A Simple High-Yield Synthesis of Gallium(I) Tetrachlorogallate(III) and the Reaction of Digallium Tetrachloride Tetrahydrofuran Solvate with 1,2-Diols

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Gallium Halides, Gallium Diolates, Oxidative Addition

Gallium(I) tetrachlorogallate(III) Ga[GaCl₄] was prepared in quantitative yield by thermal decomposition of dichlorogallane [HGaCl₂]₂, which is readily available from Et₃SiH and [GaCl₃]₂. The reaction of catechol with solutions of this gallium(I) tetrachlorogallate(III) in tetrahydrofuran leads to the evolution of hydrogen gas and affords a dinuclear gallium(III) complex with penta-coordinate metal atoms chelated and bridged by mono-deprotonated catechol ligands. In the crystalline phase tetrahydrofuran molecules are hydrogen-bonded to the hydroxy groups: [Ga(1,2-OC₆H₄OH)Cl₂(C₄H₈O)]₂. The reaction with pinacol also gives hydrogen and the analogous product [Ga(OCMe₂CMe₂OH)Cl₂(C₄H₈O)]₂. The structures of the two compounds have been determined by X-ray diffraction. A mechanism of the new reaction has been proposed which involves oxidative addition of the diol to the solvate (THF)Cl₂Ga-GaCl₂(THF) present in the tetrahydrofuran solution to give a gallium hydride intermediate.

Introduction

In the course of our current investigations in the chemistry of low-valent and low-coordinate gallium we became interested in heterocycles with the metal in a bridge position between oxygen atoms (\mathbf{A}, \mathbf{B}) . Compounds of this type and the corresponding anions (\mathbf{C}, \mathbf{D}) are analogues of the related nitrogen heterocycles which were the subject of recent preparative and structural studies in this Laboratory [1 - 3].



The chemistry of gallium alkoxides is not very well developed and the knowledge about the composition and structure of representative examples is limited [4, 5]. This is particularly true for low-valent gallium complexes. Reports in the literature about preparative routes to gallium alkoxides reflect considerable difficulties in the synthesis of pure and well-defined products [6, 7].

An important contribution by Mögele [8] has shown that "gallium dichloride" holds considerable potential as a precursor for the preparation of gallium alkoxides. Its stoichiometric reaction with methanol or ethanol (molar ratio 1:1) is reported to afford hydrogen gas, gallium trichloride and the di(alkoxy)gallium-chloride in almost quantitative yield. However, both (MeO)₂GaCl and (EtO)₂GaCl are insoluble, high-melting solids which were assumed to be coordination polymers.

In our own work this reaction was now probed with catechol and pinacol which were expected to lead to products in which the dioles or their corresponding anions are chelating the metal atom as proposed in **A** and **B**. In order to provide a suitable basis for this synthesis we also tried to optimize the preparation of the starting material "GaCl₂", which is known to be a mixed-valent salt Ga^I [Ga^{III}Cl₄] in the solvent-free solid state, but a symmetrical dinuclear Ga^{II} species (Do)Cl₂Ga-GaCl₂(Do) in donor solvents (Do = dioxane, tetrahydrofuran).

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Preparation of Gallium(I) Tetrachlorogallate(III)

Treatment of anhydrous gallium(III) chloride with trimethylsilane gives quantitative yields of dichlorogallane and trimethylchlorosilane [9]. In a more convenient variant, triethylsilane can be used instead of Me₃SiH [2]. The product of these reactions could now be shown to give quantitative yields of Ga[GaCl₄] and hydrogen gas upon heating to 150°C for 1 h. Following the reactions shown in eqs (1) and (2), carried out consecutively in the same flask, the product is now obtained in quantitative yield directly from commercial anhydrous gallium trichloride:

$$[GaCl_3]_2 + 2 Et_3SiH \rightarrow [HGaCl_2]_2 + 2 Et_3SiCl \quad (1)$$
$$[HGaCl_2]_2 \rightarrow Ga[GaCl_4] + H_2 \quad (2)$$

$$[GaCl_2]_2 \rightarrow Ga[GaCl_4] + H_2$$

The Reactions of Ga[GaCl₄] with Catechol and Pinacol

Solutions of Ga[GaCl₄] in tetrahydrofuran reaction with catechol in the molar ratio 1:1 with evolution of hydrogen gas. Work-up of the reaction mixture (after 18 h at room temperature) gives a crystalline colourless product in 34% yield. The analogous reaction with pinacol also affords colourless crystals (45 % yield) following a similar stoichiometry. (The insoluble and soluble by-products have not been identified).

 $Ga[GaCl_4] + 2 HO-E-OH \rightarrow H_2 + [Cl_2Ga(O-E-OH)]_2$ 1: $E = 1,2-C_6H_4$ **2**: $E = 1,2-Me_2C-CMe_2$

The composition of 1 and 2 was confirmed by elemental analysis. The NMR spectra of compound 1 show a multiplet for the arene hydrogen atoms and a singlet for a hydroxy hydrogen atom. Three ¹³C resonances are recorded for the arene carbon atoms. This set of data suggests symmetrically bound catechol groups, but this symmetry criterion may only be due to rapid exchange processes in solution. However, for compound 2 the CMe₂ groups of the pinacolate ligand are found to be non-equivalent suggesting an asymmetrically bound ligand. If there are any, ligand exchange processes in solution involving this ligand are slow on the NMR time scale. In the mass spectrum of compound 1 (CI mode) the cation corresponding to the monochloride is detected: m/z = 213 for $[(C_6H_4O_2H)GaCl]^+$.

Regarding the mechanism of the reaction of $Ga[GaCl_4]$ with diols, it is important to note that the mixed-valent halide is known to symmetrize in donor solvents like dioxane and tetrahydrofuran. We propose that the resulting dinuclear molecule with a Ga-Ga bond will then add the first diole molecule in an oxidative addition mode to form one monomeric unit of the product and a gallium hydride intermediate, which then reacts with a second molecule of diole (as an acid) with formation of hydrogen and the second monomeric unit. Dimerization yields the final dinuclear species:

 $Ga[GaCl_4] + 2 THF \rightarrow (THF)Cl_2Ga-GaCl_2(THF)$ (THF)Cl₂Ga-GaCl₂(THF) + HO-E-OH \rightarrow (THF)Cl₂Ga(O-E-OH) + (THF)Cl₂Ga-H (THF)Cl₂Ga-H + HO-E-OH \rightarrow (THF)Cl₂Ga(O-E-OH) + H₂

2 (THF)Cl₂Ga(O-E-OH) \rightarrow [(THF)Cl₂Ga(O-E-OH)]₂ $(E = 1, 2 - C_6H_4; 1, 2 - CMe_2 - CMe_2).$

Molecular Structures of the Complexes

Crystals of the catecholate 1 $(C_4H_8O)_2$ (from tetrahydrofuran) are monoclinic, space group $P2_1/c$, with Z = 4 formula units in the unit cell. The lattice contains dinuclear molecules as the bistetrahydrofuran solvate. These dimers have a crystallographic



Fig. 1. Molecular structure of compound 1 (ORTEP drawing with 50% probability ellipsoids; CH-atoms omitted for clarity). Selected bond lengths [A] and angles [°]: Ga-O(2) 1.911(3), Ga-O(2') 2.009(2), Ga-O(1) 2.045(3), Ga-Cl(1) 2.160(1), Ga-Cl(2) 2.158(1); O(2)-Ga-O(1) 78.95(1), O(2)-Ga-O(2') 73.70(1), Ga-O(2)-Ga' 106.30(1), Cl(1)-Ga-Cl(2) 116.08(5).

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Fig. 2. Unit cell of compound 1; CH-atoms omitted for clarity.



Fig. 3. Molecular structure of compound **2** (ORTEP drawing with 50% probability ellipsoids; CH-atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Ga-O(2) 1.898(2), Ga-O(2') 1.975(2), Ga-O(1) 2.047(2), Ga-Cl(1) 2.172(7), Ga-Cl(2) 2.195(7); O(2)-Ga-O(1) 78.79(8), O(2)-Ga-O(2') 75.46(8), Ga-O(2)-Ga' 104.54(8), Cl(1)-Ga-Cl(2) 113.88(3).

center of inversion located in the center of a Ga_2O_2 four-membered ring (Fig. 1). This ring is formed in the dimerization of neutral [(HOC₆H₄O)GaCl₂] monomers via the catecholate oxygen atoms as additional donor atoms for the gallium atoms. The metal atoms thus become five-coordinate and feature a distorted trigonal-bipyramidal configuration. O1 and O2' may be considered as axial, O2, Cl1 and Cl2 as equatorial. In total, there is a slightly puckered array of five edge-sharing six-, five- and four-membered rings.

The tetrahydrofuran molecules are hydrogenbonded to the hydroxyl groups of the catecholate ligand. In the unit cell the molecular units are stacked in columns along the c axis (Fig. 2). There are no discrete intermolecular contacts discernible. Crystals of the pinacolate $2 (C_4H_8O)_3$ (from tetrahydrofuran) are also monoclinic, space group C2/c, with Z = 8 formula units in the unit cell. The overall mode of aggregation of the monomers is similar to that of the catecholate complex 1: The two five-membered rings of the monomeric components are sharing edges with a central four-membered ring. In the dimer, the components are again related by a center of inversion (Fig. 3). Each hydroxyl group of the pinacolate ligands is hydrogen-bonded to a solvent molecule. In addition, the lattice of 2 contains a non-coordinated tetrahydrofuran molecule per dimer with its oxygen atom on a crystallographic twofold axis.

Conclusions

The present work has shown that gallium(I) tetrachlorogallate(III) can be prepared in quantitative yield in a convenient one-pot reaction from commercially available starting materials. All by-products are volatile and can be removed in a vacuum (eqs (1), (2)). The reaction of this product with 1,2-diols affords hydrogen and dinuclear dichlorogallium diolate complexes in which the ligand is only mono-deprotonated. A mechanism has been proposed for this new type of reaction which involves an oxidative addition of the diol to the adduct (THF)Cl₂Ga-GaCl₂(THF) present in tetrahydrofuran solutions of Ga[GaCl₄]. Subsequently a gallium hydride intermediate will react with the second mole of diol to give the final product. The compounds (1, 2) are dimers owing to extension of the coordination number of the metal atoms from 4 to 5. The diolate ligands are chelating and span axial/equatorial positions in distorted trigonal bipyramids. The bridging of the metal atoms occurs via the anionic oxygen centers of the ligand. These bridging atoms [O2 in Figs 1 and 3] have a planar configuration (sum of the angles at O2: 359.9° for 1, 359.5° for 2). There is well defined hydrogen bonding to two solvent molecules in each case, with standard distances, *e. g.* in complex 1, of O1-H = 0.817 and O3- -H = 1.657 Å, and with an angle O1-H--O3 = 175.0° . The NMR spectra of compound 2 show that the dimeric structure is retained in tetrahydrofuran solution at ambient temperature. By contrast, compound 1 seems to undergo ligand scrambling more readily.

Crystal data		
Formula	$C_{10}H_{13}Cl_2GaO_3$	$C_{12}H_{25}Cl_2GaO_{3.5}$
M_r	321.82	365.94
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	C2/c
$a(\mathbf{A})$	9.2248(2)	18.837(1)
b(A)	17.9982(3)	16.024(1)
c (Å)	8.3713(2)	11.441(1)
β (°)	112.750(1)	102.09(1)
$V(A^3)$	1281.75(2)	3376.7(2)
$\rho_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.668	1.440
Ζ	4	8
<i>F</i> (000)	648	1520
μ (Mo- K_{α}) (cm ⁻¹)	25.52	19.48
Data collection		
$T(\mathbf{K})$	133	133
Measured reflections	11318	6393
Unique reflections	2966 [$R_{int} = 0.0305$]	$3498 [R_{int} = 0.0313]$
Refls. used for refinement	2833	2997
Refinement		
Refined parameters	165	248
Final <i>R</i> values $[I > 2\sigma(I)]$		
$R1^{[a]}$	0.0499	0.0354
wR2 ^[b]	0.1022	0.0695
(shift/error)max	< 0.001	< 0.001
$\rho_{\rm fin}({\rm max/min})~({\rm e}{\rm \AA}^{-3})$	0.612/-0.504	0.547/-0.320

Table 1. Crystal data, data collection, and structure refinement for compounds 1 and 2.

^[a] $R = \Sigma (||F_0| - |F_c||) / \Sigma |F_0|; {}^{[b]}wR2 = \{ [\Sigma w(F_0^2 - F_c^2)^2] / \Sigma [w(F_0^2)^2] \}^{1/2}; w = 1 / [\sigma^2(F_0^2) + (ap)^2 + bp]; p = (F_0^2 + 2F_c^2)/3; a = 0.0143$ (1), 0.0195 (2); b = 4.08 (1), 8.60 (2).

Experimental Part

All reactions were routinely carried out under dry nitrogen or argon either in Schlenk vessels or in a glove-box, respectively. Solvents were dried, degassed and saturated with nitrogen, and all glassware was oven-dried and filled with nitrogen/argon. Standard equipment was used throughout. All basic chemicals were commercially available.

Gallium(I) tetrachlorogallate(III)

Anhydrous gallium trichloride (2.36 g, 6.70 mmol of dimer) is mixed with triethylsilane (1.74 g, 15.0 mol) at -13 °C and stirred for 1 h. Afterwards it is slowly allowed to warm up to 0 °C and all volatiles are removed in a vacuum to leave 1.9 g of dichlorogallane (quantitative yield). This product is slowly heated to 150 °C and evolution of hydrogen gas is observed. Heating is continued for 1 h in a vacuum. The residue (1.86 g, quantitative yield) solidifies on cooling to 20 °C. Elemental analysis (GaCl₂) calcd. Cl 50.42; found Cl 50.69. Benzene-d₆ solutions show no ¹H NMR signal, and the IR spectrum (Nujol) has no band for the Ga-H stretching vibration.

Dimeric dichlorogallium(III)(+) 1,2-catecholate(-) (1)

A solution of Ga[GaCl₄] (0.295 g, 1.05 mmol) in tetrahydrofuran (15 ml) is treated at -78 °C with a solution of catechol (0.116 g, 1.05 mmol) in the same solvent (10 ml). Gas evolution is observed. The mixture is allowed to warm to 20 °C and stirred for 18 h. The colourless precipitate is removed by filtration and the volume of the filtrate reduced to one half in a vacuum. On slow cooling to -28 °C colourless crystals are formed after a few days (0.115 g, 34% yield). NMR (THFd₈, 20 °C), ¹H: δ 6.75 (m, 2H, CH); 6.85 (m, 2H, CH); 7.97 (s, 1H, OH). ${}^{13}C{}^{1}H{}$: δ 115.8 (s, CH); 120.2 (s, CH); 146.3 (s, CO). MS (CI) m/e 213 $[(C_6H_4O_2)HGaCl]^+; 176 [(C_6H_4O_2)Ga]^+.$ Elemental analysis (C₁₀H₁₃Cl₂GaO₃) calcd. C 37.3, H 4.1: found C 35.5, H 4.2.

Dimeric dichlorogallium(III)(+) pinacolate(-) (2)

As described for 1, using Ga[GaCl₄] (0.276 g, 0.98 mmol) and pinacol (0.115 g, 0.98 mmol) in a total of 25 ml of solvent, yield 0.146 g (45%). NMR (v. s.), ¹H: δ 1.49 (s, 6H, Me); 1.63 (s, 6H, Me);

8.90 (s, 1H, OH). ${}^{13}C{}^{1}H{}: \delta$ 3.7 (s, Me); 24.2 (s, Me); 79.7 (s, CO); 80.6 (s, CO). Elemental analysis ($C_{10}H_{21}Cl_2GaO_3$) calcd. C 36.41, H 6.42: found C 38.01, H 6.70.

Crystal structure determination

Specimens of suitable quality and size of compounds 1 and 2 were mounted on the ends of quartz fibers in F06206R oil and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo-K_{α} radiation. The structures were solved by a combination of direct methods (SHELXS-97) and difference-Fourier syntheses and refined by full matrix leastsquares calculations on F^2 (SHELXL-97). The thermal motion was treated anisotropically for all nonhydrogen atoms. All solvent-hydrogen atoms were calculated and allowed to ride on their parent atoms with fixed isotropic contributions, whereas all the other hydrogen atoms were located and refined isotropically.

Further information on crystal data, data collection and structure refinement are summarized in Table 1. Important interatomic distances and angles are shown in the corresponding Figure Captions. Anisotropic thermal parameters, tables of distances and angles, and atomic coordinates have been deposited with the Cambridge Crystallographic Data Centre. The data are available on request on quoting CCDC No. 159173 1 and 159174 2.

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