (4) $[Ga_4O_2(OEt)_3Cl_3]^+$, 511 (3) $[Ga_4O_2(OEt)_2Cl_3]^+$. $C_{16}H_{40}Cl_5Ga_5O_9$ (902.33): calcd. C 21.29, H 4.43, Ga 38.88; found C 20.52, H 4.12, Ga 39.31.

The toluene solution was treated with pyridine (0.5 mL), which provided crystallization of a small crop (0.25 g) of crystals of **2**. Further storage of the mother liquor under septum resulted in its complete crystallization with the formation of needle-shaped crystals of $[PyH][GaCl_4]$ (identified by single-crystal and powder X-ray studies). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (m, 8 H, α-H-Py), 7.62 (t, J = 4.7 Hz, 4 H, γ -H-Py), 7.44 (m, 8 H, β-H-Py), 4.31 (q, J = 6.4 Hz, 8 H, H-CH_2-OEt), 4.20 (q, J = 6.5 Hz, 8 H, H-CH_2-OEt), 3.51 (q, J = 6.5 Hz, 4 H, H-CH_2-OEt), 1.46 (t, J = 6.0 Hz, 6 H, H-CH_3-OEt), 1.28 (t, J = 6.0 Hz, 12 H, H-CH_3-OEt), 0.74 (t, J = 6.0 Hz, 12 H, H-CH_3-OEt) ppm. IR (nujol): $\tilde{\nu}$ = 1611 [vs (νPy)], 1573 [w (νPy)], 1479 (s), 1299 (w), 1218 [s (δPy)], 1156 (s), 1092 (vs), 1054 (vs), 1026 (vs, br.), 889 (vs), 887 (s), 742 (vs), 691 [vs (νGa–O)], 558 [vs, br. (νGa–O)], 452 (vs), 443 (vs), 403 (vs) cm^{-1}. MS: *m/z* (%) = 957 (20) $[Ga_7O_5(OEt)_3Cl_7]^+$, 912 (6) $[Ga_7O_5(OEt)_2Cl_7]^+$, the other ions are identical to the spectrum of **1**. $C_{50}H_{80}Cl_{12}Ga_{12}N_6O_{17}$ (2299.24): calcd. C 26.15, H 3.48, Ga 36.61; found C 25.10, H 3.02, Ga 37.62.

X-ray Structure Determinations: Data collection was performed with a Bruker SMART CCD 1K diffractometer at 295(2) K, with Mo-K_α radiation (λ = 0.71073 Å; see Table 2 for details). The SAINTPLUS and the SHELXTL-NT program packages were used for data reduction and computations.[32] Empirical absorption correction was applied by using the Bruker SADABS program package. The structures were solved by direct methods. The coordinates of the heavy atoms were taken from the initial solution, and the non-hydrogen atoms were located in subsequent Fourier syntheses. The structures were refined by full-matrix least-squares techniques in an isotropic and then finally in an anisotropic approximation. The details on data collection and bonding parameters are presented in Tables 2, 3, and 4.

CCDC-650370 and -650371 (for **1**and **2**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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