On the Crystal Engineering of Organogallium Alkoxides Derived from Primary-Amine Alcohols − Relationships between Hydrogen Bonding and Donor−Acceptor Bonds

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The crystal structure analysis of model organogallium amine-alkoxides $Me_2Ga(OCH_2CH_2CH_2NH_2)$ (**2**) and $[Me_2Ga\{\mu\text{-}OCH_2CH(CH_3)NH_2\}]_2$ (**3**), demonstrate how hydrogen bonding can effectively compete with metal–ligand coordination preferences in determining the molecular and crystal structure and how conformational changes in a ligand and increased steric bulk on the carbon atom adjacent to the amine group can impart on a network morphology and molecular aggregations.

Introduction

In the last two decades, a detailed analysis of intermolecular interactions in crystals and the design of supramolecular architecture have become a rapidly expanding area.[1] Investigations of the self-assembly of organic molecules through intermolecular interactions have lead to the identification of a number of useful tools for supramolecular design, the most efficient being hydrogen bonding.[2] In spite of the large number of contributions and advances in the self-assembly of organic molecules based on noncovalent interactions, the area of organometallic compounds in this context remains largely unexplored.[3] Here we report preliminary results in aiding our understanding of relationships between intra- and intermolecular forces resulting from donor-acceptor and hydrogen bonding interactions using gallium alkoxides with primary-amine termini as model complexes.

Starting with pioneering work on the ligative possibilities of gallium alkoxides derived from amine alcohols,[4] considerable research has been devoted to the determination and understanding of the structure of this class of compounds.[5−15] Over twenty years ago Chong et al. reported the structural characterization of the dimethylgallium derivative of amine ethanol, $Me_2Ga(OCH_2CH_2NH_2)$ (**1**), and demonstrated that the latter compound exists as discrete four-coordinate monomers linked by an extensive network of N−H···O hydrogen bonds in the solid state.[6] Although the authors have not discussed in detail the hydrogen bond network, our analysis revealed a symmetrical three-dimensional architecture (structure **I**, Scheme 1). Surprisingly, to the best of our knowledge, competition between the four-coordinate complexes with an extended hydrogen bond network and the metal-ligand coordination preferences, for example the formation of the five-coordinate $[R_2Ga(O,N)]_2$-type adduct **II**, have not been studied. In order to test how the molecularity and network architecture of gallium alkoxides may be controlled by an appropriate choice of primary-amine-terminated alcohols, dimethylgallium derivatives of 3-amino-1-propanol, Me_2Ga-$(\mu\text{-}OCH_2CH_2CH_2NH_2)$ (**2**), and 2-amino-1-propanol, $\{Me_2Ga[\mu\text{-}OCH_2CH(CH_3)NH_2]\}_2$ (**3**), were synthesized and structurally characterized, and the structural features were compared with those of the previously reported 2-amino-1-ethanol analogue.
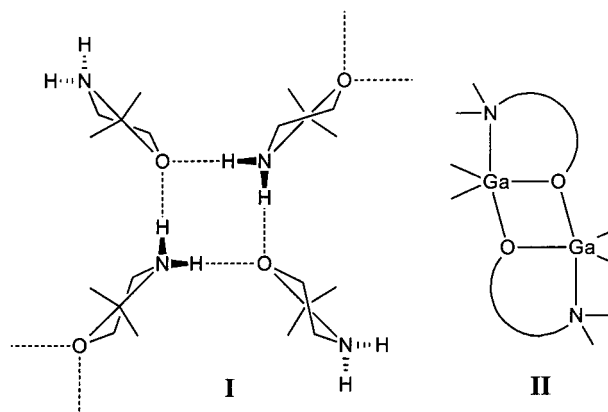
Scheme 1

Results and Discussion

The interaction of Me_3Ga with an equimolar amount of the corresponding amino alcohol in CH_2Cl_2 at -78 °C results in methane evolution and the quantitative formation of the dialkylgallium O,N-chelate complexes **2** and **3**. Single crystals suitable for an X-ray analysis were obtained from the concentrated solution at -20 °C.

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The crystal structure of **2** contains four crystallographically independent monomeric molecules with essentially the same geometry, in which each Me_2Ga moiety is chelated in a tetrahedral geometry by the amine alkoxide ligand (average Ga−O and Ga−N distances are 1.879 Å and 2.037 Å, respectively) (Figure 1). The alkoxide oxygen and amine nitrogen atoms act as complementary hydrogen donors and acceptors leading to a fully hydrogen-bonded network. The molecules in the ribbon assemble with pairs of strongly hydrogen-bonded chains (average NH···O distance is 1.90 Å; the N−H···O angles range from 170 to 176°). The chains are then cross-linked by very weak N−H···O interactions (average H···O distance is 2.45 Å and mean N−H···O angle 170°), forming the hydrogen bond network shielded by hydrophobic groups.
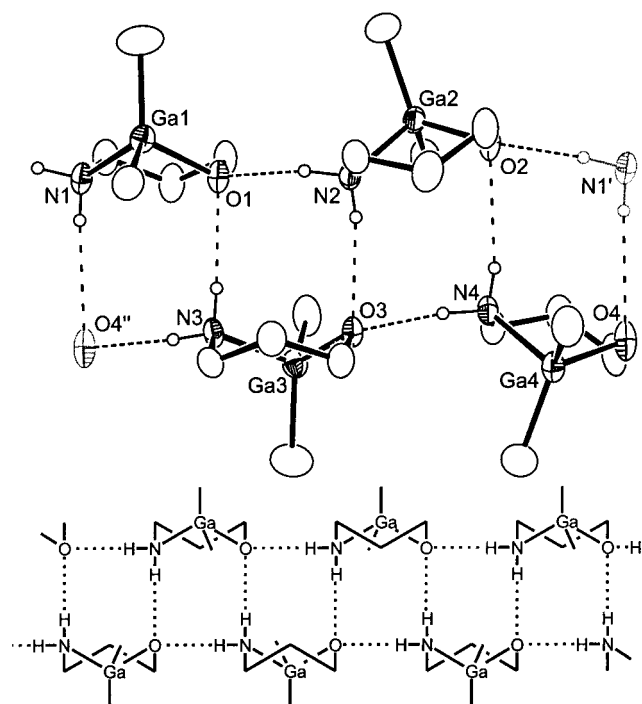
Figure 1. The hydrogen bonding observed in crystalline Me_2Ga-($OCH_2CH_2CH_2NH_2$) (**2**) showing molecular chains parallel to [010], linked together by hydrogen bonds formed by the axial amine hydrogens and alkoxide oxygens; top: the arrangement of four independent molecules; bottom: schematic representation of the hydrogen bonding network; selected bond lengths (Å) and angles (°): Ga(2)−O(2) 1.874(3), Ga(3)−O(3) 1.885(3), Ga(4)−O(4) 1.870(3), Ga(1)−N(1) 2.043(4), Ga(2)−N(2) 2.039(4), Ga(3)−N(3) 2.026(4), Ga(4)−N(4) 2.041(4), Ga(1)−O(1) 1.887(3); O(1)−Ga(1)−N(1) 91.48(15), O(2)−Ga(2)−N(2) 92.94(15), O(3)−Ga(3)−N(3) 91.65(14), O(4)−Ga(4)−N(4) 92.26(15)

The monomeric moieties in the idealized chains are related by the glide plane passing through the oxygen and nitrogen atoms. Thus, the elongation of the backbone in 3-amino-1-propanol relative to 2-amino-1-ethanol enforces the crystal structure of gallium alkoxides. An explanation of this different supramolecular behavior of **1** and **2** in the crystal is provided by an analysis of the heterocycle conformation in both compounds. The six-membered Ga-OCCCN rings in **2** adopt a chair-like conformation. As a consequence of this geometry both the amine hydrogens and oxygen lone-pairs become nonequivalent and situated in axial and equatorial positions. Inspection of the space-filling representation of the crystal structure of **2** undoubtedly shows that steric requirements favor interactions between the equatorial hydrogen and equatorial lone-pair. However, in the crystal structure involving the gallium alkoxide derived from 2-amino-1-ethanol, the five- membered GaOCCN chelate rings are slightly twisted around the C−C bond giving rise to spatial equivalency of the amine hydrogens and oxygen lone-pairs. The bisectionally positioned hydrogens and lone pairs form a symmetrical, three-dimensional, hydrogen bond network (**I**, Scheme 1).

In contrast to the four-coordinate hydrogen bonded polymeric structures of **1** and **2**, compound **3** is dimeric, being bridged by the oxygens of the chelating alkoxide ligand (Figure 2). The crystal structure of **3** comprises individual five-coordinate dimeric molecules with no unusually short intermolecular contacts. The general structural features of the molecules are consistent with those observed for related gallium alkoxides (average Ga−$O_{equatorial}$, Ga−O_{axial} and Ga−N distances are 1.923 Å, 2.113 Å and 2.348 Å, respectively).[5,13] It is worth noting that the crystal structure exhibits disorder indicating the presence of the (R^*,R^*)-[$Me_2Ga(O,N)$]$_2$ and (R,S)-[$Me_2Ga(O,N)$]$_2$ diastereomers (Figure 2). These diastereomers result from the association of monomeric moieties of the same or opposite configuration as the chiral center in the O,N-chelating ligand. Thus, the formation of the dialkylgallium alkoxide adducts derived from chiral amine-functionalized alcohols is not a stereoselective reaction, contrary to the highly stereoselective association of dialkylaluminum alkoxides derived from chiral carbonyl-functionalized alcohols recently reported by our group.[16]
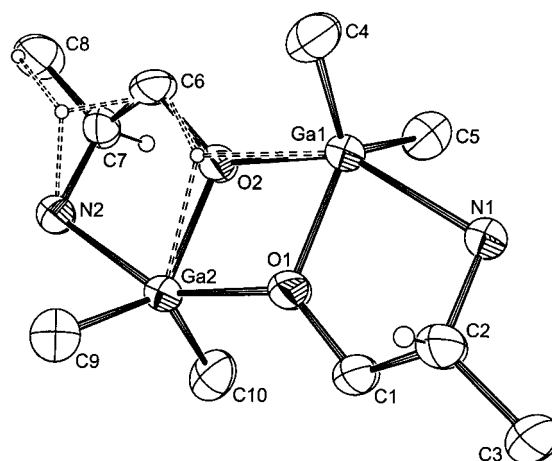

Figure 2. ORTEP view of the molecular structure of {Me_2Ga[μ-$OCH_2CH(CH_3)NH_2$]}$_2$ (**3**) showing the disordered 2-amino-1-propanolato ligands of opposite configuration as the chiral center; thermal ellipsoids are drawn at 30% probability level; selected bond lengths (Å) and angles (°): Ga(1)−O(1) 1.916(3), Ga(1)−O(2) 2.127(15), Ga(1)−N(1) 2.349(4), Ga(2)−O(2) 1.929(14), Ga(2)−O(1) 2.106(4), Ga(2)−N(2) 2.347(4); O(1)−Ga(1)−N(1) 76.57(14), O(2)−Ga(1)−N(1) 149.8(4), O(2)−Ga(2)−N(2) 75.9(4), O(1)−Ga(2)−N(2) 150.14(14)

A question arises why compounds **1** and **2** crystallize as discrete four-coordinate monomers linked by an extensive network of N−H···O hydrogen bonds and **3** occurs as a five-coordinate dimer in the solid state. It is apparent that the relative stability of the five-coordinate dimer vs. the four-coordinate, hydrogen-bonded polymer depends on the balance between the energy of coordinate bonds and hydrogen bonds; however, energy-related questions are difficult to answer at present. The reported results show that for **1** and **2** cooperative hydrogen bond interactions effectively compete with the metal ligand coordination preferences in determining the molecular and crystal structure. On the other hand, the substitution of a hydrogen by a methyl group on the carbon atom adjacent to the hydrogen donor presumably results in a weakening of the intermolecular hydrogen bond interactions and enforces the structural changes.

Conclusion

In conclusion, metal alkoxides with a primary-amine functionalized side chain provide the means to study intra- and intermolecular forces resulting from donor-acceptor and hydrogen bonding interactions. Further studies on the effects of conformational and steric changes in a subunit structure on the molecular and crystal structure of metal alkoxides are in progress.

Experimental Section

General Remarks: All reactions were carried out under dry nitrogen using standard Schlenk techniques. Solvents were dried and dis-

tilled prior to use. NMR spectra were recorded on a Varian 300 VXL spectrometer.

(3-Aminopropanolato)dimethylgallium (2): A solution of 3-amino-1-propanol (0.60 g, 8.0 mmol) in CH_2Cl_2 (10 cm^3) was cooled to −78 °C and Me_3Ga (0.92 g, 8.0 mmol) was added dropwise. After the addition was completed, the reaction mixture was warmed to room temperature and stirred for 0.5 h. Concentration of the mother solution followed by crystallization at −20 °C gave a colorless solid. Yield: 80%. − ^{1}H NMR (C_6D_6, 300 MHz): δ = −0.14 (s, 6 H, Ga−CH$_3$), 0.82−1.35 (2 H, NH$_2$), (br. m, 2 H, CH$_2$), 2.27 (br. t, 2 H, CH$_2$), 3.81 (br. t, 2 H, OCH$_2$). − $C_5H_{14}GaNO$ (173.89): calcd. C 34.53, H 8.11, N 8.05; found C 34.46, H 8.18, N 8.06.

Bis(μ-2-aminopropanolato-*N,O*)tetramethyldigallium (3): A solution of 2-amino-1-propanol (0.60 g, 8.0 mmol) in CH_2Cl_2 (10 cm^3) was cooled to −78 °C and Me_3Ga (0.92 g, 8.0 mmol) was added dropwise. After the addition was completed, the reaction mixture was warmed to room temperature and stirred for 0.5 h. Complex **3** was isolated at −20 °C as colorless crystals. Yield: 90%. − ^{1}H NMR (C_6D_6, 300 MHz): δ = −0.07 (s, 12 H, Ga−CH$_3$), 0.42 (br, 4 H, NH$_2$), 0.50 (d, 6 H, CH$_3$), 2.38 (br. m, 2 H, CH) 2.97 and 3.51 (dd, 4 H, OCH$_2$). − $C_{10}H_{28}Ga_2N_2O_2$ (347.78): calcd. C 34.53, H 8.11, N 8.05; found C 34.48, H 8.15, N 8.03.

X-ray Crystal Structure Analysis: Single crystals of **2** and **3** suitable for X-ray diffraction studies were placed in a thin-walled capillary tube (Lindemann glass 0.5 mm) in an inert atmosphere. The tube was plugged with grease, then flame-sealed and mounted on a goniometer head. Selected crystallographic data, the parameters for data collection and refinement procedures are presented in Table 1.

Compound 2: Unit cell parameters and intensity data for compound **2** were collected with a P3 Siemens diffractometer employing graphite monochromated Mo-K_α radiation. The crystal classes and the orientation matrices were obtained by the least-squares refinement of 30 well-centered reflections randomly selected in the 2θ range 16−29°. The intensities were collected in the ω−2θ mode

Table 1. Crystal data and data collection parameters for **2** and **3**

Compound	**2**	**3**
Empirical formula	$C_5H_{14}GaNO$	$C_{10}H_{28}Ga_2N_2O_2$
Molecular weight	173.89	347.78
Temperature [K]	293(2)	293(2)
Wavelength [Å]	0.71073 (Mo-K_α)	0.71073 (Mo-K_α)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/a$
Unit cell dimensions	$a = 16.171(2)$ Å	$a = 8.663(2)$ Å
	$b = 10.9828(14)$ Å	$b = 11.738(2)$ Å
	$c = 20.146(3)$ Å	$c = 16.293(3)$ Å
	$\beta = 111.411(12)°$	$\beta = 94.17(3)°$
Volume [Å^3]	3331.1(8)	1652.4(6)
Z	16	4
Density [Mg/m^3]	1.387	1.398
Absorption coefficient [mm^{-1}]	3.227	3.253
$F(000)$	1440	720
Crystal size [mm^3]	0.64 × 0.19× 0.15	0.30 × 0.26× 0.14
θ range for data collection	2.1 to 25.0°	3.0 to 27.4°
Index ranges	$0 \leq h \leq 19, 0 \leq k \leq 13, -24 \leq l \leq 22$	$0 \leq h \leq 11, 0 \leq k \leq 15, -21 \leq l \leq 21$
Independent reflections	5863 ($R_{int} = 0.0142$)	3752
Absorption correction type	Gaussian	Semi-empirical
Data/restraints/parameters	5863/0/364	3752/20/190
Final R indices $[I > 2\sigma(I)]$[a]	$R1 = 0.0381, wR2 = 0.0681$	$R1 = 0.0549, wR2 = 0.1098$
Goodness-of-fit on F^2[b]	0.920	1.089
R indices (all data) [a]	$R1 = 0.0863, wR2 = 0.0789$	$R1 = 0.0844, wR2 = 0.1271$
Extinction coefficient	0.00029(5)	0.0035(6)
Largest diff. peak and hole	0.37 and −0.29 e·Å^{-3}	0.91 and −0.81 e·Å^{-3}

[a] $R1 = \Sigma|F_o-F_c|/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2-F_c^2)/\Sigma wF_o^4]^2$. − [b] Goodness of fit $S = [\Sigma w(F_o^2-F_c^2)^2/\Sigma(n-p)]^{1/2}$.

and corrected for Lorentz-polarization effects and crystal decomposition (3.8%). A Gaussian absorption correction based on the crystal shape was applied, which resulted in transmission factors ranging from 0.531 to 0.634. The structure was solved by direct methods using the SHELXS-86 program.[17] The distribution of the peaks showed that compound **2** crystallizes with four independent molecules in the asymmetric unit. The structure of **2** was refined by full-matrix least-squares on F^2 using the program SHELXL-97.[18] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of the methyl groups C(25) and C(35) were refined as disordered groups with two positions rotated by 60° about the C−C bond. The remaining hydrogen atoms were located from the Fourier-difference map and isotropically refined.

Compound 3: Diffraction data were collected at room temperature on a Nonius Kappa diffractometer equipped with a CCD area detector. The structure was solved by direct methods (SHELXS-86 program[17]). Compound **3** crystallizes with one independent dimeric molecule in the asymmetric unit. Full-matrix least-squares refinement was carried out on F^2 (SHELXL-97[18]). All non-hydrogen atoms were refined anisotropically. The O(2)C(6)C(7)C(8)N(2) ligand revealed substantial disorder, which was modeled in terms of two sets of OCH$_2$CH(CH$_3$)NH$_2$ atoms (two moieties of opposite configuration as the chiral center) with adjusted occupancy factors of 0.61(1) and 0.39(1), respectively. Both disordered moieties were refined anisotropically using similarity restraints for the chemically equivalent C−C, C−O and C−N distances. Hydrogen atoms were added to the structure model at geometrically idealized coordinates with fixed isotropic temperature factors.

[1] J.-M. Lehn, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 89; G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier, Amsterdam, **1989**; J.-M. Lehn, *Supramolecular Chemistry, Concepts and Perspectives*, VCH, Weinheim, **1995**; C. V. K. Sharma, G. R. Desiraju, *Perspectives in Supramolecular Chemistry. The Crystal as a Supramolecular Entity*, Wiley, Chichester, **1996**.

[2] G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, **1997**; C. B. Aakeröy, K. R. Seddon, *Chem. Soc. Rev.* **1993**, 397−407; J. C. MacDonald, G. M. Whitesides, *Chem. Rev.* **1994**, *94*, 2383−2420.

[3] D. Braga. F. Grepioni, G. R. Desiraju, *Chem. Rev.* **1998**, *98*, 1375−1405; D. Braga. F. Grepioni, *Coord. Chem. Rev.* **1999**, *183*, 19−41.

[4] G. E. Coates, R. G. Hayter, *J. Chem. Soc.* **1953**, 2519−2524.

[5] S. J. Rettig, A. Storr, J. Trotter, *Can. J. Chem.* **1975**, *53*, 58−66.

[6] K. S. Chong, S. J. Rettig, A. Storr, J. Trotter, *Can. J. Chem.* **1979**, *57*, 586−590.

[7] S. J. Rettig, A. Storr, J. Trotter, K. Uhrich, *Can. J. Chem.* **1984**, *62*, 2783−2792.

[8] E. C. Onyiriuka, S. J. Rettig, A. Storr, J. Trotter, *Can. J. Chem.* **1987**, *65*, 782−788.

[9] G. D. Gracey, S. J. Rettig, A. Storr, J. Trotter, *Can. J. Chem.* **1987**, *65*, 2469−2477.

[10] W. T. Tao, Y. Han, Y. Z. Huang, X. L. Jin, J. Sun, *J. Chem. Soc., Dalton Trans.* **1993**, 807−809.

[11] H. Schumann, S. Wernik, F. Girgsdies, R. Weimann, *Main Group Metal Chemistry* **1996**, *19*, 331−338.

[12] K.-H. Thiele, E. Hecht, T. Gelbrich, U. Dümichen, *J. Organomet. Chem.* **1997**, *540*, 89−94.

[13] E. Hecht, T. Gelbrich, S. Wernik, R. Weiman, K.-H. Thiele, J. Sieler, H. Schumann, *Z. Anorg. Allg. Chem.* **1998**, *624*, 1061−1066.

[14] H. S. Sun, Q. Zhao, Y. J. Liu, H. M. Hu, X. Z. You, Z. Y. Zhou, *J. Coord. Chem.* **1999**, *47*, 459−465.

[15] J. Z. Tian, J. Q. Zhang, X. Shen, H. X. Zou, *J. Organomet. Chem.* **1999**, *584*, 240−245.

[16] J. Lewiński, J. Zachara, I. Justyniak, *Chem. Commun.* **1997**, 1519−1520; J. Lewiński, J. Zachara, I. Justyniak, *Organometallics* **1997**, *16*, 3859−3862; J. Lewiński, I. Justyniak, Z. Ochal, J. Zachara, *J. Chem. Soc., Dalton Trans.* **1999**, 2909−2911.

[17] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.

[18] G. M. Sheldrick, *SHELXL 97, Program for Refinement of Crystal Structures*, University of Göttingen, **1993**.