

Does *C*-methylcalix[4]resorcinarene always adopt the crown shape conformation? A resorcinarene/bipyridine/decamethylruthenocene supramolecular clathrate with a novel framework structure†

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Decamethylruthenocene acts as the template for the self-assembly of a 2:4:1 *C*-methylcalix[4]resorcinarene/bipyridine/decamethylruthenocene supramolecular structure with large hydrophobic cavities.

As part of a survey of candidates for time-resolved diffraction studies of excited state structures we have previously reported binary phases of 4,4'-dihydroxybenzophenone and *p*-amino-*p'*-nitrobiphenyl and photoinactive 'spacer' molecules.^{1,2} Molecular dilution achieved in host-guest crystals has several advantages in time-resolved work, as discussed elsewhere.³ We report here, on a complex crystalline phase containing decamethylruthenocene (DMR), which has a long-lived triplet state.

MacGillivray *et al.* reported the entrapment of acetylated ferrocene derivatives within the supramolecular deep cavity *C*-methylcalix[4]resorcinarenes (CMCR)/4,4'-bipyridine.^{4,5} Though decamethylruthenocene is larger than diacetylferrocene, the cavity formed by *C*-methylcalix[4]resorcinarene, which is extended through hydrogen bonding with the bipyridine molecules, appeared sufficiently flexible to accommodate larger guests.

Needle shape orange crystals of CMCR/4,4'-bipyridine/DMR crystal were grown by slow cooling (one day) of a boiling 96% ethanol (3 mL) solution of *C*-methylcalix[4]resorcinarene (27.2 mg, 0.05 mmol), 4,4'-bipyridine (15.6 mg, 0.10 mmol) and decamethylruthenocene (18.5 mg, 0.05 mmol). Low temperature X-ray structure determination⁶ shows an arrangement in which one DMR, two water and two ethanol solvent molecules are located in cavities within a hydrogen-bonded framework formed by the host molecules, with a 2:4:1 CMCR/bipyridine/DMR ratio, as illustrated in Fig. 1. The clathrated DMR molecules occupy one of two center-of-symmetry related positions in a disordered arrangement.

The *C*-methylcalix[4]resorcinarene (CMCR) molecules have a 'flattened cone' conformation (Fig. 2), using the terminology introduced by Gutsche⁷ (Fig. 2), different from the crown shape of all the other reported X-ray structures of CMCR. Intramolecular hydrogen bonding is absent in this conformation. While *C*-methylcalix[4]resorcinarene derivatives adopting the 'flattened cone' conformation occur when their hydroxy groups are substituted by ethoxy⁸ or trimethylsilyloxy groups,⁹ or the hydroxy groups are coordinated with metal,¹⁰ which eliminates the possibility of intramolecular hydrogen bonding, this is the first observation of a non-substituted non-metal-atom-containing *C*-methylcalix[4]resorcinarene in this conformation.¹¹

Four O–H...O hydrogen bonds link pairs of neighboring resorcinarenes into columns parallel to the crystallographic [011] direction,¹² while O–H...N hydrogen bonds to the nitrogen atoms at each end of the interspersed bipyridine molecules link the columns into 'skewed-brick' sheets parallel to the (1 $\bar{1}$ 1) plane.¹³ The DMR molecules serve as templates for the self-assembly of the framework, which is isomeric to MacGillivray's one dimensional polymer.¹⁴ The template-

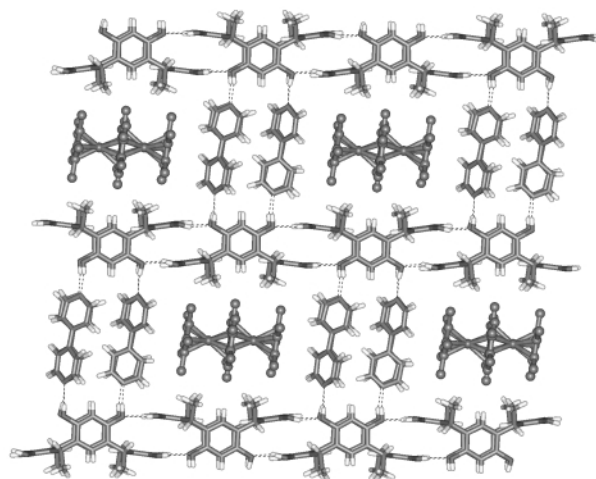


Fig. 1 Hydrogen-bonded layers showing columns of *C*-methylcalix[4]resorcinarene linked by 4,4'-bipyridine molecules. The two half-occupancy decamethylruthenocene molecules are shown. Solvent molecules omitted for clarity.

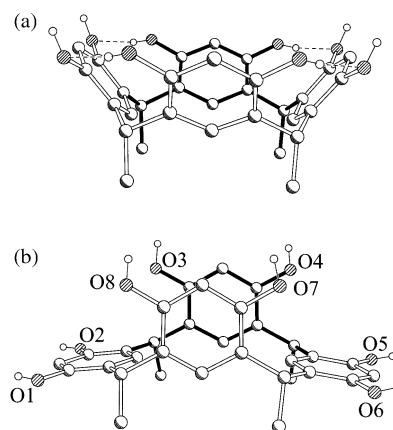


Fig. 2 (a) The bowl-shaped (based on coordinates from ref. 4) and (b) the flattened cone conformation of *C*-methylcalix[4]resorcinarene as determined by X-ray diffraction.

induced architecture of the host framework is of much current interest.¹⁵ Large hydrophobic cavities, in which the guest molecules are located, occur in the space between the bipyridyl molecules (Fig. 3). Successive sheets perpendicular to (1 $\bar{1}$ 1) are linked by weaker interactions, including C–H...O hydrogen bonds. The two independent bipyridine molecules are twisted by 32.04(14)° and 17.15(20)°, respectively.

Though crystals of neat DMR are disordered at ambient temperature,¹⁶ low temperature X-ray analysis shows the structure to be fully ordered at 90 K, with a doubling of the unit cell.⁶ Comparison of the DMR molecules in the two structures shows only negligible differences, the Ru–Cp distances averag-

† Electronic supplementary information (ESI): colour version of Fig. 1. See <http://www.rsc.org/suppdata/cc/b0/b004783j/>

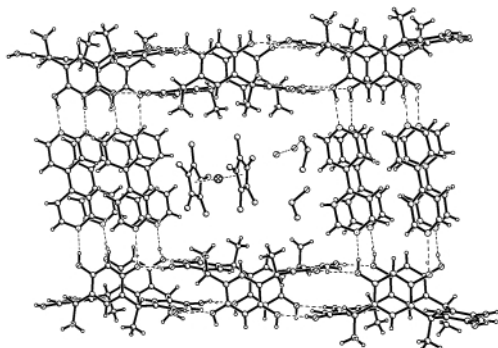


Fig. 3 Detailed view of the cavity including the solvent molecules. Only one of the two center-of-symmetry related positions of the guest molecules is shown.

ing 1.805(16) and 1.792(7) Å respectively in the complex, compared with 1.800(3) and 1.800(3) Å in the neat DMR structure.

The impetus for the current study was the long lifetime of the 3E_1 triplet state of DMR, reported as 627 μ s (4.2 K), compared with 127 μ s for ruthenocene (1.5 K).¹⁷ Spectroscopic experiments^{18,19} and calculations^{20,21} indicate a significant change in inter-ring distance on excitation of ruthenocene, which is to be investigated by time-resolved synchrotron diffraction methods. Using equipment described elsewhere,²² we have measured the 16 K lifetimes of the DMR triplet state in both the resorcinarene/DMR complex and neat DMR as 492 and 460 μ s, respectively. While the DMR concentration is much lower in the complex crystal (0.602 vs. 3.71 M in the neat crystal), the difference could reflect a slightly different temperature.²³ Other measurements on lifetimes in host-guest complexes show no clear relation between excited-state lifetime and molecular concentration.²⁴

In summary, decamethylruthenocene acts as the template for the self-assembly of the 2:4:1 C-methylcalix[4]resorcinarene/bipyridine/decamethylruthenocene supramolecular crystal. The crystal has a layered structure with two-dimensional planes of hydrogen-bonded molecules, and contains 'flattened cone' shaped calix[4]resorcinarene molecules. The decamethylruthenocene molecules are located in hydrophobic cavities lined by the C-methyl groups and the bipyridyl hydrogen atoms. It is likely that other hydrophobic molecules of comparable size can be similarly accommodated in this type of structure, thus suggesting additional applications in crystal engineering and supramolecular chemistry. We have already obtained C-methylcalix[4]resorcinarene/bipyridine/benzophenone crystals with similar framework and 'flattened cone' shaped calix[4]resorcinarene molecules.²⁵

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- 13 O8...N1^{III} 2.723(3) Å, O8-H8D...N1^{III} 165(4)° (III = x, y + 1, z); O4...N2^{IV} 2.730(3) Å, O4-H4D...N2^{IV} 167(4)° (IV = -x, -y + 1, -z); O3...N3^V 2.729(3) Å, O3-H3D...N3^V 168(4)° (V = x - 1, y + 1, z); O7...N4^{VI} 2.707(3) Å, O7-H7D...N4^{VI} 169(4)°.
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