

The self-assembly between C_2 -symmetric (methanol)₆ or S_6 -symmetric (ethanol)₆ cyclohexamers and paddle-wheel dinuclear copper units leads to unique 1D polymer chains†

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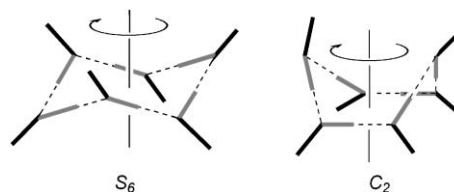
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The first crystallographic evidences of the theoretically suggested C_2 -symmetric cyclohexameric form of liquid methanol and the S_6 -symmetric cyclohexameric form of liquid ethanol are reported, trapped inside a hydrophilic pocket shielded by *tert*-butyl groups.

The assessment of the structure of liquid compounds is highly valuable and enjoys increasing interest within the scientific community.¹ It is indeed important to gain knowledge of the nature of weak intermolecular interactions, such as hydrogen bonds in protic solvents, since they govern the physicochemical properties of molecular systems in the condensed phase.² In that context, clusters are aggregates of atoms and/or molecules which are held together *via* binding interactions, from weak hydrogen bonds to strong covalent bonds. Clusters are therefore regarded as the bridging gap between the single molecules in the gas phase and the condensed matter, namely the liquid or the solid phase.³ Therefore, molecular clusters are crucial to understand important physical phenomena, like nucleation or phase transitions.^{4,5} Considerable efforts have been devoted to the study of small methanol clusters.⁶ At -110 °C, solid crystalline methanol forms infinite H-bonded zigzag chains.⁷ Above its melting point, these chains are broken up to linear and/or cyclic (MeOH)_{*n*} oligomers with *n* ranging from 3 to 20.⁸ It has been established that the cyclic methanol hexamer, already mentioned in 1962 by Pauling,⁹ is predominant in liquid methanol at room temperature,^{10,11} while a tetrameric methanol cluster is observed in the vapour.¹² Two conformers of this methanol cyclohexamer apparently exist in solution, namely the S_6 and the C_2 symmetric forms (Scheme 1).⁶ Wiegardt *et al.* have reported the first and only crystallographic evidence of the S_6 assembly of (MeOH)₆.¹³ To date, the C_2 conformation has not been characterized by X-ray crystallography. Similarly, the structure of liquid ethanol is being investigated,^{14,15} and Sarkar *et al.* have pointed out the possible existence of cyclic hexamers of ethanol at room temperature.¹⁶

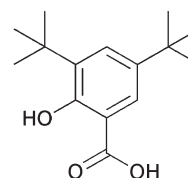
In the present study, the crystal structures of [Cu₂(HL)₄(MeOH)₂]₄MeOH **1**† and [Cu₂(HL)₄(EtOH)₂]₄EtOH **2**† are



Scheme 1 Cyclic hexameric forms of liquid methanol.

reported where HL represents mono-deprotonated 3,5-di-*tert*-butylsalicylic acid (Scheme 2, H₂L). The reaction of H₂L with copper(II) acetate monohydrate (2 : 1) in methanol affords, after slow evaporation of the solvent for a week in air, green rectangular crystals of **1** in 85% yield. The crystal structure determined by X-ray diffraction (Fig. S1)† shows a dinuclear Cu^{II} unit bridged by four carboxylate HL ligands. The symmetry related Cu(1) and Cu(1a) ions are in a Jahn–Teller distorted octahedral environment formed by four oxygen atoms from four different HL ligands, an axial methanol molecule, and a metallic center. The in-plane CuO bond lengths ranging from 1.961(3) to 1.986(3) Å can be considered as normal, as well as the basal angles, close to 90°, varying from 88.47(14) to 90.53(14)°. The methanolic O(1) atom is located at a longer distance of 2.155(4) Å, characteristic of a Jahn–Teller axially elongated bond. The short Cu(1)–Cu(1a) distance of 2.586(1) Å is typical for strongly antiferromagnetically coupled Cu(II) ions; as determined by magnetic measurements the coupling $2J$ equals -355 cm⁻¹.† In addition, in complex **1**, each ligand exhibits strong/intermediate O–H⋯O salicylate-type intramolecular hydrogen bonding, between the non-coordinated phenolic proton and one carboxylate oxygen atom, [O⋯O = 2.575(6) Å and O(27)⋯O(21) = 2.565(6) Å; O–H⋯O angles of 146 and 131°, respectively, for the two crystallographically independent ligands.¹⁷

The most fascinating feature of this species is that C_2 -symmetric (MeOH)₆ units are trapped within the coordination network. Indeed, each copper ion of the dinuclear core is axially bound to a methanol molecule belonging to a methanol cyclohexamer. These coordinative/H-bonding interactions give rise to the formation of a



Scheme 2 3,5-Di-*tert*-butylsalicylic acid (H₂L).

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† Electronic supplementary information (ESI) available: Experimental procedures for the preparation of **1** and **2**, ORTEP representations of the corresponding crystal structures, and magnetic susceptibility measurements for **1**. See DOI: 10.1039/b608220c

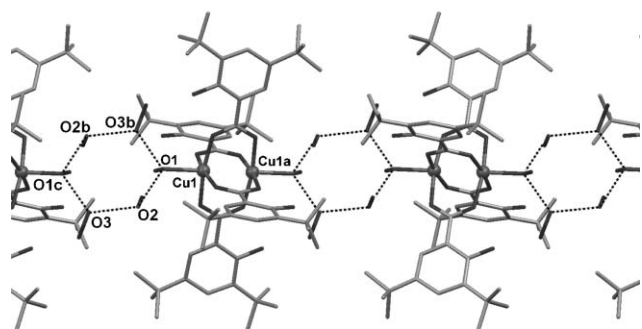


Fig. 1 1D polymer assembled from $[\text{Cu}_2(\text{HL})_4]/(\text{MeOH})_6$ units. $\text{O}(1)\cdots\text{O}(2)$ 2.548(8) Å, $\text{O}(1)\cdots\text{O}(3b)$ 3.037(9) Å, $\text{O}(2)\cdots\text{O}(3)$ 2.603(12) Å.

unique 1D polymer with alternating $[\text{Cu}_2(\text{HL})_4]$ and $(\text{MeOH})_6$ entities, as depicted in Fig. 1. As clearly evidenced in Fig. 1 and 2, the six methanol molecules form a C_2 -symmetric cyclic structure by means of moderate to strong hydrogen bonds [$\text{O}(1)\cdots\text{O}(2) = 2.548(8)$ Å; $\text{O}(1)\cdots\text{O}(3b) = 3.037(9)$ Å; $\text{O}(2)\cdots\text{O}(3) = 2.603(12)$ Å], in the range of the $\text{O}\cdots\text{O}$ contacts reported by Wiegardt for the S_6 - $(\text{MeOH})_6$ conformer.¹³ The $\text{D}-\text{H}\cdots\text{A}$ angles vary from 145 to 169°, which are typical for moderate to strong H bonds.¹⁷ Strikingly, the present methanol hexamer adopts a twisted-boat conformation (Fig. 2b). This distortion from the predicted boat conformation of $(\text{MeOH})_6$ present in liquid methanol (Scheme 1) is most likely due to (a) the fact that the oxygen atoms $\text{O}(1)$ and $\text{O}(1a)$ are coordinated to copper ions (Fig. 1), and (b) the hydrophobic outer *tert*-butyl shell which cages in the methanol molecules, as evidenced by the orientation of the methanolic methyl groups pointing outside the hydrophilic core (Fig. 3a). However, this C_2 -symmetric structure represents the first crystallographic evidence of the second, energetically favoured form of liquid methanol. Indeed, a thorough search on the Cambridge Structural Database (CSD version 5.27, January 2006) reveals that, out of all 310 structures that contain at least two hydrogen-bonded methanol molecules (2.0 Å $<$ $\text{O}\cdots\text{O}$ $<$ 3.2 Å), only three of them were found to contain methanol cyclohexamers all of which have a chair conformation (CSD refcodes FEZTUA, YAHYIG, and NILCUG). Interestingly, nine examples of cyclic tetramers have been found (CSD refcodes AHIHII, HIKJUG, IMUZAR, IPASUN, QEFDAG, QIRYIZ, RECTAU, RECTAU01, and VIQHOS), which are also considered as major components of liquid methanol.⁵

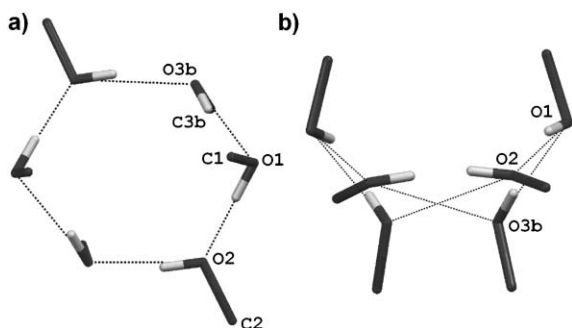


Fig. 2 Views of (a) the cyclic methanol hexamer in **1** and (b) the C_2 -symmetric twisted boat conformation of this cyclohexamer.

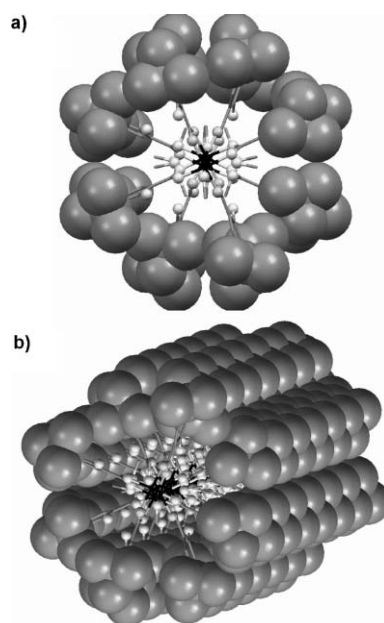


Fig. 3 (a) Hydrocarbon shell generated by the *tert*-butyl groups (shown in the space filling style); (b) 16 Å wide infinite nanocylinder exhibiting an inner hydrophilic cavity. C atoms in grey, O atoms in light grey and Cu atoms in black.

Each dinuclear copper complex is staggered by 45° from its two neighbouring dicopper units, giving rise to a hydrocarbon cylindrical shell formed by the *tert*-butyl groups, and with a diameter of 1.6 nm (Fig. 3a and 3b). The inner part of the cylinder is a hydrophilic core wherein methanolic, phenolic, and carboxylic oxygen atoms are confined (light grey atoms in Fig. 3).

The reaction of H_2L with copper(II) acetate monohydrate (2 : 1) in ethanol leads to the formation of green rectangular crystals of **2** in 73% yield. As revealed by X-ray diffraction studies, complex **2** is isostructural to **1**, with a $\text{Cu}(1)\cdots\text{Cu}(1a)$ distance of 2.599(1) Å (Fig. S2).† The coordination environments of both copper ions are related to the ones of **1**, with $\text{Cu}-\text{O}$ bond lengths ranging from 1.961(4) to 2.154(4) Å. Remarkably, a similar coordination/H-bond network is realised between $[\text{Cu}_2(\text{HL})_4]$ and $(\text{EtOH})_6$ units (Fig. 4). The resulting 1D polymer entraps cyclic ethanol

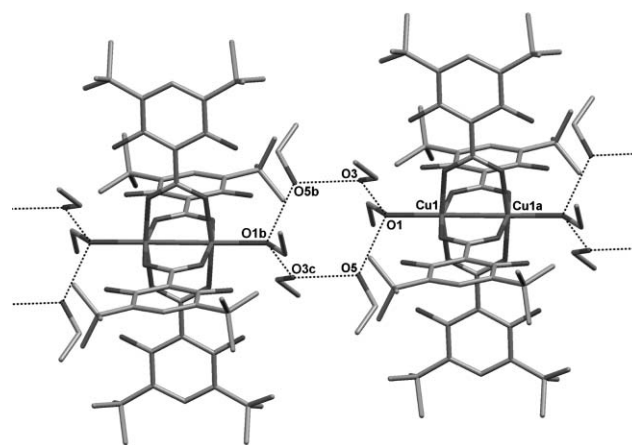


Fig. 4 1D polymer assembled from $[\text{Cu}_2(\text{HL})_4]/(\text{EtOH})_6$ units. $\text{O}(1)\cdots\text{O}(3)$ 2.778(7) Å, $\text{O}(1)\cdots\text{O}(5)$ 2.729(7) Å, $\text{O}(3)\cdots\text{O}(5b)$ 2.637(8) Å.

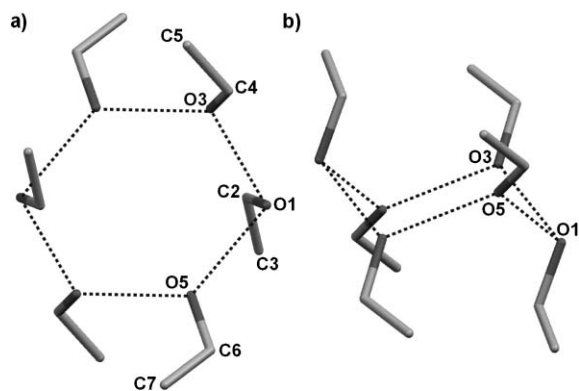


Fig. 5 View of the (a) cyclic ethanol hexamer and (b) the S_6 -symmetric chair conformation of this cyclohexamer.

hexamers, this time, in a chair cyclohexane conformation (Fig. 5). The S_6 -symmetric structure arises from strong hydrogen-bonding interactions [O(1)⋯O(3) = 2.778(7) Å; O(1)⋯O(5) = 2.729(7) Å; O(5b)⋯O(3) = 2.637(8) Å] between six ethanol molecules, with D–H⋯A angles varying from 155 to 173°.¹⁷ Once again, the methylene groups are pointing towards the outer shell, where they are interacting with the *tert*-butyl groups. The ethanolic oxygen atoms constituting the hexagonal rings are located in the hydrophilic core, containing the copper ions and the oxygen atoms of the ligands. Contrary to **1**, the dinuclear copper units are not staggered by 45°, but are perfectly stacked. This supramolecular structural difference is most likely due to the longer hydrocarbon chains of the ethanol molecules which consequently do not sterically allow the rotation of the copper complexes. This S_6 -symmetric structure corresponds to the first crystallographic evidence of a cyclohexameric form of liquid ethanol, which is expected to be one of its energetically favoured constituting units. No example of cyclic ethanol hexamer has been found in the CSD (version 5.27, January 2006).

As suggested by spectroscopic and computational studies,^{6,18} liquid methanol is constituted of H-bonded oligomers (from trimer to decamer), with two low energy configurations for the dominant cyclohexameric form, *i.e.* the S_6 and C_2 symmetry.⁵ The crystallographic data reported by Wiegardt,¹³ as well as the present ones support the theoretically predicted structures. Indeed, the two forms have now been crystallographically characterised in two different compounds, which suggest the presence of this oligomer in the liquid phase of methanol, as foreseen by Pauling more than 40 years ago.⁹ Although the structure of liquid ethanol has been comparatively less studied,^{15,16} the present study indicates that cyclohexamers are also present in this phase. Furthermore, these investigations show that the herein reported paddle-wheel copper complex is able to trap the liquid, hydrogen-bonded form of protic solvents.

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Notes and references

‡ *Crystal data:* for [Cu₂(HL)₄(CH₃OH)₂] \cdot 4CH₃OH (**1**): C₆₆H₁₀₈Cu₂O₁₈, blue, rectangular plate, $M = 1316.60$, monoclinic, space group $P2/c$, $a = 12.295(3)$, $b = 12.971(3)$, $c = 22.984(5)$ Å, $\beta = 103.57(3)^\circ$, $V = 3563.1(13)$ Å³, $Z = 2$, $D_c = 1.227$ g cm⁻³, $T = 173(2)$ K, $F(000) = 1412$, $\mu(\text{Mo-K}\alpha) = 0.661$ mm⁻¹. A transparent green rectangular single crystal of $0.04 \times 0.08 \times 0.08$ was mounted on a glass fiber using oil drop method. 91220 independent reflections (8179 unique; $R_{\text{int}} = 0.097$) were collected on a Bruker-Nonius Kappa CCD diffractometer. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically. The hydrogen atom of the coordinated methanol OH-group was located from the difference Fourier map. All other H-atoms were geometrically placed and refined as part of a riding model. The final agreement factors are $R_1 = 0.076$ for 4778 data with $F > 4\sigma(F)$ and $R_1 = 0.138$, $wR_2 = 0.220$ for 8179 data.

Crystal data: for [Cu₂(HL)₄(CH₃CH₂OH)₂] \cdot 4CH₃CH₂OH (**2**): C₇₂H₁₁₆Cu₂O₁₈, green, rectangular plate, $M = 1396.73$, triclinic, space group $P-1$, $a = 11.809(4)$, $b = 13.022(3)$, $c = 13.094(3)$ Å, $\beta = 96.47(3)^\circ$, $V = 1994.6(9)$ Å³, $Z = 1$, $D_c = 1.163$ g cm⁻³, $T = 173(2)$ K, $F(000) = 750$, $\mu(\text{Mo-K}\alpha) = 0.594$ mm⁻¹. A transparent green rectangular single crystal of $0.32 \times 0.32 \times 0.02$ was mounted on a glass fiber using the oil drop method. 30961 independent reflections (9135 unique; $R_{\text{int}} = 0.086$) were collected on a Bruker-Nonius Kappa CCD diffractometer. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically. The hydrogen atom of the coordinated ethanol OH-group was located from the difference Fourier map. All other H-atoms were geometrically placed and refined as part of a riding model. The final agreement factors are $R_1 = 0.089$ for 4750 data with $F > 4\sigma(F)$ and $R_1 = 0.172$, $wR_2 = 0.248$ for 9135 data.

CCDC 610529 (**1**), 610530 (**2**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b608220c

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