2 : 1 Ba/Ti(IV) Heterobimetallic complex based on two calix[6]arenes

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Reaction of *p*-Bu^t-calix[6]arene with barium metal in methanol then [Ti(OPr^i)_4] affords a heterobimetallic complex with a central Ti(IV) attached to two calix[6]arenes in the 1,3-alternate conformation, each with an *endo*-barium sharing common phenolate groups with the titanium centre.

The relevance of alkali and alkaline earth metal cation π-arene solvation in biology[1] and chemistry[2] has recently provoked a number of theoretical and experimental investigations into these interactions. There is ample structural evidence for the solvation of alkali metals by aromatic systems.[3] However, there are few structural examples of analogous interactions for alkaline earth metals,[4,5] with most studies limited to theoretical[6] or gas phase studies.[7] Stabilisation of such interactions in the condensed phase is possible using macrocycles capable of three dimensional π-solvation, whereby the metal is drawn over the face of arene rings through classical coordination elsewhere within the macrocycle.

Calixarenes have the ability to encourage metal···π-arene interactions through phenolate coordination. They are macrocyclic ligands usually comprised of 4 to 8 phenol moieties, linked by methylene bridges at their *ortho*-positions, that can be organised with shape-specific π-rich cavities. Complexes of the lowest oligomer in the series, calix[4]arene, adopt the cone conformation,[8] except for some group 13 organometallic systems.[9] The cone conformation has two binding sites, either *endo*- or *exo*- to the cavity. In the *endo*- case metal ions may interact with the π faces of the aromatic groups while simultaneously interacting with the calix[4]arene phenol groups, whereas in the *exo*- case metal ions can interact with up to four phenol groups. The difference in these binding sites allows access to heterobimetallic complexes, with several examples extant of *endo*-alkali metals with *exo*-transition metals,[10] whereas there is only one structurally authenticated example of an *endo*- group 2 complex.[11] Complexation of larger group 2 metals, in particular, is inherently difficult due to the relatively low coordination saturation afforded by the macrocycle.

For the larger calix[6]arenes greater coordination of group 2 metal ions is possible, but this is at the expense of the increased conformational flexibility of the calixarene, and controlling this is a challenge, as is controlling the number of metal ions complexing to a larger number of *exo*- binding sites. Whilst strategies for synthesis of calix[4]arene complexes are generally well defined, this is not the case for calix[6]arene. Herein we show that barium forms a heterobimetallic Ti(IV) complex with *p*-^tBu-calix[6]arene, **1**, eqn. (1). Interestingly the structural organisation of the calix[6]arene occurs not only through barium and titanium phenoxo coordination, but also through barium π-complexation. Significantly the synthesis represents a new methodology for the construction of heterobimetallic complexes based on calix[6]arene.
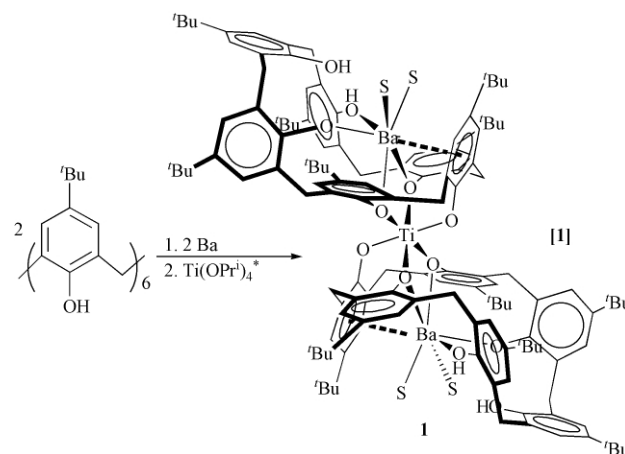
Complex **1** was prepared in 88% yield by the reaction of one equivalent of barium with one equivalent of *p*-^tBu-calix[6]arene in methanol, followed by the addition of 1 : 1 solution of Ti(OPr^i)_4 and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) in methanol.† It was necessary to mix the Ti(OPr^i)_4

with the TMEDA before addition of methanol, to avoid precipitation of titanium hydroxides/methoxides.

The structure of **1** contains four un-ionised phenol OH groups, so we were interested to explore the chemistry by attempting to introduce additional alkali metal or alkaline earth cations at these sites. All such attempted reactions in methanol were unsuccessful and **1** decomposed to the starting calixarene.

The solid-state structure of **1** suggests that the ^{1}H NMR spectrum should contain three sets of methylene doublets. Three such doublets (one slightly broad) are indeed observed when solid **1** is desolvated under vacuum, before the NMR solution (CDCl_3) sample is prepared. In contrast, the ^{1}H NMR spectrum of as-obtained methanol solvate **1** in chloroform shows only one of the expected doublets, the others presumably being broadened into the baseline. These results suggest that the presence of methanol results in rapid intramolecular re-organisation on the NMR time scale. Signals for the residual phenolic OH protons are not observable in either spectrum.
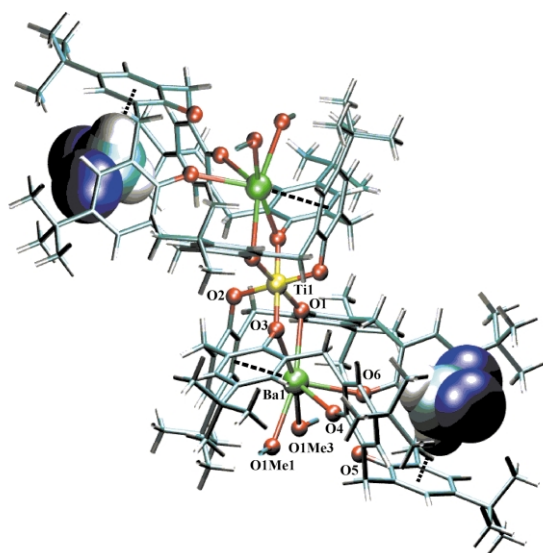
The atom-to-atom connectivity in **1** in the solid state was established by a single crystal diffraction study. The complex crystallises in space group $P2_1/n$ with the asymmetric unit comprised of half a molecule, the other half generated by an inversion centre, Fig. 1.[12,13] The calix[6]arenes are in the 1,3-alternate conformation, as in recently authenticated monocyclopentadienyltitanium(IV) complexes of the same calixarene.[14] The symmetry of the molecule imposes a linear arrangement of the three metal centres, so that the cavities devoid of metal ions are pointing in opposite directions. Each such cavity contains a molecule of dichloromethane solvent, Fig. 1, and the complex acts as a divergent receptor. Interestingly the chlorinated solvent molecules fit snugly in the cavities and show C–H···π interactions, the closest CH···centroid distance being 2.61 Å, which is comparable to previously reported values for dichloromethane inclusion complexes of calix[4]arene (2.46, 2.48, 2.61 Å)[15] and calix[6]arene (2.49 Å).[14]

Scheme 1 * Ti(OPr^i)_4 premixed with one equivalent of TMEDA in methanol. S = Methanol.

The central Ti(IV) is coordinated octahedrally by three contiguous phenolate groups from each calix[6]arene, the two 1,3-arranged groups from each calixarene bridging also to its proximate barium centre. The aromatic rings of the unique non-bridging phenolates are involved in Ba···π-arene interactions, with Ba(1)–C(12–17) distances ranging from 3.28–3.53 Å (Ba-arene centroid 3.10 Å). If bonding distances are arbitrarily construed to be ≤3.45 Å, an η⁴ coordination of the arene ring is indicated. A previously reported compound Ba₂(Odpp)(μ-Odp)₃[4] (Hodpp = 2, 6-diphenylphenol) possesses four significant Ba-arene interactions with Ba-arene centroid distances of similar length to **1** (3.02–3.28 Å). The barium centres also bind to two other phenol moieties, and on charge balance considerations one of these for each calixarene must be protonated, assuming that all groups around titanium are deprotonated (as expected for a polarising quadrivalent metal centre). Two coordinated methanol ligands complete each barium environment, thus the barium centres are seven coordinate, counting a π-arene as occupying one coordination site. The barium π-arene interaction in **1** represents only the third example of cationic π-bonding to the inner faces of calix[6]arene[16] and the first example of barium π-arene bonding. Unfortunately the large nature of the structure determination precluded location of hydrogen atoms, and any attempt to assign the phenolic group would be purely speculative.

Our simple synthetic approach gives access to a novel heterobimetallic complex, and this approach may lend itself to other combinations of metals. Moreover, the Ba···π-arene interaction has implications in designing other calixarene complexes, with other complex ligands, as well as offering a model for the solvation of alkaline earth ions in aromatic rich systems.

Fig. 1 Projection of **1** with spacefilling dichloromethane molecules, broken lines represent Ba···π and CH···π interactions. Selected interatomic distances (Å) and angles (°):Ti(1)–O(1, 2, 3) 1.930(4), 1.940(4), 1.944(4), Ba(1)–O(1, 3, 4, 6, 1Me1, 1Me3) 2.725(4), 2.674(4), 2.847(4), 2.805(4), 2.752(2), 2.715 (5), Ba(1)–C* 3.10, O(1)–Ti(1)–O(1^i, 2, 2^i, 3, 3^i) 180.0, 89.8(2), 90.2(2), 84.0(2), 96.0(2), O(2)–Ti(1)–O(2^i, 3, 3^i) 180.0, 89.7(2), 90.3(2), O(3)–Ti(1)–O(3^i) 180.0, O(1)–Ba–O(3, 4, 6, 1Me1, 1Me3) 57.4(1), 121.5(1), 91.3(1), 163.5(1), 116.5(2), O(3)–Ba–O(4, 6, 1Me1, 1Me3) 88.6(1), 124.1(1), 109.6(1), 163.9(1), O(4)–Ba–O(6, 1Me1, 1Me3) 68.8(1), 64.2(1), 106.3(1), O(6)–Ba–O(1Me1, 1Me3) 105.0(1), 68.4(1), Ba(1)–O(1, 3)–Ti(1) 107.5(2), 109.0(2), C*–Ba(1)–O(1, 3, 4, 6, 1Me1, 1Me3) 78.6, 78.5, 144.7, 144.6, 89.2, 85.8. C* is the centroid of the arene ring interacting with barium.

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