Hydrogen bonded assemblies of a cyclic trimeric hydroxy gallium(III) derivative: $[\{Me_2Ga(\mu\text{-}OH)\}_3\cdot 3H_2O]_2\cdot$18-crown-6

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Addition of hydrolysed trimethylgallium to an excess of 18-crown-6 in water affords an alkyl μ-hydroxo bridged Ga(III) trimer in solution (pH *ca.* 6) and the solid, isolated as the hydrogen bonded assembled supermolecule $[\{Me_2Ga(\mu\text{-}OH)\}_3\cdot 3H_2O]_2\cdot$18-crown-6.

The oxidation and reaction of group 13 alkyl compounds with water is often extremely exothermic and under controlled conditions it is possible to isolate some metal oxide/hydroxide intermediate compounds *en route* to complete hydrolysis to the alkane and metal hydroxides.[1] These compounds have provided information about the hydrolysis reactions and certain derivatives have also been found to function as co-catalysts in the Ziegler–Natta polymerisation of olefins.[2] The oxide, hydroxide and mixed oxide–hydroxide chemistry of aluminium, and also indium, has been extensively studied.[3] In contrast, there have been relatively few studies concerning analogous gallium chemistry.[3–11] The first organogallium–oxo compound reported $[Bu^tGa(\mu_3\text{-}O)]_9$ was characterised by mass spectrometry and NMR spectroscopy,[12] soon followed by the synthesis and structural authentication of the only known cyclic trimeric hydroxy derivative of gallium, $[Bu^t_2Ga(\mu\text{-}OH)]_3$.[5] This compound was originally identified as an impurity formed during the synthesis of $[Bu^t_2Ga(\mu\text{-}PH_2)]_3$.[13] More recently, the structural characterisation of the largest galloxane hydroxide isolated thus far, $[Ga_{12}Bu^t_{12}(\mu_3\text{-}O)_8(\mu\text{-}O)_2(\mu\text{-}OH)_4]$, has been described.[4] Further studies on the stabilization and structural characterisation of controlled hydrolysis products of $[Ga(2,4,6\text{-}Me_3C_6H_3)_3]$ by deprotonation reactions involving alkyllithium reagents have also been reported.[14]

In addressing the difficulties associated with isolating the intermediates formed during the hydrolysis of substitutionally labile alkyl metal compounds from aqueous solution we use a crown ether to promote supramolecular complexation and crystallisation. A similar technique has been used to crystalise a known dinuclear aqua cation formed during the hydrolytic polymerisation of Cr(III).[15] In the present study we show that using this supramolecular self assembly approach results in the formation of a new alkyl μ-hydroxo bridged Ga(III) trimer, $[\{Me_2Ga(\mu\text{-}OH\}_3\cdot 3H_2O]_2\cdot$18-crown-6, which has been characterised in solution and in the solid state.

Addition of an aqueous solution of hydrolysed trimethylgallium to 2 equiv. of 18-crown-6 in water at room temperature (pH of the mixture *ca.* 6) results in the formation of colorless crystals of $[\{Me_2Ga(\mu\text{-}OH)\}_3\cdot 3H_2O]_2\cdot$18-crown-6 (Fig. 1)† suitable for X-ray crystallography. It is noteworthy that the product yield is enhanced by increasing the concentration of 18-crown-6 relative to hydrolysed Me_3Ga in the reaction mixture; molar ratios for 18-crown-6: hydrolysed Me_3Ga of 2 : 1, 1 : 1 and 0.5 : 1 afford the trimer in 70, 40 and 20% yield respectively. The ^1H NMR spectrum of the complex in acetone exhibits a singlet at $\delta -0.45$, assigned to the Me_2Ga units, a less intense singlet at δ 4.46, assigned to the GaOH protons, and a singlet at δ 3.59 assigned to the ethylene groups of the 18-crown-6. The integration, 6 : 1 : 4 respectively, is consistent with the proposed formulation. In acetone hydrogen bonding interactions (Fig. 2) between GaOH groups and solvent are likely and in this context we note that in chloroform the singlet for GaOH shifts to δ 1.43. The trimeric complex was found to be insoluble in hexane and water which contrasts with previous findings for the *tert*-butyl analogue $[Bu^t_2Ga(\mu\text{-}OH)]_3$.[6]

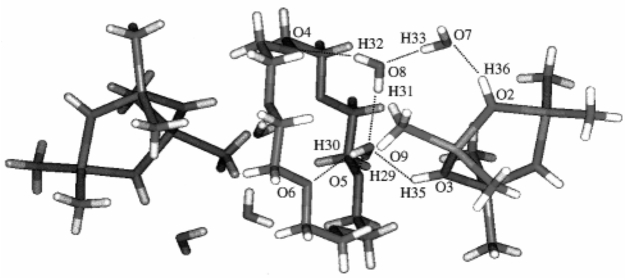

Fig. 1 The molecular structure of $[\{Me_2Ga(\mu\text{-}OH)\}_3\cdot 3H_2O]_2\cdot$18-crown-6.

The variable-temperature ^1H NMR spectra of the complex show shifts in the singlet due to GaOH from δ 4.4 (+30 °C) to a doublet (2 : 1) at 5.2 (−60 °C) which may be due to the hydrogen bonding interactions of two of the three possible bridging OH groups with water molecules hydrogen bonded to the crown ether (Fig. 1). This change was not observed in the variable-temperature ^1H NMR spectra of $[Bu^t_2Ga(\mu\text{-}OH)]_3$[6] and is consistent with the presence of the crown ether complex in solution. Addition of D_2O to the complex in acetone results in the spontaneous disappearance of the O–H signal, indicating very fast proton exchange on the bridging OH groups. By comparison the OH signal for $[Bu^t_2Ga(\mu\text{-}OH)]_3$ in D_2O disappeared slowly over 120 h (slow proton exchange).[6] This is to be expected since terminal methyl groups sterically crowd the bridging OH groups less thus providing greater access to the bulk solvent (for exchange) than *tert*-butyl groups on the same gallium trimer.

The $^{13}C\{^1H\}$ NMR spectrum at 20 °C contains two singlets at δ 11.04 and 71.40 due to 18-crown-6 and Me_2Ga groups, respectively. The positive ion electrospray mass spectrum (ESMS) confirmed the trimeric nature of the complex in the gas phase $\{[Me_2Ga(OH)]_3 = 350.1\ u\}$. IR spectroscopic data confirm the presence of the O–H and C–O (18-crown-6) groups ($\nu_{O\text{–}H}$ 3420 cm^{-1}, $\nu_{C\text{–}O}$ 1110 cm^{-1}).

The compound crystallises in the space group $P\bar{1}$ with the asymmetric unit comprised of one $[GaMe_2(OH)]_3$ cluster and half a crown ether molecule, bound together by a chain of three hydrogen bonded water molecules (Fig. 1).‡ Crystallographic symmetry places one cluster on each side of the crown ether

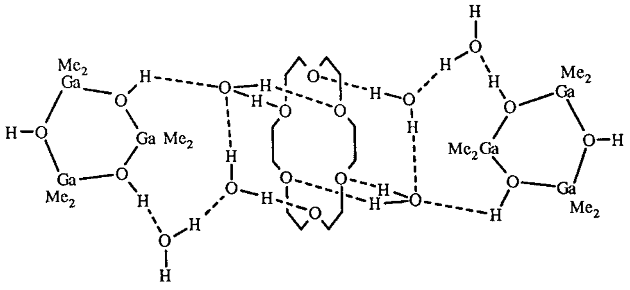

Fig. 2

Table 1 Hydrogen bonding distances (Å) and angles (°) in the supermolecule

A	H	B	A···B	A–H	H···B	A–H···B
O(2)	H(36)	O(7)	2.693(3)	0.950(2)	1.940(3)	134.5(2)
O(3)	H(35)	O(9)	2.824(4)	0.950(2)	2.104(3)	131.5(2)
O(7)	H(33)	O(8)	2.687(5)	0.85(4)	1.84(5)	173(4)
O(7)	H(34)	O(2)	2.887(4)	0.86(6)	2.07(6)	158(5)
O(8)	H(31)	O(9)	2.767(5)	0.80(5)	2.00(5)	163(5)
O(8)	H(32)	O(4)	2.834(4)	0.75(4)	2.11(4)	164(4)
O(9)	H(29)	O(5)	2.882(4)	0.91	1.98	177.1
O(9)	H(30)	O(6)	2.816(5)	0.66	2.16	170.9

molecule which is arranged with adjacent oxygen atoms alternating between pointing towards one of the gallium clusters and to its symmetry relative, *i.e.* three up and three down. Two water molecules hydrogen-bond with each face of the crown, the first bridging two crown ether oxygens, O···O 2.88(1) and 2.82(1) Å, while the second bridges the first water molecule O···O 2.68(1) Å and the remaining crown ether oxygen O···O 2.83(1) Å. The hydrogen bonding sphere of the first water molecule is completed by a hydrogen bond to one of the hydroxy groups from the gallium cluster O···O 2.82(1) Å while a third water molecule connects the second water molecule and the gallium cluster *via* hydrogen bonding to a second hydroxy of the cluster O···O 2.69(1) Å. Hydrogen bonding distances and angles in the supermolecule are shown in Table 1.

In conclusion we have shown the supramolecular hydrogen bonded self assembly of a novel cyclic trimeric hydroxy gallium(III) derivative with 18-crown-6 $[\{Me_2Ga(\mu\text{-}OH)\}_3\cdot 3H_2O]\cdot$18-crown-6. Evidence for the presence of the supermolecule was obtained from both solid state and solution studies. Furthermore, X-ray crystallographic data showed that in the solid state each supermolecule exists as a discrete unit comprising of two gallium trimer clusters hydrogen bonded through six lattice water molecules to a central crown ether. We are currently investigating using this approach to crystallise other group 13 alkyl hydroxy compounds from aqueous solution.

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Notes and references

† Synthesis and characterisation of $[\{Me_2Ga(\mu\text{-}OH)\}_3\cdot 3H_2O]_2\cdot$18-crown-6: Me_3Ga (1 ml) was added to distilled water (30 ml) in an extremely exothermic reaction (**CAUTION!**) Aliquots of this solution were taken and added to aqueous solutions of 18-crown-6 such that the ratio of 18-crown-6 to hydrolysed Me_3Ga was 2 : 1 at pH *ca.* 6. This resulted in the formation of colorless crystals over a period of a week. Yield: 70% with respect to Ga. Mp 64–66 °C. Insoluble in hexane and water; soluble in acetone and chloroform. IR (KBr disk): 3420m br, 2956m, 2912m, 1637w, 1473vw, 1353w, 1253vw, 1202w, 1109s, 962m, 838vw, 802vw, 734m, 583m, 532m cm^{-1}. ^1H NMR [300.07 MHz, 20 °C, $(CD_3)_2CO$] δ −0.45 [s, 18H, $(Me_2Ga)_3$], 3.59 (s, 24H, 18-crown-6), 4.46 {s, 3H, $[Ga(OH)]_3$}. ^1H NMR (200.13 MHz, 20 °C, CD_3Cl) δ −0.34 [s, 18H, $(Me_2Ga)_3$]), 1.43 {s, 3H, $[Ga(OH)]_3$}, 3.68 (s, 24H, 18-crown-6). $^{13}C\{^1H\}$ NMR (75.45 MHz, 20 °C, $(CD_3)_2CO$] δ 11.04 (s, 18-crown-6), 71.40 [s, $(Me_2Ga)_3$]. ESMS (MI, Me_2CO), *m/z* 480.1 $\{[Me_2Ga(OH)]_3\cdot Me_2CO\cdot 4H_2O\}$, 408.1 $\{[Me_2Ga(OH)]_3\cdot Me_2CO\}$, 363.2 ($Me_2Ga\cdot$18-crown-6), 350.1 $\{[Me_2Ga(OH)]_3\}$. Anal. Calc. for $[Ga_3O_9C_{12}H_{39}]_2$: C, 26.84; H, 7.27. Found: C, 2701; H, 7.40%.

‡ Data collected on an Enraf Nonius CCD diffractometer at 123 K using graphite-monochromated Mo-Kα radiation (λ = 0.71013 Å) were corrected for Lorenzian and polarisation but not absorption. The structure was solved using TEXSAN. All non-hydrogen atoms were refined using a full-matrix least-squares refinement against *F*. All hydrogen atoms, other than those attached to water molecules, were included at calculated positions with a riding model. Those hydrogen atoms attached to water molecules were included by the detection of electron density between heteroatoms situated at hydrogen-bonded distances *i.e.* < 2.9 Å and refined. *Crystal data.* $C_{23}H_{78}O_{18}Ga_6$. M_r = 1073.18, triclinic, space group $P\bar{1}$, a = 8.9725(3), b = 11.3120(3), c = 12.8986(5) Å, α = 77.522(1), β = 75.876(1), γ = 67.686(6)°, U = 1163.35(6) $Å^3$, Z = 2, μ = (Mo-Kα) = 8.935 mm^{-1}, 3139 reflections, 242 parameters, R_1 = 0.0309, wR = 0.0338. CCDC 182/1106. See http://www.rsc.org/suppdata/cc/1999/153/ for crystallographic files in .cif format.

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