

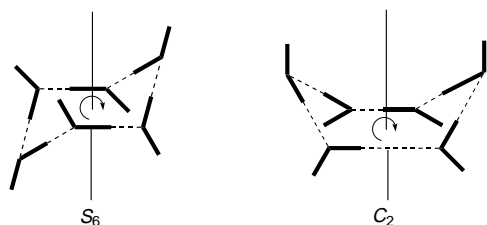
The structure of the S_6 -symmetric methanol hexamer assembled in a supramolecular hydrophobic cavity

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The structure of the cyclic S_6 -symmetric hexamer of methanol has been established by X-ray crystallography in crystals of $[\text{GaLF}_3](\text{MeOH})_{6/2} \cdot (\text{MeOH})_3 \cdot \text{CH}_2\text{Cl}_2$ **1**; the hexamer has been proposed to be the dominant species in liquid methanol.⁴

Crystalline, solid methanol consists of infinite zigzag chains of hydrogen bonded methanol molecules with an $\text{O} \cdots \text{O}$ distance of 2.66 Å at -110 °C.¹ Upon melting long chains and/or cyclic oligomers $(\text{MeOH})_n$ form ($n = 3-20$).² In his famous book *The Nature of the Chemical Bond*, Pauling has depicted the cyclic hexamer $(\text{MeOH})_6$ with six $\text{O}-\text{H} \cdots \text{O}$ bonding contacts as an example.³ This cluster has later been proposed to be the dominant species in liquid methanol at room temperature⁴ and its structure and vibrational spectrum in the gas phase have been repeatedly calculated.⁵ Two conformers of nearly equal energy apparently exist: an S_6 and a C_2 symmetric form (Scheme 1) both of which have been generated by the method of size selection of clusters by momentum transfer in a scattering experiment with atoms in the gas phase.^{5a,6} Upon vaporization of methanol the tetramer $(\text{MeOH})_4$ has been shown to be the major component of the vapour.⁷ To date none of these cyclic structures has been found in the solid state and, consequently, they have not been characterized by single crystal X-ray crystallography.



Scheme 1

We report here the crystal structure of $[\text{GaLF}_3](\text{MeOH})_{6/2} \cdot (\text{MeOH})_3 \cdot \text{CH}_2\text{Cl}_2$ **1**† where L represents the neutral pendent arm macrocycle 1,4,7-tris(2-amino-3,5-di-*tert*-butylbenzyl)-1,4,7-triazacyclononane. In crystals of **1** the cyclic $(\text{MeOH})_6$ hexamer is assembled in a hydrophobic ligand cavity.

The reaction of L with $\text{GaF}_3 \cdot 3\text{H}_2\text{O}$ (1 : 2) in refluxing ethanol produces colourless microcrystals of $[\text{GaLF}_3]$ upon addition of water to the above mixture. Colourless crystals of **1** were obtained from a dichloromethane–methanol (1 : 5 v/v) solution of $[\text{GaLF}_3]$ at -20 °C. Details of the ligand and complex syntheses will be reported elsewhere.

The solid state structure of **1** consists of neutral $[\text{GaLF}_3]$ molecules shown in Fig. 1 where the 1,4,7-triazacyclononane backbone of the macrocycle L is bound to a GaF_3 fragment. The three 2-amino-3,5-di-*tert*-butylbenzyl arms are not coordinated. A *cis*- $\text{N}_3\text{F}_3\text{Ga}$ octahedron is formed. The molecule possesses C_3 symmetry. The three uncoordinated pendent arms adopt a conformation where they are folded upwards toward the coordinated nine-membered 1,4,7-triazacyclononane ring. An approximately circular bowl-shaped hydrophobic ‘surface’ is formed with six bulky tertiary butyl groups at the rim of this

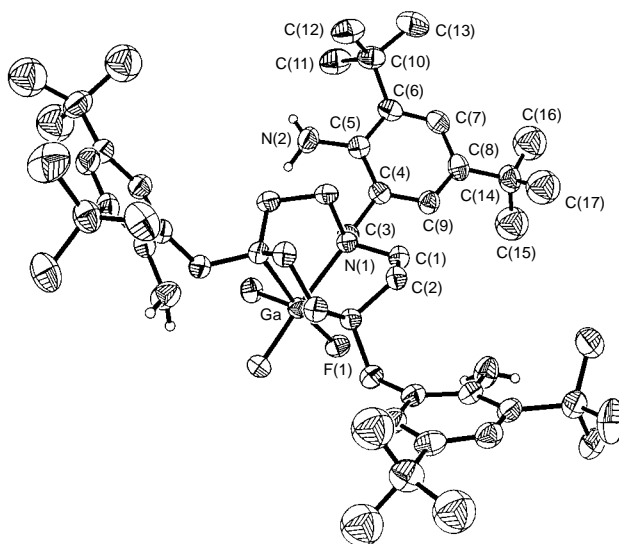


Fig. 1 Molecular structure of the neutral $[\text{GaLF}_3]$ complex in crystals of **1**. Selected distances (Å) and angles (°): Ga–N(1) 2.147(3), Ga–F(1) 1.849(2), C(5)–N(2) 1.397(6), F(1)–Ga–F(1') 94.1(1), N(1)–Ga–N(1') 82.8(1), N(1)–Ga–F(1) 88.7(1).

bowl. Two such $[\text{GaLF}_3]$ molecules are then packed together in a fashion which brings the two hydrophobic bowl-shaped surfaces facing each other. The two sets of three pendent arms are staggered. This ‘dimer’ is held together by van der Waals forces only. Roughly, its shape may be viewed as clam-like with S_6 symmetry. The inner surface of this clam is of purely hydrophobic nature since it comprises exclusively phenyl rings and methylene hydrogen atoms of the two ligands L. The disc-shaped cavity inside is filled with six methanol molecules as is shown in Fig. 2. Fig. 3 shows the six MeOH molecules forming a cyclic structure *via* six $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonding contacts [$\text{O} \cdots \text{O}$ 2.62(1) Å]. The methyl groups are staggered; the hexamer adopts S_6 symmetry. The methyl groups form weak van der Waals contacts to the hydrophobic inner

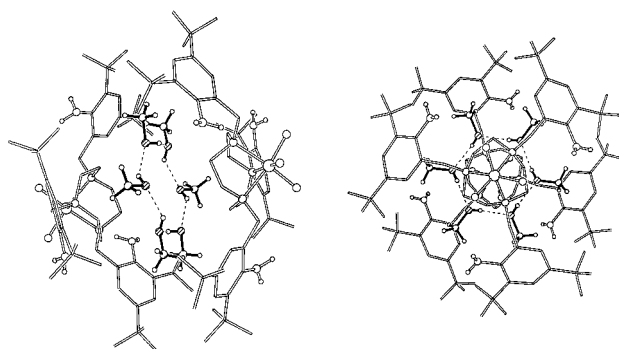


Fig. 2 Schematic representation of the $[\text{GaLF}_3]_2 \cdot (\text{MeOH})_6$ unit in **1**. Left: side-view looking into the ‘clam’ composed of two $[\text{GaLF}_3]$ shells. Right: view down the S_6 axis on which the two Ga^{3+} ions (only one is seen) lie.

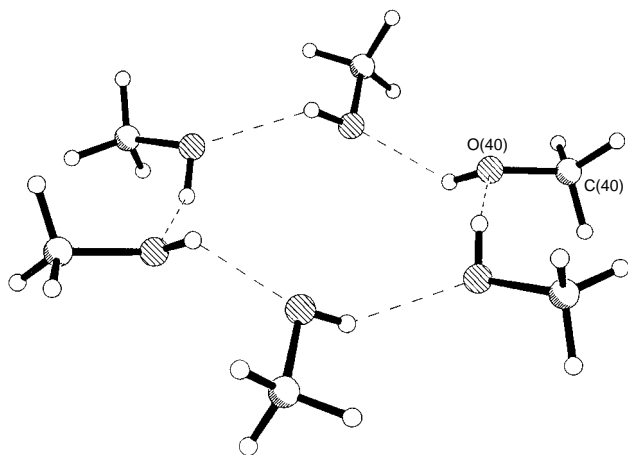


Fig. 3 Schematic representation of the S_6 symmetric methanol hexamer in **1**. Selected distances (Å): O(40)···O(40') 2.62(1), O(40)–C(40) 1.394(9).

surface of the cavity only. The O–H···O bonds are asymmetric and the twelve-membered ring is puckered.

The outer surface of the clam exposes two sets of (a) three fluoro ligands and (b) of three amino groups; it is 'sticky'. Three additional methanol molecules per GaLF₃ unit form each a strong O–H···F contact at 2.58(1) Å and two somewhat weaker O···H–N interactions with the amino groups at 2.94(1) and 3.39(1) Å. The latter two interactions enforce an ordered packing of the clams relative to each other in the solid state ('inter-clam' contacts).

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Notes and References

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† *Crystal data*: **1**: C₅₈H₁₁₀Cl₂F₃GaN₆O₆, $M = 1185.14$, trigonal, space group $R\bar{3}$, $a = b = 18.940(3)$, $c = 33.672(6)$ Å, $U = 10461(3)$ Å³, $Z = 6$, $D_c = 1.129$ Mg m⁻³, $\mu(\text{Mo-K}\alpha) = 0.53$ mm⁻¹, $F(000) = 3840$. A transparent colorless block of $0.56 \times 0.49 \times 0.28$ mm was mounted in a sealed capillary. 3517 independent reflections were collected on an Enraf-Nonius CAD4 diffractometer [graphite monochromated Mo-K α radiation, 293(2) K] using ω -scan technique. The structure was solved by direct methods and all non-hydrogen atoms were refined anisotropically using full-matrix least squares based on F^2 . Carbon atoms C(15), C(16), C(17) belonging to a *tert*-butyl group were disordered by rotation and a split atom model was applied. The CH₂Cl₂ solvent molecule was found to be disordered on a crystallographic threefold axis. Owing to evaporation, its occupancy factor was reduced to one third of the complete molecule (1/9 for carbon and 2/9 for chlorine). The methyl, methylene and phenyl ring hydrogen atoms were placed at calculated positions whereas all OH and NH₂ hydrogen atoms were located in a difference electron density map around a circle which represents the possible loci for a fixed O–H, or N–H distance and C–N(O)–H angle. Final $R_1 = 0.072$, $wR_2 = 0.196$, 2740 $F_o > 4\sigma(F_o)$, $2\theta \leq 50^\circ$, 233 parameters. CCDC 182/747.

- 1 J. K. Tauer and W. N. Lipscomb, *Acta Crystallogr.*, 1952, **5**, 606.
- 2 D. L. Wertz and R. K. Kruh, *J. Chem. Phys.*, 1967, **47**, 388; A. H. Narten and A. Habenschuss, *J. Chem. Phys.*, 1984, **80**, 3387; M. Magini, G. Paschina and G. Piccaluga, *J. Chem. Phys.*, 1982, **77**, 2051.
- 3 L. Pauling, in *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, NY, 1962, p. 474.
- 4 S. Sarkar and R. N. Joarder, *J. Chem. Phys.*, 1993, **99**, 2032.
- 5 (a) U. Buck, B. Schmidt and J. G. Siebers, *J. Chem. Phys.*, 1993, **99**, 9428; (b) U. Buck, *Ber. Bunsenges. Phys. Chem.*, 1992, **96**, 1275; (c) U. Buck and B. Schmidt, *J. Chem. Phys.*, 1993, **98**, 9410; (d) U. Buck and I. Ettischer, *J. Chem. Phys.*, 1994, **100**, 6974.
- 6 U. Buck, *J. Phys. Chem.*, 1994, **98**, 5190.
- 7 W. Weltner, Jr. and K. S. Pitzer, *J. Am. Chem. Soc.*, 1951, **73**, 2606.

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