

Methanolysis as a Route to Gallium(III) Clusters: Synthesis and Structural Characterization of a Decanuclear Molecular Wheel

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Treatment of a methanolic solution of gallium(III) nitrate with lithium hydroxide in the presence of benzoic acid resulted in the decanuclear cluster $[\text{Ga}(\text{OMe})_2\{\text{O}_2\text{CC}(\text{OH})\text{Ph}_2\}]_{10}$ (**1**). The metal and the organic components have assembled to form a cyclic molecule that adopts the structure of a wheel. The 10 Ga^{III} ions are approximately coplanar and are coordinated in a distorted octahedral manner by six oxygen atoms. The integrity of the molecular wheel is retained in solution, as evidenced by the ¹NMR spectrum of **1** in DMSO-*d*₆, while no signal in the ⁷¹Ga NMR could be detected.

The chemistry of Ga(III) compounds in aqueous solutions is dominated by their tendency to undergo hydrolysis.^{1–5} Several studies on the hydrolytic behavior of Ga(III) have shown that the hydrolysis of $[\text{Ga}(\text{OH})_6]^{3+}$ starts from acidic pH values (i.e., lower than 2), and at pH ≥ 4, the dominant species is the water soluble $[\text{Ga}(\text{OH})_4]^-$.^{5,6} As the pH rises from very acidic to the value of 4, the soluble hydrolysis species that have been observed are the Ga(OH)(aq)²⁺ and Ga(OH)₂(aq)⁺¹ ions, followed by the formation of a gel with the composition Ga(OH)₃, which transforms to the white

solid GaO(OH) with further addition of base.² A tridecanuclear cluster with the composition $[\text{GaO}_4\text{Ga}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ has been suggested to form just before the formation of the gel.^{2,3} Unfortunately, the products of hydrolysis cannot be readily crystallized.

In organometallic reaction systems, exposure of a dry reaction solution in organic solvents to air or addition of small quantities of water are enough to promote hydrolysis of the Ga(III) species, producing oxo/hydroxo-bridged tri-,⁶ tetra-,^{6d,6e,7} hexa-,⁸ octa-,⁹ nona-,¹⁰ deca-,¹¹ and dodecanuclear¹² complexes. In contrast, in nonorganometallic reaction systems, addition of a base is usually necessary to promote hydrolysis. Polynuclear Ga(III) complexes as products of the hydrolytic process of nonorganometallic reaction systems are rare and only recently have been structurally characterized. This family of oxo/hydroxo polynuclear Ga(III) complexes includes tetra-, octa-, and tridecanuclear complexes supported by multidentate N,O ligands,¹³ a nonanuclear hydroxo cage based on a bis-β-diketonate ligand,¹⁴ a cucurbit[6]uril co-crystallized 32-metal cluster,¹⁵ and two ligand unsupported tridecanuclear complexes.^{15,16}

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(1) Brown P. L. *J. Chem. Soc., Dalton Trans.* **1989**, 399–402.

(2) Bradley, S. M.; Kydd, R. A.; Yamdagni, R. *J. Chem. Soc., Dalton Trans.* **1990**, 413–417.

(3) Bradley, S. M.; Kydd, R. A.; Yamdagni, R. *J. Chem. Soc., Dalton Trans.* **1990**, 2653–2656.

(4) Diakonov I.; Pokrovski, G. S.; Benezeth, P.; Schott, J.; Dandurand, J.-L.; Escalier J. *Geochim. Cosmochim. Acta* **1997**, *61*, 1333–1343.

(5) Benezeth, P.; Diakonov, I. I.; Pokrovski, G. S.; Dandurand, J.-L.; Schott, J.; Khodakovskiy I. L. *Geochim. Cosmochim. Acta* **1997**, *61*, 1345–1357.

(6) (a) Naiini, A. A.; Young, V.; Han, Y.; Akinc, M.; Verkade J. G. *Inorg. Chem.* **1993**, *32*, 3781–3782. (b) Atwood, D. A.; Cowley, A. H.; Harris, P. R.; Jones, R. A.; Koschmieder, S. U.; Nunn, C. M. *Organometallics* **1993**, *12*, 24–29. (c) Nichols, P. J.; Papadopoulos, S.; Raston, C. L. *Chem. Commun.* **2000**, 1227–1228. (d) Schnitter, C.; Roesky, H. W.; Albers, T.; Schmidt, H.-G.; Ropken, C.; Parisini, E.; Sheldrick, G. M. *Chem.—Eur. J.* **1997**, *3*, 1783–1792. (e) Zhao, Q.; Sun, H.; Chen, W.; Duan, C.; Liu, Y.; Pan, Y.; You, X. *Organometallics* **1998**, *17*, 156–160.

(7) (a) Hodge, P.; Piggott, B. *Chem. Commun.* **1998**, 1933–1934. (b) Wiberg, N.; Amelunxen, K.; Lerner, H.-W.; Noth, H.; Ponikvar, W.; Schwenk, H. *J. Organomet. Chem.* **1999**, *574*, 246–251. (c) van Poppel, L. H.; Bott, S. G.; Barron, A. R. *Polyhedron* **2002**, *21*, 1877–1882.

(8) (a) Neumuller, B.; Gahlmann, F. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1701–1702. (b) Store, J.; Belgardt, T.; Stalke, D.; Roesky, H. W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1244–1246. (c) Feher, F. J.; Budzichowski, T. A.; Ziller, J. W. *Inorg. Chem.* **1997**, *36*, 4082–4086. (d) Croucher, P. D.; Drljaca, A.; Papadopoulos, S.; Raston, C. L. *Chem. Commun.* **1999**, 153–154. (e) Hoefelmeyer, J. D.; Brode, D. L.; Gabbai, F. P. *Organometallics* **2001**, *20*, 5653–5657.

(9) Capparelli, M. V.; Hodge, P.; Piggott, B. *Chem. Commun.* **1997**, 937–938.

(10) Store, J.; Klemp, A.; Roesky, H. W.; Fleischer, R.; Stalke, D. *Organometallics* **1997**, *16*, 3074–3076.

(11) Kim, S.-J.; Yang, N.; Kim, D.-H.; Kang, S. O.; Ko, J. *Organometallics* **2000**, *19*, 4036–4042.

(12) (a) Landry, C. C.; Harlan, C. J.; Bott, S. G.; Barron, A. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1201–1202. (b) Swenson, D. C.; Dagorne, S.; Jordan R. F. *Acta Crystallogr.* **2000**, *C56*, 1213–1215.

(13) (a) Schmitt, W.; Anson, C. E.; Sessoli, R.; van Veen, M.; Powell, A. K. *J. Inorg. Biochem.* **2002**, *91*, 173–189. (b) Goodwin, J. C.; Teat, S. J.; Heath, S. L. *Angew. Chem., Int. Ed.* **2004**, *43*, 4037–4041. (c) Lah, M. S.; Gibney, B. R.; Tierney, D. L.; Penner-Hahn, J. E.; Pecoraro, V. L. *J. Am. Chem. Soc.* **1993**, *115*, 5857–5858.

COMMUNICATION

A methoxo-bridged hexanuclear Ga(III) cluster is also known to form upon treatment of a dry methanolic dibenzoyl-methane/GaCl₃ solution with sodium methoxide.¹⁷

Herein we present the first example of a new synthetic route to alkoxide-containing Ga(III) clusters, which is based on the alcoholysis of a gallium(III) salt in the presence of a carboxylate ligand. We describe the synthesis, crystal structure, and spectroscopic characterization of the novel decanuclear Ga(III) complex [Ga(OMe)₂{O₂CC(OH)Ph₂}]₁₀·2MeOH·0.5H₂O (1·2MeOH·0.5H₂O) that adopts the structure of a wheel.

A Ga(NO₃)₃·9H₂O (0.17 g, 0.4 mmol)/benzoic acid [Ph₂C(OH)CO₂H] (0.092 g, 0.4 mmol)/LiOH·H₂O (0.042 g, 1.0 mmol) (1:1:2.5 molar ratio) reaction mixture in MeOH (10 mL) resulted in a clear colorless solution from which X-ray quality colorless crystals of 1·2MeOH·0.5H₂O (X-ray crystal data: C₁₆₂H₁₇₉Ga₁₀O_{52.5}, fw = 3663.36, triclinic, *P* $\bar{1}$ (No. 2), *a* = 12.614(7) Å, *b* = 21.78(1) Å, *c* = 21.25(1) Å, α = 110.09(2)°, β = 105.81(2)°, γ = 109.57(2)°, *V* = 4643(4) Å³, *Z* = 1, *T* = 298 K, *d*_{calc} = 1.310 g/cm³; R₁ [*I* > 2σ(*I*)] = 0.0648, wR₂_{all data} = 0.2053, GOF = 1.079, *T*_{min}/*T*_{max} = 1.889/−0.604.) were grown in a closed vial within a period of a week in ca. 60% yield. We utilized an excess of LiOH·H₂O, aiming at doubly deprotonating the organic ligand, although hydrolysis and formation of entirely hydroxo or/oxo species could not be ruled out. Contrary to our expectations, the ligand stabilizing the Ga(III) wheel is the monoanion of benzoic acid, while instead of hydrolysis products (OH[−] or O^{2−}), we found MeO[−] anions in the crystal structure of **1**. Although some of the known Ga(III) clusters were prepared in methanolic solutions,^{14,16} this is the first time that alcoholysis took place instead of hydrolysis. The 1:1:1, 1:1:1.5, 1:1:2, 1:2:1, and 1:2:2 reaction systems yield the same decanuclear complex in lower yields, while addition of more than 2.5 equiv of LiOH·H₂O per Ga^{III} creates a white turbidity that cannot be isolated by filtration. Complex **1** is soluble in many organic solvents (i.e., acetone, chloroform, dichloromethane, tetrahydrofuran, acetonitrile, nitromethane, dimethylformamide, and dimethyl sulfoxide), while it is insoluble in water and alcohols. Complex **1** hydrolyzes in moist air, as evidenced by the decrease of its solubility in the organic solvents mentioned above with time and by IR spectroscopy.

Complex 1·2MeOH·0.5H₂O crystallizes in the triclinic space group *P* $\bar{1}$. A perspective view of the molecular structure of **1** is shown in Figure 1. Ten Ga^{III} ions, 10 benzilate(−1) ligands, and 20 MeO[−] anions have assembled to form a cyclic molecule that adopts the structure of a wheel. Although there are few other cyclic Ga(III) complexes,^{17,18} **1** is the only “carbon copy” of Lippard’s molecular ferric

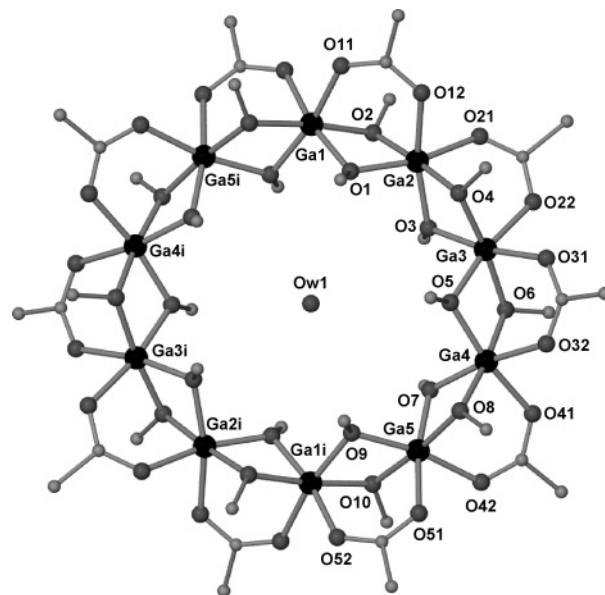


Figure 1. Perspective view of 1·2MeOH·0.5H₂O. Hydrogen atoms, most of the benzoate atoms, and the solvate MeOH molecules have been omitted for clarity. Selected interatomic distances (Å) and angles (deg): Ga2–O1 1.944(4), Ga2–O2 1.938(4), Ga2–O3 1.941(4), Ga2–O4 1.932(4), Ga2–O12 2.038(5), Ga2–O21 2.010(5), O1–Ga2–O21 167.9(2), O2–Ga2–O4 176.6(2), O3–Ga2–O12 167.0(2), Ga1–O1–Ga2 98.6(2), Ga1–O2–Ga2 98.9(2) (*i*: 1 − *x*, 1 − *y*, 2 − *z*).

wheel,¹⁹ and joins a very small family of cyclic decanuclear wheels of the same type.^{19,20} Complex **1** is the first Ga(III) member in this family. Table 1 summarizes the most important structural parameters of representative members of the [M(OR)₂(O₂CR′)]₁₀ family.

The molecular wheel of **1** is placed on a center of inversion. The 10 Ga^{III} ions are nearly coplanar, with an average deviation of ca. 0.0165 Å from the best least-squares plane passing through them. This coplanarity has been also observed in the known Fe(III),^{19,20c–20f} V(III),^{20a} Cr(III),^{20b} and Cr(III)/Mn(III)^{20g} decanuclear wheels. The closest Ga···Ga distances are almost identical, ranging from 2.953 to 2.963 Å. The Ga···Ga···Ga angles range from 142.0° to 147.0°, averaging 144°, which is the ideal value required by ring-closure considerations for a planar 10-membered ring. The diameter of the wheel calculated by averaging the distance between Ga^{III} ions on opposite sides of the ring is 9.569 Å.

Each Ga^{III} ion adopts a distorted octahedral geometry with four methoxo and two carboxylato oxygen atoms from two

(14) Albrecht, M.; Dehn, S.; Frohlich, R. *Angew. Chem., Int. Ed.* **2006**, *45*, 2792–2794.

(15) Gerasko, O. A.; Mainicheva, E. A.; Naumov, D. Y.; Kuratieva, N. V.; Sokolov, M. N.; Fedin, V. P. *Inorg. Chem.* **2005**, *44*, 4133–4135.

(16) Rather, E.; Gatlin, J. T.; Nixon, P. G.; Tsukamoto, T.; Kravtsov, V.; Johnson, D. W. *J. Am. Chem. Soc.* **2005**, *127*, 3242–3243.

(17) Abbati, G. L.; Brunel, L.-C.; Casalta, H.; Cornia, A.; Fabretti, A. C.; Gatteschi, D.; Hassan, A. K.; Jansen, A. G. M.; Maniero, A. L.; Pardi, L.; Paulsen, C.; Serge, U. *Chem.—Eur. J.* **2001**, *7*, 1796–1807.

(18) Kim, I.; Kwak, B.; Lah, M. S. *Inorg. Chim. Acta* **2001**, *317*, 12–20.

(19) (a) Taft, K. L.; Lippard, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 9629–9630. (b) Taft, K. L.; Delfs, C. D.; Papaefthymiou, G. C.; Foner, S.; Gatteschi, D.; Lippard, S. J. *J. Am. Chem. Soc.* **1994**, *116*, 823–832.

(20) (a) Laye, R. H.; Murrie, M.; Ochsenbein, S.; Bell, A. R.; Teat, S. J.; Raftery, J.; Gudel, H.-U.; McInnes, E. J. L. *Chem.—Eur. J.* **2003**, *9*, 6215–6220. (b) McInnes, E. J. L.; Anson, C.; Powell, A. K.; Thomson, A. J.; Poussereau, S.; Sessoli, R. *Chem. Commun.* **2001**, 89–90. (c) Bewnelli, C.; Parsons, S.; Solan, G. A.; Winpenny, R. E. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *36*, 1825–1827. (d) Frey, M.; Harris, S. G.; Holmes, J. M.; Nation, D. A.; Parsons, S.; Tasker, P. A.; Teat, S. J.; Winpenny, R. E. P. *Angew. Chem., Int. Ed.* **1998**, *37*, 3246–3248. (e) Kooijman, H.; Spek, A. L.; Bouwman, E.; Micciche, F.; Warzeska, S. T.; Reedijk, J. *Acta Crystallogr.* **2002**, *E58*, m93–m95. (f) Canada-Vilalta, C.; Pink, M.; Christou, G. *Chem. Commun.* **2003**, 1240–1241. (g) Helliwell, M.; Smith, A. A.; Teat, S. J.; Winpenny, R. E. P. *Inorg. Chim. Acta* **2003**, *354*, 49–53.

Table 1. Average Interatomic Distances (Å) and Angles (deg) in [M(OR)₂(O₂CR)]₁₀ Complexes

parameter	V ₁₀ ^a	Cr ₁₀ ^b	Fe ₁₀ ^c	Ga ₁₀ ^d
M···M	3.014 3.009 ^e	2.989 2.991 ^e	3.028	2.958
M–M–M	143.85 143.97 ^e	143.99 143.98 ^e	144	144
M–OR _O	1.975 ^f 2.002 ^g 1.972 ^{e,f} 1.996 ^{e,g}	1.964 ^f 1.963 ^g 1.962 ^{g,e,f} 1.964 ^{e,g}	1.975 ^f 1.987 ^g	1.941 ^f 1.942 ^g
M–OR _{COO}	2.036 2.029 ^e	1.986 1.994 ^e	2.057	2.023
M–OR _O –M	99.46 ^f 97.69 ^g 99.42 ^{e,f} 97.84 ^{e,g}	99.12 ^f 99.16 ^g 99.34 ^{e,f} 99.19 ^{e,g}	100.08 ^f 99.27 ^g	99.3 ^f 99.1 ^g
deviation from best M ₁₀ mean plane	0.1266 0.0266 ^e	0.0150 0.0196 ^e	0.0088	0.0165
ring diameter	9.735 9.735 ^e	9.671 9.677 ^e	9.979	9.569

^a [V(OMe)₂(O₂CMe)]₁₀, ref 20a. ^b [Cr(OMe)₂(O₂CMe)]₁₀, ref 20b. ^c [Fe(OMe)₂(O₂CCH₂Cl)]₁₀, ref 19. ^d [Ga(OMe)₂{O₂CC(OH)Ph₂}]₁₀, this work. ^e Two crystallographically independent molecules. ^f “Inner” RO[−]. ^g “Outer” RO[−].

benzilate ligands in a cis arrangement. The edge-sharing octahedral nearest neighboring Ga^{III} ions are bridged by two μ_2 -methoxo oxygen atoms, which define the common edge, and one μ_2 -benzilate ligand acting in a 1,3-syn,syn fashion. The benzilate ligands are alternatively arranged above and below the metal ring with an average deviation of 1.045 Å (ring mean plane···O_{carboxylate}). The methoxo ligands are divided into two sets: one set pointing above and one pointing below the metal ring (average ring mean plane···O_{methoxo} 1.057 Å). Each of the two sets of the methoxo ligands is subdivided into two other sets: one pointing inward and one directed outward the metal ring. Therefore, there are five methoxo ligands in each side of the metal ring that point inward creating a small cavity where a water molecule is trapped (Ow1, with 50% occupancy, closest Ow1···H_{methoxo} 3.466 Å). Complex **1** joins a handful of methoxo-bridged Ga(III) complexes.^{17,21}

In the IR spectrum of **1** in KBr, the $\nu_{as}(\text{COO})$, $\nu_s(\text{COO})$, and $\nu(\text{OMe})$ modes appear at 1570, 1411, and 1057 cm^{−1}, respectively. The IR spectrum of **1** that has been exposed to moist air for a period of a month exhibits a decrease in the intensity of the $\nu(\text{OMe})$ band, suggesting hydrolysis. The ¹H NMR of the free benzilate(−1) ion (in the form of its sodium salt) in DMSO-*d*₆ exhibits two distinct groups of resonances in the 7.3–7.5 ppm region corresponding to the phenyl protons. In the ¹H NMR of **1** in DMSO-*d*₆, the 10 phenyl protons of the benzilate anion resonate at 7.7 (doublet, 1H), 7.5 (doublet, 3H), and 7.2 ppm (multiplet, 6H), while the CH₃− protons of the methoxo ligands appear as a broad band (two overlapping singlets) at 3.2 ppm. The difference of the two spectra in the aromatic region suggests that the phenyl protons of the benzilate anion in **1** are in a quite different chemical environment as compared with the free

ligand. This observation suggests that the benzilate anion is coordinated to Ga^{III} ions in solution. The fact that no other peaks were observed, suggesting more than one species in solution, let us conclude that the structure of the Ga₁₀ cluster is retained in the DMSO solution. The pattern of the ¹H NMR spectrum remains unchanged for a period of a week, and after that, a white cloudiness appears suggesting hydrolysis of the Ga₁₀ in solution. Attempts to obtain the ⁷¹Ga NMR spectrum in DMSO-*d*₆ at ca. 25 °C and at ca. 80 °C and in CDCl₃ at ca. 25 °C were unsuccessful, probably due to line width broadening which is influenced by the quadrupolar moment and the symmetry at the gallium ion.²³

Complex **1** is the second molecular wheel based on the benzilate anion. The Fe(III) analogue, namely, [Fe(OMe)₂{O₂CC(OH)Ph₂}]₁₂²² (**2**), is known to form under similar conditions with those used for the preparation of **1**. Surprisingly, **1** is decanuclear while **2** is dodecanuclear, despite the striking similarities between Fe(III) and Ga(III), i.e., ionic radii, coordination preferences, etc. Both wheels are planar, with similar M···M distances but not M···M···M angles. The methoxo and benzilate ligands adopt the same coordination modes in both complexes, while both metals are octahedral. The base used to promote alcoholysis in both reaction systems was the same (LiOH·H₂O), thus excluding the possibility of templating effects that could have differentiated the nuclearity of the two wheels. The Ga(III) and Fe(III) wheels crystallize in different crystal systems and space groups (triclinic, *P* $\bar{1}$, and monoclinic, *P*2₁/*c*, for Ga and Fe, respectively), in addition to the difference of the dimensions of their unit cells. Those discrepancies indicate that Fe^{III} doping within Ga^{III} crystals¹⁷ might not always work as expected. Preliminary results on doping with Fe(III) the Ga(III) **1** wheel show that a yellowish crystal [the color indicates the presence of Fe(III)] made from the 1:1:2:5 (Fe(III)/Ga(III)/benzilate acid/LiOH·H₂O) has the unit cell of the parent wheel (Ga₁₀).

In conclusion, we presented here the synthesis, crystal structure, and spectroscopic characterization of the first Ga(III) molecular wheel. The initial results presented in this work illustrate the value of methanolysis reactions of a Ga(III) salt in the presence of carboxylate groups as a means to prepare polynuclear complexes and suggest that a rich source of such clusters might await discovery. We are currently exploring the possibility of synthesizing analogous molecular wheels of other trivalent metal ions and lanthanides with benzilate acid, as well as utilizing other α -hydroxy acids and amino acids for the construction of such species. We also plan alcoholysis reactions of preformed small nuclearity Ga_x clusters.

Supporting Information Available: X-ray crystallographic data (CIF), spectroscopic data (IR, ¹H NMR), and preparative details of **1** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(21) (a) Cleaver, W. M.; Barron, A. R.; McGuffey, A. R.; Bott, S. G. *Polyhedron* **1994**, *13*, 2831–2846. (b) Hossain, M. B.; Jalal, M. A. F.; van der Helm, D. *J. Chem. Cryst.* **1998**, *28*, 57–60.

(22) Raptopoulou, C. P.; Tangoulis, V.; Devlin, E. *Angew. Chem., Int. Ed.* **2002**, *41*, 2386–2389.