Influence of lower rim C-methyl group on crystal forms and metal complexation of resorcinarene bis-crown-5

Kaisa Helttunen, Tiia-Riikka Tero and Maija Nissinen

C-methyl resorcinarene bis-crown-5 (I) with pendant methyl groups at the lower rim was prepared and crystallized in various solvent mixtures with and without selected metal salts. The crystal structures of two polymorphic forms of unsolvated 1 (I-I and I-II), three solvates (acetonitrile, chloroform and dichloromethane-methanol), and three metal complexes with silver and cesium salts were obtained. The lower rim methyl groups and the block shape of the host promote crystal packing in brick-wall type assemblies, in which the binding cavities are efficiently filled by the crown bridges. Thus, solvents are found in the interstitial space or coordinated to the crown bridges on top of the cavity, whereas more strongly binding metal cations are able to occupy the cavity. The chloroform solvate proved to be a relatively labile crystal form, which transformed to unsolvated form (I-I) over time. Resorcinarene monocrown-5 (2) was obtained as a minor product of the bridging reaction. Two solvate structures (acetonitrile and chloroform-water) of 2 are also reported, providing an example of the effect of the missing crown bridge on the solvate structures.

Introduction

Resorcinarenes, macrocycles with a concave aromatic binding site, are well-known supramolecular hosts for ammonium and alkali metal cations, and small organic molecules. The resorcinarene cavity consists of four resorcinol rings, which are usually in a bowl-like rcce crown conformation supported by a circle of intramolecular hydrogen bonds between the hydroxyl groups at the upper rim (Fig. 1). Resorcinarene conformation affects its ability to adapt to the shape and size of the guest leading to a great variety in complexation capacity and, even more so, in the solid state structures of resorcinarenes. The most remarkable solid state resorcinarene structures include hydrogen bonded dimeric and hexameric capsules, as well as tubular assemblies mediated by π···π interactions. Inclusion of guests, such as ammonium cations or alcohols within the resorcinarene cavity has an important role in the formation of these assemblies.

Hydroxyl group functionalization affects the ability of the resorcinarene to assume different conformations by interfering with the intramolecular hydrogen bonding, or by restricting the conformation to a permanent crown or boat in resorcinarene cavitands and in crown ether bridged resorcinarenes, respectively. The lower rim alkyl chain length also has an effect on the resorcinarene conformation, since rcce C-methyl resorcinarenes crystallize in the boat conformation more readily than C-ethyl or C-propyl resorcinarenes, and other, more rare conformations, such as scoop, rect chair, and rect diamond have been reported in addition to a typical crown conformation. The conformational variation has made the C-methyl resorcinarene a versatile building block for 2-D and 3-D supramolecular networks, in which resorcinarenes are connected by hydrogen bonding linkers and the lattice cavities are filled with guests, such as ferrocene, ruthenocene, m-xylene and benzophenone, or solvents.

Partially O-alkylated resorcinarenes have a reduced amount of hydrogen bond donating and functionalization sites at the upper rim, which simplifies the synthetic modification, such as the preparation of crown ether bridged resorcinarenes. C$_2$ symmetric tetramethoxy resorcinarenes were first synthesized by McIlwrie et al. and the series of different lower rim

Figure 1. C-methyl resorcinarene in a rcce crown conformation (A, top) and in a rcce boat conformation (A, bottom) showing typical hydrogen bonding schemes with dashed bonds. The covalently locked crown and boat conformations are shown in (B).
alkyl chain lengths was recently completed with a C-methyl derivative.²⁸ The longer alkyl chain tetramethoxy resorcinarenes (C₂H₅–C₁₃H₂₅) have previously been used as starting materials for resorcinarene bis- and mono-crown-5 derivatives, which are synthesized by attaching one or two tetra(ethyleneglycol) bridges to the hydroxyl groups at the upper rim.²⁹,³⁰ The crown ether bridged resorcinarene derivatives with a fixed boat conformation have shown a reasonable affinity towards ammonium cations,³¹ alkali metals (K⁺, Rb⁺, Cs⁺)²⁹,³⁰,³² and silver cations.³³ Versatile packing motifs, including layers,³⁰,³²,³³,³⁴ capsules,²⁹,³⁰,³³ nanorods,³³ and a helical chain,²⁹ especially for the metal complexes of C-ethyl resorcinarene bis-crown-5, have been observed. The comparison of the C₂H₅–C₁₃H₂₅ derivatives of resorcinarene bis-crown-5 has indicated that lower rim alkyl chain affects the self-assembly and crystal packing of the bis-crown-5, but also the complexation properties of the host probably due to solubility differences.³⁰,³⁴ These results prompted us to study how the conformational properties of the C-methyl resorcinarene manifest in the resorcinarene crown ether derivatives C-methyl bis-crown-5 and mono-crown-5, which turned out to show remarkably different solvate formation and crystal packing properties than their longer alkyl chain analogues.

Results and discussion

Inherently chiral C-methyl resorcinarene bis-crown-5 (1, Fig. 2) and mono-crown-5 (2) were synthesized from tetramethoxy resorcinarene²⁸ using the protocol previously applied for the long alkyl chain bearing resorcinarenes.²⁹ In both cases the resorcinarene framework adopts a permanent boat conformation due to bridging, in which the dihedral angles between the opposing aryl rings describe the openness of the binding cavity. In bis-crown 1, the dihedral angles between the horizontal rings are typically bent over 180° and the angles between the vertical rings are negative reducing the apparent cavity size in solid state. In mono-crown 2 the crown bridge encloses only one end of the cavity and the other end is open leaving the binding site more exposed.

Unsolvated crystal structures of bis-crown 1

The unsolvated crystal forms of 1 were obtained from 1-propanol and by rapid evaporation of chloroform-acetone solution containing traces of DMF (structures I-I in P2₁/c and I-II in P-1, respectively). Form I-I was also obtained from ethyl acetate and several co-crystallization experiments with silver and alkali metal salts, which indicates the stability of this crystal form. Previously, unsolvated crystal forms have only been obtained for C-butyl and C-pentyl resorcinarene bis-crown derivatives,³⁰ whereas C-ethyl derivative has crystallized as various solvate structures.²⁹,³⁵

The conformation of 1 in polymorph 1-I is a twisted boat with an 8.8° tilt angle between the vertically aligned aryl rings and a 12.3° twist angle with respect to the methine bridges (Fig. 3, Table 1). The conformation of polymorph 1-II is less twisted.
The vertically aligned aryl rings in both polymorphs are leaning towards the cavity with dihedral angles of -8.4° and -12.0°, thus reducing the cavity size, which is typical for unsolvated and unoccupied cavities in resorcinarene bis-crowns. As previously observed for the C-butyl and C-pentyl resorcinarene bis-crowns, the empty space inside the binding cavity is filled by the crown ether bridges, which fold on top of the resorcinarene cavity in I-I and I-II. In addition, an inward pointing O-methyl group C(33) in I-I fills the rest of the cavity void.

Due to the short methyl groups at the lower rim, the overall shape of the molecule I is block-like leading to a compact brick-wall type of assembly in I-I when viewed above (Fig. 4). Weak hydrogen bonds from the lower rim methyl group C(30) to the upper rim O(25), and from C(40) to O(27) and C(51) to O(13) (3.36–3.49 Å) connect the rows of I. A side view of the packing reveals a sheet like assembly, in which weak hydrogen bonds C(49)···O(11) connect the brick-wall layers. In I-II the molecules are more clearly aligned to dimers, which are connected by intermolecular π···π stacking between the aryl rings (C(1)-C(6); Fig. 4) and by weak hydrogen bonds between the methoxy carbon and the crown ether bridge (C(34)···O(56), 3.53 Å). The crown ether bridge connecting O(4) and O(11) extends more on horizontal direction creating weak hydrogen bonds between C(43)···O(45) of the adjacent molecules. The disorder of the crown ether bridge (C(41)-O(42)) indicates steric freedom in the bridge conformation. A side view of the layers shows resemblance to a shifted capsule packing of the enantiomers, which is a common packing motif for C-ethyl bis-crown and C-ethyl mono-crown solvates.29,31,35

Solvate structures of bis-crown 1

Very stable (stable in solution for several months) 1:1 acetonitrile solvate of compound I (I-III in P-I) was obtained by recrystallization from hot acetonitrile. In contrast to the acetonitrile solvate of C-ethyl resorcinarene bis-crown which

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**Table 1. Conformational properties of I-I – I-V.**

<table>
<thead>
<tr>
<th>Structure</th>
<th>I-I</th>
<th>I-II</th>
<th>I-III</th>
<th>I-IV</th>
<th>I-V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal composition</td>
<td>Twisted boat</td>
<td>Twisted boat</td>
<td>Twisted boat</td>
<td>Twisted boat</td>
<td>Twisted boat</td>
</tr>
<tr>
<td>Conformation*</td>
<td>CH₃CN</td>
<td>CH₃OH</td>
<td>(CHCl)₂</td>
<td>CH₃CN</td>
<td>CH₃OH</td>
</tr>
<tr>
<td>Tilt (°)</td>
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<td>4.65</td>
</tr>
<tr>
<td>Distance / Å</td>
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<td>8.00</td>
<td>7.89</td>
<td>-1.09</td>
<td>-1.48</td>
</tr>
<tr>
<td>Dihedral angle between opposite rings</td>
<td>N.D.</td>
<td>N.D.</td>
<td>188.1</td>
<td>191.4</td>
<td>207.3</td>
</tr>
</tbody>
</table>

* A twisted boat has twist/tilt angles > 5°. Centroid-centroid distance between the opposite aromatic rings. Dihedral angle between the horizontal aryl rings cannot be determined due to twisting. Average cavity diameter from O–O distances.

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Figure 4. Crystal packing of 1-I (A-B) and 1-II (C-D) showing top and side views of packing of the block shaped molecules. Weak hydrogen bonds are shown as blue lines and π···π stacking with black dashed lines. Dashed parallelogram in the top view indicates the molecules shown in the side view, and thick green dashed line a shifted capsule in 1-II. Hydrogen atoms and disordered atoms omitted for clarity.
encapsulates three acetonitrile molecules inside the cavity,\(^{29}\) acetonitrile in I-III is confined in the interstitial space between the hosts and connected by weak hydrogen bonds from acetonitrile -\(\text{CH}_3\) to the crown bridge O(50). As in unsolvated forms the resorcinarene cavity is filled by a folded and disordered crown ether bridge facing a horizontal aromatic ring (H(40A)···Ar 3.12 Å). The conformation of the host is nearly ideal boat conformation, and the molecules pack in a brick-wall type assembly as in I-I (Fig. 5). The molecules are connected by weak hydrogen bonds between methoxy groups (C(36)···O(13) and C(34)···O(27)) and the “brick” layers further by weak hydrogen bonds (C(31)···O(50)).

A completely different packing motif was found from a dichloromethane-methanol solvate (I-IV) crystallized in P2\(_1/c\) with one molecule of dichloromethane, one methanol and resorcinarene I in the asymmetric unit. Both of the crown ether bridges and dichloromethane molecules are disordered, and dichloromethane and methanol are located on top of the binding cavity via weak hydrogen bonds to the crown ether bridge (O(39) and O(42)). Molecules of I are connected in two antiparallel chains by C-H···O bonds (C(44)···O(56) and C(36)···O(18), 3.29–3.57 Å, Fig. 6A). Furthermore, instead of previous layered assemblies the chains are located at a 68.5° angle and connected by short contacts between the crown ether bridge and the lower rim side of the aryl rings. In addition, the upper rim interface of two resorcinarene chains forms an apparent dimer assembly (Fig. 6B), which, however, does not have direct or solvent mediated contacts between the upper and lower resorcinarene molecules.

Slow evaporation crystallization of I from chloroform-methanol and chloroform-ethanol solutions afforded thin needle crystals within few days. A thicker rod-shaped crystal allowed the structural determination of a chloroform solvate I-V in P2\(_1/c\) with 3:1 ratio of chloroform and resorcinarene I in the asymmetric unit (Fig. 7). The conformation of I is a twisted boat, in which two aryl rings overbend below a horizontal plane giving a curved shape for the molecule. Overbending of the resorcinarene core has been observed in some rare cases for longer alkyl chain derivatives, such as in sodium complex of C-ethyl resorcinarene bis-crown (196.7°),\(^{29}\) and in C-ethyl resorcinarene bis-thiacrowns (195–198°).\(^{36}\) The cavity of the resorcinarene I is again fairly closed by the folded crown ether bridges, which bend toward the interior and are held by two intramolecular weak hydrogen bonds to the aromatic rings (C(41)···O11 and C(52)···O25), 3.51–3.52 Å). The crystal packing of the host could be described as a puckered layer, in which the crown ether bridges form weak hydrogen bonds (C(44)···O53 and C(55)···O(42)). The layers of I alternate with the layers of chloroform throughout the crystal lattice.
After several months of storage in solution 1-V turned into clear block crystals, which were found to be crystals of 1-I. Thus, 1-V is a kinetically controlled crystal form, whereas very stable crystals 1-I and acetonitrile solvate 1-III are thermodynamically stable phases. The stability difference between the two solvates probably arises from the solubility of 1. Host 1 is soluble in chloroform (and DCM) at room temperature and in acetonitrile with heating, but it does not dissolve completely in alcohols even upon heating at approximately 0.5 mg/ml concentration used for crystallizations. Therefore, ethanol or methanol acts as an anti-solvent for chloroform solvated 1 enhancing the nucleation of the crystals of kinetically controlled chloroform solvate 1-V.

**Solvate structures of mono-crown 2**

C-methyl resorcinarene mono-crown (2) has one crown-ether bridge and two free resorcinol hydroxyl groups available for hydrogen bonding. Two solvates, one with CDCl3/water (2-I) and one with acetonitrile (2-II) were obtained for 2, which allow the comparison of the solvate structures and inclusion properties of the resorcinarene cavity with bis-crown 1. Compound 2 crystallized rapidly from an NMR sample with two molecules of 2, two molecules of water, and one molecule of CDCl3 in the asymmetric unit (2-I, P-1). The host adopts an overbent boat conformation (Table 2) and the crown ether bridge folds inside the cavity forming an exocavity pocket, which binds a chloroform molecule with a bifurcated C-H···O hydrogen bond (Fig. 8). A water molecule is hydrogen bonded to the open end of the resorcinarene cavity and connects two molecules of 2 in a horizontal direction. In addition, a hydrogen bond from a resorcinol ring to the crown ether bridge (O(18)···O(39)) of an opposite facing resorcinarene connects a dimer structure in a vertical direction similarly to previous C-ethyl mono-crown structures. The crown ether bridged binding cavity, however, remains empty unlike in the crystal structures of C-ethyl resorcinarene mono-crown, where water, methanol and acetonitrile occupy the crown pocket, and the dihedral angles between the horizontal aryl rings are smaller (145–158°).

![Figure 7. A twisted boat conformation of the labile chloroform solvate 1-V showing weak hydrogen bonds between chloroform and 1 with blue lines and C-H–π interaction with black dashed line (A). A side view shows puckered layers of 1 and chloroform with a space fill model (B). Hydrogen atoms are not shown for clarity.](image)

![Figure 8. A vertical hydrogen bonded dimer of 2-I (A), a top and a side view as a CPK model (B), and horizontal chains (C); the second molecule of 2 in the asymmetric unit is not shown. Hydrogen bonded horizontal chains of 2-II (D).](image)

**Table 2. Conformational properties of 2.**

<table>
<thead>
<tr>
<th>Structure Crystal composition</th>
<th>2-I</th>
<th>2-II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal</td>
<td>2(CDCl3)0.5·H2O</td>
<td>2 CH3CN</td>
</tr>
<tr>
<td>Conformation</td>
<td>Boat</td>
<td>Boat</td>
</tr>
<tr>
<td>Tilt (°)</td>
<td>4.1</td>
<td>2.2</td>
</tr>
<tr>
<td>Twist (°)</td>
<td>4.0</td>
<td>3.4</td>
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<td>Distance/Å</td>
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<td>5.06/8.00</td>
</tr>
<tr>
<td>Dihedral angle between opposite rings/°</td>
<td>4.87</td>
<td>4.81</td>
</tr>
</tbody>
</table>

4 Centroid-centroid distance between the opposite aromatic rings. 5 Average cavity diameter from the O···O distances.
neighboring molecule (O(18)H···O(4)), which is rotated sideways on top of the cavity. The disordered acetonitrile molecule is located at the open end of the binding site forming weak hydrogen bonds to 2.

The solvate structures of 1 and 2 indicate that the resorcinarene cavity is not used for inclusion of the solvent molecules, but the crown ether bridge folds inwards filling the cavity and short methyl chains allow compact packing in layers or chains.

**Metal complexes of host 1**

Previously, the complexation studies with tetramethoxy resorcinarene bis-crowns have shown that the binding cavity is suitable for the complexation of relatively large alkali metal cations (K⁺, Rb⁺, Cs⁺), 29,30,32 and silver (Ag⁺) 33,34 by cation···π and ion-dipole interactions. Based on the previous affinity studies the strongest binding cesium and silver cations were chosen for complexation studies with 1 as their PF₆⁻ salts. Metal complexation was not attempted with mono-crown 2, since mono-crowns are weak hosts for alkali metals. 31

Composition of CsPF₆ with 1 provided a 1:2 host-to-guest complex with two guest cations and one PF₆⁻ anion inside the binding cavity of 1(1-Cs2, P-1 Fig. 9). A molecule of acetone with occupancy of 0.5 and second PF₆ are filling the interstice in the crystal lattice. The cations are coordinated by three M···O bonds (3.09–3.25 Å) to the crown ether bridge, by two bonds to the OCH₃ group (3.21–3.31 Å), and, in addition, by cation···π interactions to the center of the horizontal aryl rings (cation-centroid distances of 3.33 and 3.44 Å) similarly to the previously obtained cesium complexes of C-ethyl and C-propyl bis-crown derivatives. 30,32 Difference to the structures of the longer alkyl chain resorcinarenes lie in the conformation of 1 (Table 3) which is less twisted than C-propyl bis-crown but more twisted than C-ethyl bis-crown. In addition, 1 has a larger dihedral angle of 161.0° between the horizontal aromatic rings than C-ethyl and C-propyl derivatives (152.6° and 148.8°), which leads to a longer Cs···Cs distance (6.90 Å) than in previous complexes (6.42 Å and 6.57 Å for C-ethyl and C-propyl derivatives, respectively). A wider distance of included cations enables the formation of a capsule-like pairs of right-handed and left-handed enantiomers by Cs···F coordination (3.25 Å), which was not possible with the shorter Cs···Cs distance. However, the overall packing of the capsules still resembles the layered packing of C-propyl resorcinarene bis-crown, which formed solvent mediated shifted capsules.

Since twisting of the resorcinarene framework leads to interesting capsule and nanorod structures of C-ethyl resorcinarene bis-crown-5 silver complexes, 33 a considerable effort was placed on the investigation of the C-methyl resorcinarene bis-crown-5 silver complexes. Crystallization from pure alcohols provided very small or low quality crystals, likely due to low solubility of the host. Successful crystallization experiments were done in solvent mixtures with AgPF₆ and AgCF₃SO₃ salts. Crystallization with AgPF₆ in acetone yielded a host-guest complex (1-Ag2, C2/c), in which two silver cations are located inside the cavity, one PF₆⁻ on top of the cavity, and the other one between two crown bridges and a lower rim of the third resorcinarene (Fig. 10A). The complexation with AgCF₃SO₃ in acetone-ethanol-DCM, on the other hand, gave a crystal structure of 1:1 complex (1-Ag1, Pnma), in which an anion and solvent connect a dimeric capsule (Fig. 10B).

In 1:2 complex the silver cations are bound by two M···O bonds to the crown ether bridge (2.36—2.51 Å) and by one coordination bond to the OCH₃ group (2.54 Å) similarly to the previous C-ethyl and C-propyl bis-crown AgPF₆ complexes. In addition, silver is connected by π coordination bond to the OCH₃ group (2.54 Å) similarly to the previous C-ethyl and C-propyl bis-crown AgPF₆ complexes. Consequently, the Ag···Ag distance is relatively short, 7.10 Å, which is likely
due to the interactions with the PF\textsubscript{6} anion on top of the cavity. In previous bis-crown silver complexes silver cations were interacting with coordinated solvent molecules (methanol, ethanol, 1- or 2-propanol, or acetone) and the distance between the metals was significantly longer ($\text{Ag} \cdots \text{Ag} = 8.8$–$10.8$ Å)\textsuperscript{33,34}. In addition, in C-ethyl bis-crown silver complexes the conformation of the host varied from a slightly twisted to significantly twisted boat depending on the size of the solvent coordinated to the included metal. In contrast, the boat conformation of host I is rather pinched with the horizontal aryl rings overbent in a 200° dihedral angle and the vertical aryl rings leaning slightly towards each other making the shape of I a compact block. The crystal packing of 1-Ag2 is composed of symmetric brick-wall type of sheets when viewed from front, in which each layer constitutes of a single enantiomer.

In 1:1 complex silver is coordinated by two $\text{Ag} \cdots \text{O}$ bonds (2.43–2.44 Å) to the crown ether bridge and by $\eta^1$-metal-arene coordination (2.50–2.61 Å) to the distal edge of the aromatic ring resembling the earlier examples of silver complexes (Figure 10).\textsuperscript{33,34} In addition, a water molecule forms a coordination bond (2.31 Å) to the cation on an open side of the binding pocket. The empty side of the cavity is filled by the inward leaning vertical aryl rings (dihedral angle -12.2°) and a folded crown ether bridge in contrast to 1:1 silver complex of C-ethyl bis-crown capsule, in which the second binding pocket was filled with methanol and water molecules. Two enantiomeric 1:1 complexes form ethanol, water and triflate anion mediated capsules, in which the silver cations are located on top of each other.

**Conclusions**

C-methyl resorcinarene bis-crown-5 (I) and mono-crown-5 (2) with the shortest possible alkyl chains at the lower rim were synthesized. The short methyl chain induces interesting structural and packing properties in solid state, namely, the ability to adapt to different conformations and an overbent boat conformation. The conformation of the resorcinarene bis-crowns and mono-crowns is always locked to a boat conformation but, nevertheless, there are possibilities to conformational variation, such as twisting and tilting, which play interesting role in the crystal packing of resorcinarene bis-crowns.

C-methyl bis-crown-5 (I) crystallized readily in two solvent-free brick-wall assemblies, 1-I and 1-II, due to the block-like shape of the molecule, in which the crown ether bridges are folded inside the cavity. Three different solvate structures for I were obtained, in which the solvent molecules occupy the interstitial space between hosts in the crystal lattice. The chloroform solvate (1-V) formed a crystal with alternating solvent and host layers, but transformed to the crystal form 1-I over time in solution indicating the thermodynamic stability of the polymorph 1-I. The mono-crown-5 solvates 2-I and 2-II also had solvents only outside the binding pocket in contrast to C-ethyl mono-crown solvates, in which the cavity was used for solvent inclusion. The results indicate that the short methyl groups at the lower rim induce a conformation that does not favor solvent inclusion. In addition, the twisting observed in 1-I occurs readily and leads to the efficient packing of the molecules in solvent-free crystals.

Host I was co-crystallized with cesium and silver salts producing three different metal complex structures. In the cesium complex 1-Cs2, long Cs–Cs distance and large dihedral angle between horizontal aryl rings enabled crystal packing into a dimeric capsule. In the silver complex 1-Ag2, overbending of the boat conformation along with short Ag–Ag distance was observed. In 1:1 host-silver complex 1-Ag1, the unoccupied binding pocket was efficiently filled with a folded
crown bridge. Thus, the unique conformational tendencies of C-methyl resorcinarene affect the complexation properties of resorcinarene bis-crown-5 in the solid state when compared to hosts with same binding site and longer pendant alkyl chains.

Experimental

Crystallography

Single crystal X-ray data were recorded on a Nonius Kappa CCD diffractometer with Apex II detector using graphite monochromated CuKα (λ = 1.54178 Å) radiation for structures I-II and I-III. The data were processed and absorption correction was made with Denzo-SMN v.0.97.638. Single crystal X-ray data for structures I-1, I-IV 1-Ag1, 1-Ag2, 1-Cs2 and 2-II was collected on an Agilent Supernova Dualsource diffractometer using an Agilent Atlas CCD detector with monochromated CuKα (λ = 1.54180 Å), and for structures I-V and I-on a Supernova diffractometer with monochromated MoKα (λ = 0.71070 Å). The data were processed and empirical absorption correction was made with CrystAlisPro. The structures were solved using SHELX-97 software package or Olex2 (olex2.solve with charge flipping or SHELXS with direct methods). The structure refinement was made with Olex2 using XL refinement package with least squares minimization. The hydrogen atoms were calculated to their idealized positions with isotropic temperature factors (1.2 or 1.5 times the C temperature factor) and refined as riding atoms unless otherwise mentioned. CCDC 1042079–88 contains the supplemental crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1-I: Single crystals of C$_2$H$_7$O$_4$ (M = 917.06 g/mol) were crystallized from 1-propanol. Crystal form 1-I was also obtained from crystallization in acetone with AgPF$_6$, in acetonitrile-2-propanol (1:1) with AgBF$_4$, in acetone-chloroform (1:2) with AgPF$_6$, and in CDCl$_3$-acetonitrile-d$_6$ (1:12) with AgPF$_6$. Colourless needle crystal 0.3 × 0.1 × 0.05 mm, monoclinic, P2$_1$/c (no. 14), a = 11.0209(1) Å, b = 16.0930(2) Å, c = 26.6261(4) Å, β = 90.074(1)°, V = 4722.38(10) Å$^3$, Z = 4, T = 123.00(10) K, μ(Cu Kα) = 0.760, D(calc) = 1.290 mg/mm$^3$, 28596 reflections measured (6.42 ≤ 2θ ≤ 148.94), 9459 unique (R(int) = 0.0314), R = 0.0499 (>2σ(I)), wR$^2$ = 0.1455 (all data), GoF = 1.023.

1-II: Single crystals of C$_2$H$_7$O$_4$ (M = 917.06 g/mol) crystallized rapidly from CHCl$_3$-acetone (8:2) solution with a trace of DMF after evaporation of the solvent. Colourless rod crystal 0.1 × 0.02 × 0.02 mm, triclinic, P1-1 (no. 2), a = 11.3557(13) Å, b = 13.3242(2) Å, c = 16.537(3) Å, α = 108.171(8)°, β = 94.406(8)°, γ = 92.266(7)°, V = 2365.0(6) Å$^3$, Z = 2, T = 173 K, μ(Cu Kα) = 0.759, D(calc) = 1.288 mg/mm$^3$, 11456 reflections measured (5.64 ≤ 2θ ≤ 133.8), 8121 unique (R(int) = 0.0815), R = 0.0556 (>2σ(I)), wR$^2$ = 0.1503 (all data), GoF = 1.027. C41-O42 (-CH$_2$O-) are disordered over two positions (0.87:0.13) and restrained with SADI, DELU and SIMU.

1-III: Single crystals of C$_2$H$_5$O$_4$C$_2$H$_7$N$_2$ (M = 958.12 g/mol) were crystallized from acetonitrile solution. Colourless block crystal 0.1 × 0.1 × 0.1 mm, triclinic, P-1 (no. 2), a = 8.9268(3) Å, b = 14.4126(7) Å, c = 20.6525(11) Å, α = 85.264(2)°, β = 85.152(2)°, γ = 73.771(3)°, V = 2537.3(2) Å$^3$, Z = 2, T = 173 K, μ(Cu Kα) = 0.735, D(calc) = 1.254 mg/mm$^3$, 12142 reflections measured (6.40 ≤ 2θ ≤ 133.86), 8756 unique (R(int) = 0.0486), R$_1$ = 0.0526 (>2σ(I)), wR$^2$ = 0.1393 (all data), GoF = 1.018. C41-O42-C43 (-CH$_2$OCH$_3$-) are disordered over two positions (0.84:0.16), restrained with SADI, DELU, and SIMU, and constrained with EADP (C41-C41B).

1-IV: Single crystals of C$_2$H$_5$O$_4$C$_2$H$_7$-CH$_2$O (M = 1034.03 g/mol) were crystallized from dichloromethane layered with NaN$_3$O$_4$ in methanol. Colourless plate crystal 0.3 × 0.2 × 0.1 mm, monoclinic, P2$_1$/c (no. 14), a = 17.9718(4) Å, b = 19.32153(5) Å, c = 15.5981(2) Å, β = 102.1831(17)°, V = 5294.30(16) Å$^3$, Z = 4, T = 123.01(10) K, μ(Cu Kα) = 1.658, D(calc) = 1.297 g/mm$^3$, 17795 reflections measured (6.8 ≤ 2θ ≤ 148.5), 10237 unique (R$_{int}$ = 0.0321), R$_1$ = 0.0932 (>1σ(I)), wR$_2$ = 0.2966 (all data), GoF = 1.075. O42-C43 (-OCH$_2$-) are disordered over two positions (0.88:0.12), restrained with SADI, DELU, and SIMU, and constrained with EADP (O42-O42A). C48-C49-O50-C51-C52 are disordered over two positions (0.69:0.31) and restrained with SADI, DELU, and SIMU. CH$_2$Cl$_2$ is disordered over two positions (0.78:0.22), restrained with DFIX 1.79 and constrained with EADP for C12.

1-V: Single crystals of C$_2$H$_5$O$_4$Cl$_3$ (M = 1275.17 g/mol) were crystallized from ethanol-chloroform (3:2) solution as needles and rods. The crystals transformed into polymorphic form 1-I after several months in solution. Colourless rod crystal 0.4 × 0.1 × 0.1 mm, monoclinic, P2$_1$/c (no. 14), a = 17.5687(4) Å, b = 23.0884(5) Å, c = 15.7904(3) Å, β = 108.034(2)°, V = 6090.5(2) Å$^3$, T = 173 K, Z = 4, μ(Mo Kα) = 0.475, D(calc) = 1.391 mg/mm$^3$, 21409 reflections measured (5.96 ≤ 2θ ≤ 53.38), 11877 unique (R$_{int}$ = 0.0251), R$_1$ = 0.0860 (>2σ(I)), wR$_2$ = 0.2632 (all data), GoF = 1.022. Largest difference peak 1.28 e Å$^{-3}$ located 1.16 Å from C101 indicates residual electron density around CHCl$_3$. Disorder model for solvates did not improve the structure model and was therefore not used in the final refinement.

1-Cs2: Single crystals of [C$_5$][PF$_6$][C$_2$H$_5$O$_4$C$_2$H$_7$O$_4$] ([PF$_6$] (C$_2$H$_5$O)$_{2.5}$ (M = 1501.86 g/mol) were crystallized from acetone-DCM (10:1) with excess of CsPF$_6$. Colourless block crystal 0.16 × 0.05 × 0.05 mm, triclinic, P-1 (no. 2), a = 13.2706(3) Å, b = 15.2318(3) Å, c = 16.1051(4) Å, α = 80.059(2)°, β = 89.360(2)°, γ = 88.922(2)°, V = 3205.86(13) Å$^3$, Z = 2, T = 123.01(10) K, μ(Cu Kα) = 10.169 mg/mm$^3$, D(calc) = 1.556 mg/mm$^3$, 21759 reflections measured (8.72 ≤ 2θ ≤ 151.98), 12904 unique (R$_{int}$ = 0.0303), R$_1$ = 0.0408 (>2σ(I)), wR$_2$ = 0.1138 (all data), GoF = 1.029. C55-O56-C57 (-CH$_2$OCH$_3$-) was disordered over two positions (0.66:0.34) and restrained with DELU and SIMU. F1-F6 are restrained with DELU and SIMU. Acetone molecule was refined with occupancy of 0.5 and restrained with ISOR and DANG.
I-Ag1: Single crystals of [Ag₂(C₂₅H₃₄O₁₄)]CaF₂(OCH₃)₂ (M = 1242.08 g/mol) were crystallized from acetone-ethanol-DCM (1:0.2:0.2) solution at 30 °C. Colourless plate crystal 0.1 × 0.1 × 0.04 mm, orthorhombic, Pnma (no. 62), a = 21.0806(5) Å, b = 37.7868(8) Å, c = 14.1827(3) Å, V = 11297.5(4) Å³, Z = 8, μ(Cu Kα) = 3.941, Dcalc = 1.461 g/mm³, 26573 reflections measured (7.86 ≤ θ ≤ 153.3), 11658 unique (Rint = 0.0348), R1 = 0.0869 (>2σ(I)), wR2 = 0.2731 (all data), GoF = 1.041. DFIX was disordered over two positions (0.5:0.5) and restrained with DFIX, DELU and SIMU. EADP constrain is used for C101, N100, C102, and C105. OH hydrogens were located from electron density map and restrained using DFIX 0.82.

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Notes and references


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[This page contains scientific text related to crystallography and chemical synthesis, including experimental details and data analysis, with references to original research papers and other sources for further reading.]


