Self-assembling of *p-tert*-butylcalix[4]arene into supramolecular structures using transition-metal derivatization

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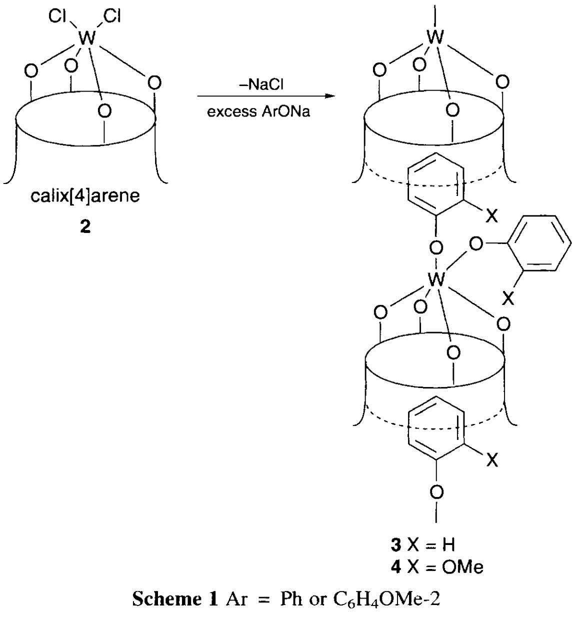
The functionalization of tungsten bonded over a calix[4]arene oxomatrix with phenoxo groups leads to the self-assembling of metal–calix[4]arenes into a columnar structure.

The self-assembling of calix[*n*]arenes[1] into supramolecular structures has never been obtained thus far by a clear methodology. A single case of self-assembling, though not structurally supported, was achieved *via* a very elaborate derivatization of the upper rim of the calixarene structure.[2] We approached the self-assembling of calix[4]arene units taking advantage of two major facts: (*i*) the propensity of the calix[4]arene cavity[5c] to host aromatic rings *via* the so-called aliphatic–aromatic interaction[3] and (*ii*) the possibility to shape the calix[4]arene cavity by transition-metal derivatization.[4,5] This shaping is strongly dependent on the size of the metal ion and its coordination number.[5c] The model compounds we refer to and have used, within this context, are [WO(L)], **1**,[†] in its unsolvated form, and [$WCl_2(L)$], **2**[5c] {H_4L = *p-tert*-butylcalix[4]arene} containing the same metal in the same oxidation state, but with a different coordination number. Both **1** and **2**, although showing very different cavity shapes, can host either benzene or toluene.[5c,‡] Taking into account toluene and benzene complexation into a calix[4]arene cavity, we used six coordinate tungsten complexes containing aryl substituents to see whether a self-organization of the various monomeric units into a columnar structure would occur.

Complex **2** was treated with sodium phenolate or catecholate in THF (Scheme 1), and the resulting solids **3** or **4** were recrystallized from *n*-hexane.

The anticipated polymeric structures of **3** and **4**[§] have been established by X-ray analysis, although details are reported only for **3**.[¶] It should be emphasized that recrystallization was from *n*-hexane, which is non-competitive as a guest towards the calix[4]arene cavity.



Scheme 1 Ar = Ph or C_6H_4OMe-2

The propensity of calixarene compounds to exhibit host–guest interactions is emphasized in the present complex by its peculiar packing mode, the aromatic ring of a phenato anion [O(5), C(51)–C(56)] protrudes into the cavity of a neighbouring molecule giving rise to a chain of molecules along the [100] axis (Fig. 1). Within a chain the molecules are related by a simple translation, and therefore the 'reference' planes determined by the bridging methylene carbons are parallel. The guest aromatic ring enters the cavity with the C(52)–C(55) vector essentially parallel to the direction of the molecular axis [W···C(55)···C(52) 179.5(2)°]. The dihedral angle between the W···C(55)···C(52) line and the normal to the reference plane is 175.4(1)°. The guest ring plane is nearly parallel to the B and D rings [dihedral angle 25.3(2)°] and perpendicular to the A and C rings [dihedral angle 90.0°] of calixarene. The shortest host–guest contacts involve the *tert*-butyl carbons [C(51)···C(36A) 3.488(17), C(52)···C(36A) 3.618(17)Å], but disorder affecting these groups prevents a more detailed discussion. The complex has an imposed *m* symmetry, the mirror plane running through the metal and the O(1) and O(3) oxygen atoms of calixarene. The W–O(1) and W–O(2) bond distances [mean value, 1.923(5) Å] are similar to those observed in complex **1**, while the W–O(3) distance [1.862(5) Å] is significantly shorter, indicating some degree of double bond character, in accord with the linearity of the W–O(3)–C(20) system [176.9(5)°]. This value is also in good agreement with the W–O(5) [1.871(5) Å] and W–O(7) [1.859(5) Å] bond distances involving the phenato ligand where an approximately linear behaviour of the W–O–C units is also observed.

The octahedral coordination geometry of the metal, the best equatorial plane being defined by O(1), O(3), O(5) and O(7), produces a rearrangement in the orientation of the aromatic rings of the calixarene removing the planarity of the O_4 core. Compared with complex **1**, complex **3** shows two phenyl rings (A and C) pushed away from the macrocycle and two (B and D) towards the macrocycle to define an elliptical cone section cavity elongated along the O(1)···O(3) direction. The dimension of the cavity can be expressed by the values of the C(4)···C(17) [10.304(12) Å] and C(10)···C(10′) [7.458(9) Å] distances (′ = *x*, 0.5 − *y*, *z*). The W–O–C units are almost linear for O(3), O(5) and O(7), in agreement with a very significant M–O π interaction.

The orientation of the C(51)···C(56) aromatic ring inside the cavity of the complex molecule translated along [100] is such that H(54) [attached to C(54)] is pointed toward the centre of the adjacent C ring [the distance between H(54) and the centroid of the ring is 2.71 Å]. The C(55)–H(55) bond, which enters the cavity in the direction of the calixarene molecular axis, gives rise to different contacts with O(1) and O(3) [H(55)···O(1) 2.62 Å, C(55)–H(55)···O(1) 137°].

The results reported here are a significant contribution on how to plan the self-assembling of calix[4]arene moieties into

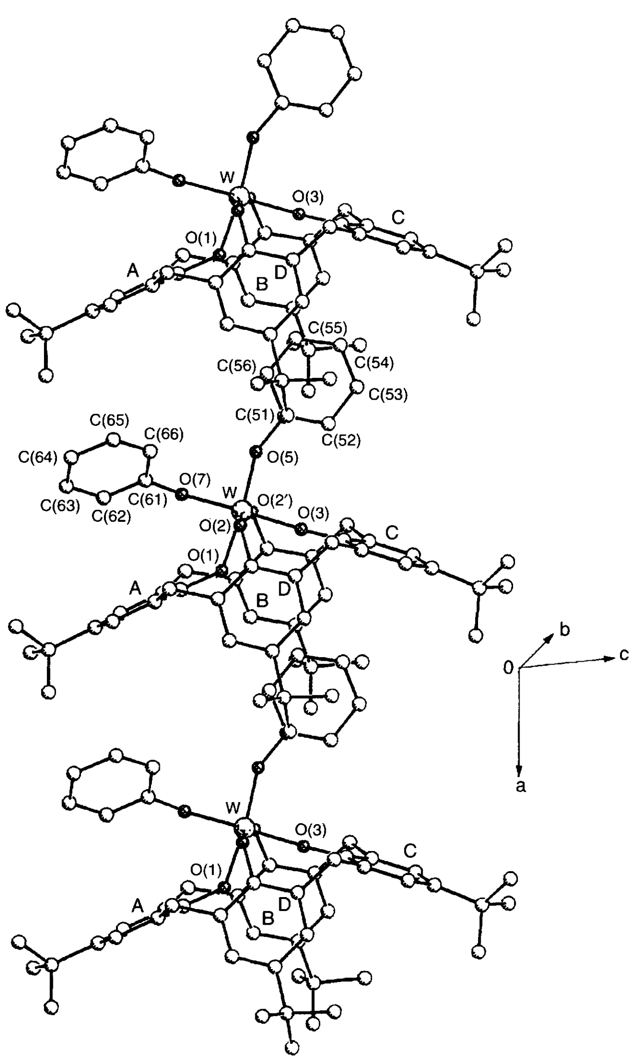


Fig. 1 SCHAKAL view of the chaining of the molecules along the [100] axis in complex **3**. Prime denotes a transformation of x, $0.5 - y$, z. Disorder omitted for clarity. Selected bond distances (Å) and angles (°): W–O(1) 1.920(6), W–O(2) 1.926(3), W–O(3) 1.862(5), W–O(5) 1.871(5), W–O(7) 1.859(5), O(5)–W–O(7) 87.8(2), W–O(1)–C(1) 133.8(5), W–O(2)–C(13) 125.0(3), W–O(3)–C(20) 176.9(5), W–O(5)–C(51) 153.9(5), W–O(7)–C(61) 144.9(4).

columnar-type structures. Work is in progress along two directions: (*i*) how to tune the host–guest interaction and (*ii*) how to form self-assembled structures in the presence of competitive solvents.

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Footnotes

† *Synthesis and spectroscopic data* of **1**: Bu^{n}Li (22.6 cm^3, 1.69 mol dm^{-3} in *n*-hexane, 38.0 mmol) was added dropwise to a benzene (350 cm^3) suspension of H$_4$L (6.20 g, 9.55 mmol) and the reaction mixture was stirred at room temp. for 1 h. Then WOCl$_4$ (3.27 g, 9.56 mmol) was added and the resulting dark violet suspension was refluxed for 16 h. The benzene suspension was concentrated *in vacuo* to 100 cm^3 and the solid residue recovered and extracted with toluene (150 cm^3) for 2 days. **1** was obtained from toluene as a yellow solid (34%). δ_H (200 MHz, CD$_2$Cl$_2$, room temp.): δ 1.19 (s, 36 H, Bu^t), 2.34 (s, 3 H, C*H*$_3$Ph), 3.34 (d, 4 H, J = 12 Hz, *H*CH), 4.59 (d, 4 H, J = 12 Hz, HC*H*), 7.18 (m, 13 H, H$_{arom}$). Satisfactory elemental analysis was obtained. Crystals suitable for X-ray analysis were obtained by slow cooling of a saturated toluene solution (from reflux to room temp.).

‡ Various solvated forms have been reported in ref. 5(*c*) while here we are referring to the unsolvated form containing toluene in the cavity.

§ *Synthesis and spectroscopic data* of **3** and **4**. **3**: PhONa (2.98 g, 25.7 mmol) was added to a suspension of [WCl$_2$(L)] (5.25 g, 4.79 mmol) in THF (250 cm^3) and the mixture stirred at room temp. for 18 h. The resulting red solution was evaporated to dryness *in vacuo* and the residue was extracted with *n*-hexane (250 cm^3). The hexane solution was then cooled to 0 °C and [W(OPh)$_2$(L)] obtained as a red solid (65%). δ_H (200 MHz, CD$_2$Cl$_2$, room temp.): δ 1.21 (s, 18 H, Bu^t), 1.33 (s, 18 H, Bu^t), 3.45 (d, 4 H, J = 14 Hz, *H*CH), 4.55 (d, 4 H, J = 14 Hz, HC*H*), 6.83 (m, 6 H, H$_{arom}$), 7.83 (m, 12 H, H$_{arom}$). Satisfactory elemental analysis was obtained. Complex **4** was synthesized by the same procedure as **3**. δ_H (200 MHz, CD$_2$Cl$_2$, room temp.): 1.21 (s, 18 H, Bu^t), 1.32 (s, 18 H, Bu^t), 3.41 (d, 4 H, J = 14 Hz, *H*CH), 3.60 (s, 6 H, OCH$_3$), 4.62 (d, 4 H, J = 14 Hz, HC*H*), 6.77 (m, 6 H, H$_{arom}$), 7.11 (m, 10 H, H$_{arom}$). Satisfactory elemental analysis was obtained.

¶ *Crystal data* for complex **3**; C$_{56}$H$_{562}$O$_6$W, M = 1015.0, monoclinic, space group $P2_1/m$, a = 9.592(4), b = 15.315(2), c = 18.591(2) Å, β = 104.73(2)°, U = 2641.3(12) Å^3, Z = 2, D_c 1.276 g cm^{-3}, $F(000)$ = 1040, Mo-Kα radiation (λ = 0.71069 Å), μ(Mo-Kα) = 22.76 cm^{-1}, crystal dimensions 0.13 × 0.21 × 0.95 mm. The structure was solved by the heavy-atom method and anisotropically refined for all non-hydrogen atoms, except for those affected by disorder. The methyl carbon atoms of three *tert*-butyl groups [C(30)–C(32), C(34)–C(36), C(38)–C(40)] were affected by high thermal parameters indicating the presence of disorder, which was solved by splitting the atoms over two positions. The aromatic ring of the phenato group [C(61)–C(66)] was found to be statistically distributed over two positions related by the mirror plane. All the disordered atoms were isotropically refined with a site occupation factor of 0.5. The hydrogen atoms, except those associated with the disordered atoms, which were ignored, were located from difference Fourier maps and introduced as fixed contributors in the last stage of refinement (U_{iso} = 0.08 Å^2). During the refinement the C–C bond distances within the disordered *tert*-butyl groups were constrained to be 1.54(1) Å. For 4210 unique observed reflections [$I > 2\sigma(I)$] collected at 295 K ($6 < 2\theta < 54°$) on a Enraf-Nonius CAD4 diffractometer and corrected for absorption the conventional R is 0.036 ($wR2$ = 0.082). All calculations were carried out on an IBM PS2/80 personal computer and on an Encore E91 computer. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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