

E-mail: clraston@chem.uwa.edu.au

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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 $\cdots\pi$ -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 η^4 coordination of the arene ring is indicated. A previously reported compound Ba₂(Odp)(μ -Odp)₃⁴ (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]arene¹⁶ 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 $\cdots\pi$ -arene interaction has implications in designing other calixarene

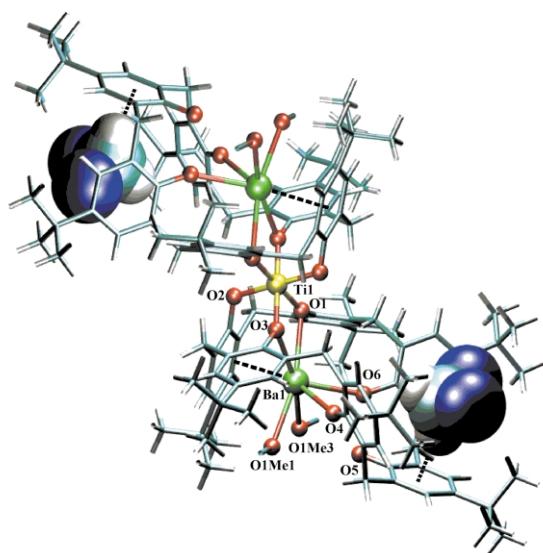


Fig. 1 Projection of **1** with spacefilling dichloromethane molecules, broken lines represent Ba $\cdots\pi$ and CH $\cdots\pi$ interactions. Selected interatomic distances (Å) and angles (°): Ti(1)–O(1, 2, 3) 1.930(4), 1.940(4), 1.944(4), Ba(1)–O(1, 3, 4, 6, 1Me1, 1Me3) 2.725(4), 2.674(4), 2.847(4), 2.805(4), 2.752(2), 2.715 (5), Ba(1)–C* 3.10, O(1)–Ti(1)–O(1ⁱ, 2, 2ⁱ, 3, 3ⁱ) 180.0, 89.8(2), 90.2(2), 84.0(2), 96.0(2), O(2)–Ti(1)–O(2ⁱ, 3, 3ⁱ) 180.0, 89.7(2), 90.3(2), O(3)–Ti(1)–O(3ⁱ) 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.

complexes, with other complex ligands, as well as offering a model for the solvation of alkaline earth ions in aromatic rich systems.

Notes and references

[†] **Synthesis:** **1** To a suspension of *p*-Bu-L[OH]₆ (1.0 g, 1.03 mmol) in methanol (100 ml) was added barium metal (0.16 g, 1.17 mmol). The mixture was stirred affording a white suspension on complete consumption of the barium. Ti(OPr)₄ (0.2 ml, 97%, 0.65 mmol) and TMEDA (0.15 ml, 1 mmol) were mixed together and then diluted in ~10 ml methanol and this mixture was added to the barium calix[6]arene complex. **1** formed as a pale orange crystalline solid, yield 1.2 g, 88%. Crystals of **1** suitable for X-ray structure determination were grown from a mixture of dichloromethane and methanol. ¹H NMR (CDCl₃, 300 MHz, 298 K) **1** (sample dried *in vacuo*) δ 7.15 (s, 4 H, aryl), 7.02 (s, 8 H, aryl), 7.01, (s, 4 H, aryl), 6.89 (s, 4 H, aryl), 6.54, (s, 4 H, aryl), 4.95 (b, 4 H, CH₂), 4.36 (d, 4 H, *J* = 15 Hz, CH₂), 3.97 (d, 4 H, *J* = 15 Hz, CH₂), 3.28 (d, 4 H, *J* = 15 Hz, CH₂), 3.19 (d, 4 H, *J* = 15 Hz, CH₂), 3.06 (b, 4 H, CH₂), 1.25 (s, 54 H, ^tBu), 1.20 (s, 18 H, ^tBu), 1.15 (s, 36 H, ^tBu). **1** was collected at 150 K on a Bruker-AXS SMART 1000 CCD diffractometer with Mo–K α radiation. The structure was solved by direct methods (SIR92) and refined with a full matrix least-squares refinement on *F* (RAELS). C₆₆H₈₀BaTi_{0.5}O₆·1.25(CH₂Cl₂)·3(CH₃OH), *M* = 1332.9, monoclinic, *a* = 14.674(3), *b* = 14.360(3), *c* = 33.624(7) Å, β = 99.936(4)°, *U* = 6979(4) Å³, *T* = 150 K, space group *P*2₁/*n*, *Z* = 4, μ (Mo–K α) = 0.767 mm^{–1}, 69102 reflections measured, 16640 unique (*R*_{int} = 0.040). The final *R* = 0.048, and *wR* = 0.060 (observed data). CCDC 205214. See <http://www.rsc.org/suppdata/cc/b3/b302346j/> for crystallographic data in .cif or other electronic format.

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