

# A heterobimetallic $K_2Ti_2$ complex incorporating two calix[5]arenes: A diverse array of metal–ligand interplay

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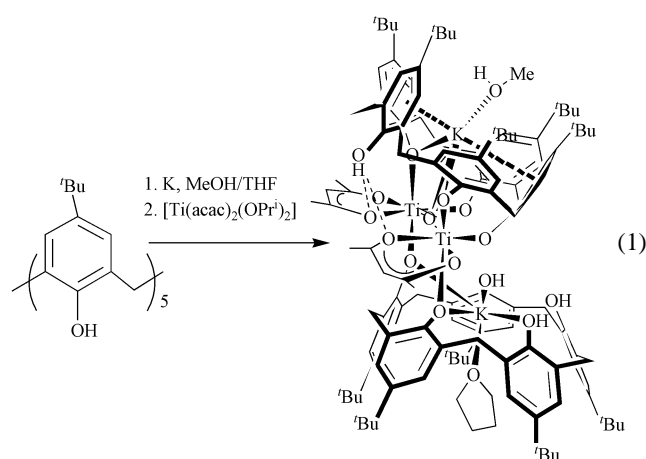
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Reaction of *p*-<sup>t</sup>Bu-calix[5]arene with potassium metal in a mixture of methanol and THF followed by  $[Ti(acac)_2(OPr^i)_2]$  affords an unsymmetrical dimeric 1:1 K/Ti complex built up from a central Ti–O–Ti core with each titanium(IV) centre octahedrally coordinated, bearing an acac and a calix[5]arene encapsulating a potassium ion.

Calixarenes can bind metal ions in a variety of ways for both pristine calixarenes as well as upper and lower rim functionalised analogues.<sup>1</sup> For the former, complexation studies have mainly centred on calix[4]arenes, which usually adopt the cone conformation with the four phenolic O-centres poised to bind to metal ions. In contrast, the larger calix[6–8]arenes exhibit considerable conformational flexibility which complicates their coordination chemistry and, not surprisingly, there are few reports of such complexes.<sup>2</sup> The intermediate sized calix[5]arenes also have few structurally authenticated metal complexes, those being based on large metal ions (W,<sup>3</sup> U<sup>4</sup> and Ln<sup>5</sup>). Like calix[4]arenes, calix[5]arenes are predisposed to the cone conformation both in solution and in the solid state through the formation of strong intramolecular hydrogen bonds. However unlike calix[4]arene, the five O-phenolato donors are too widely spaced for simultaneous coordination to one small metal ion. Moreover, the dispositions of the O-centres in the symmetrical cone conformation, or unsymmetrical conformations, lack complementarity with common binding geometries for transition metal ions.

Herein we report the synthesis† and structural elucidation of a titanium bridged calix[5]arene complex, **1**, eqn. (1),



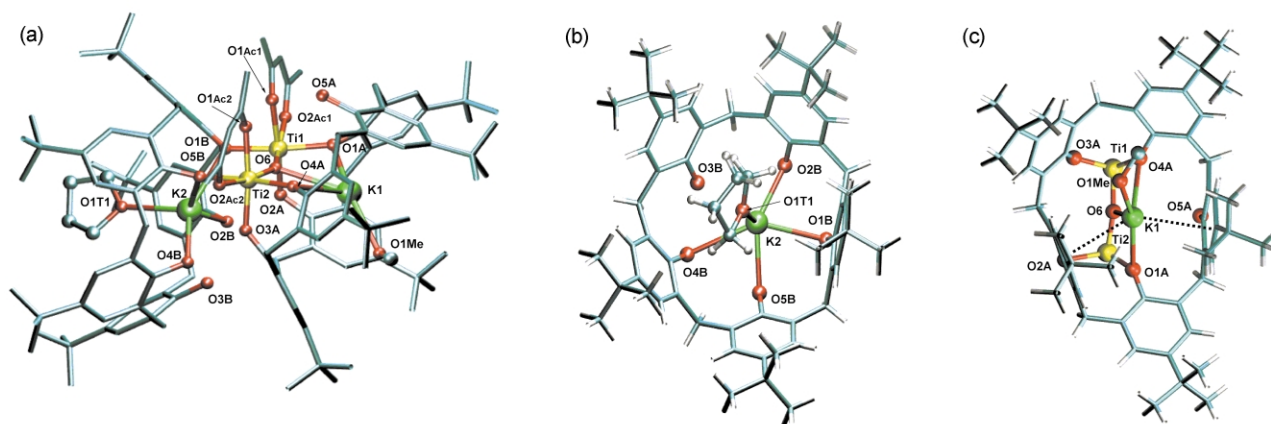
incorporating potassium ions, which has unusual metal–ligand interplay and disposition of the phenolic/phenolate groups. These include (i) two potassium ions bind *endo* to each calix[5]arene, the first such example for a calix[5]arene, (ii) one potassium cation binds to phenyl rings of the inner faces of a calix[5]arene, facilitated by the pinched conformation conferred upon it by also binding titanium(IV); the other *endo* potassium cation is positioned closer to the oxygen periphery of its associated calix[5]arene, and (iii) two calix[5]arenes accom-

modate two octahedral titanium(IV) centres bridged by an oxo-moiety.

Complex **1** was prepared in 76% yield by the addition of one equivalent of  $[Ti(acac)_2(OPr^i)_2]$  to a solution formed by reacting one equivalent of potassium metal with *p*-<sup>t</sup>Bu-calix[5]arene in methanol/THF, eqn. (1). The atom-to-atom connectivity and arrangement of ligands in the solid state was established by a single crystal diffraction study, Fig. 1(a). The complex crystallises in the space group *P1*. Two oxo-bridged octahedrally coordinated titanium atoms link the two calix[5]arenes, the angle subtended by the two titanium centres being  $151.1(2)^\circ$ . One calix[5]arene binds the two titanium centres, each with two adjacent O-centres which are necessarily *cis*-on the metal centres. Its remaining phenolic group is not associated with either titanium or potassium centre. This calix[5]arene has a pinched conformation, Fig. 1(c),<sup>6</sup> with the 1,3 phenyl groups essentially orientated in the same direction, these being  $\pi$ -bound to the associated potassium ion, K1. The other calix[5]arene binds through only two adjacent O-centres, one to each titanium, with the macrocycle in a more symmetrical cone conformation, Fig. 1(b).<sup>6</sup> Both these O-centres, and two others of this calix[5]arene are bound to the associated potassium centre, K2, and like the other calixarene, one phenol group is uncomplexed. The octahedral coordination of each titanium is fulfilled by a bidentate acetylacetonate (acac) ligand.

The charge of the metal centres is balanced by the oxo- and acac ligands, and calixarenes with different levels of deprotonation. All phenolic groups attached to titanium are assumed to be deprotonated (as expected for a polarising quadrivalent metal centre), which gives the calix[5]arenes 4- and 2- charges to satisfy the molecular charge balance. The uncomplexed phenolic groups of each calixarene are undoubtedly protonated, and the same should apply to those uniquely attached to K2.

The overall arrangement of ligands and metal centres approximates to *C<sub>s</sub>* symmetry, with the potassium centres and oxo-moiety lying on the 'symmetry element'. The pinched calix[5]arene binds the K1 atom in its cavity where the tilting of the 1,3 phenyl rings is associated with bis- $\eta^6$ - $\pi$ -arene cation interaction. One of these rings has its associated O-centre bound to a titanium, with the K1- $\eta^6$ -arene(centroid) distance at 3.346 Å. The other aromatic ring O-centre is not coordinated and presumably here tilting towards K1 is favoured by maximising the  $\pi$ -arene–potassium interaction, which is reflected in a shorter K1- $\eta^6$ -arene(centroid) distance: 3.125 Å. Added to this are potential tilting constraints associated with hydrogen bonding of this phenolic OH group to O1Ac1 and O1Ac2 oxygens of the acac ligands, O(H)⋯O5–O1Ac1, O1Ac2 distances being 2.988 and 2.942 Å respectively. Both K<sup>+</sup>– $\eta^6$ -arene(centroid) distances are within the realms for values reported for a mixed *endo*/*exo* potassium *exo* titanium dimeric calix[4]arene complex, *viz.* 3.217 Å.<sup>7</sup> This K1 centre also interacts significantly with the oxygen atoms of the two splayed, 1,3-disposed, phenolate rings of the pinched calix[5]arene as well as the oxo-ligand bridging the two titanium centres, and one methanol molecule which resides snugly in the cavity of the calixarene. Thus K1 is six coordinate counting each K<sup>+</sup>– $\pi$ -arene interaction as one sterically demanding coordination site. The



**Fig. 1** (a) Molecular projection of **1** with hydrogen atoms omitted for clarity, (b) top view of the symmetrical cone configured calix[5]arene, (c) top view of pinched calix[5]arene. Selected interatomic distances (Å) and angles (°): Ti(1)–O(1A, 2A, 1B, 1Ac1, 2Ac1, 6) 1.906(4), 1.927(4), 1.873(4), 2.051(4), 2.105(4), 1.874(4), Ti(2)–O(1Ac2, 2Ac2, 3A, 4A, 5B, 6) 2.043(4), 2.080(4), 1.986(4), 1.913(4), 1.913(4), 1.824(4), K(1)–O(1A, 1Me, 4A, 6) 2.929, 2.845(8), 2.797(4), 2.763(4), K(2)–O(1B, 2B, 4B, 5B, 1T1) 2.906(4), 2.668(4), 2.926(4), 2.650(4), 2.617(6), O(1A)–Ti(1)–O(2A, 1B, 1Ac1, 2Ac1, 6) 89.0(2), 169.6(2), 91.1(2), 84.6(2), 93.6(2), O(2A)–Ti(1)–O(1B, 1Ac1, 2Ac1, 6) 87.3(2), 170.7(2), 90.4(2), 97.6(2), O(1B)–Ti(1)–O(1Ac1, 2Ac1, 6) 91.0(2), 85.6(2), 96.5(2), O(1Ac1)–Ti(1)–O(2Ac1, 6) 80.3(2), 91.6(2), O(2Ac1)–Ti(1)–O(6) 171.7(2), O(1Ac2)–Ti(2)–O(2Ac2, 3A, 4A, 5B, 6) 80.9(2), 173.8(2), 91.7(2), 89.9(2), 87.6(2), O(2Ac2)–Ti(2)–O(3A, 4A, 5B, 6) 94.7(2), 81.1(2), 84.4(2), 167.5(2), O(3A)–Ti(2)–O(4A, 5B, 6) 91.9(2), 85.2(2), 97.2(2), O(4A)–Ti(2)–O(5B, 6) 164.9(2), 94.5(2), O(5B)–Ti(2)–O(6) 100.6(2), O(1A)–K(1)–O(1Me, 4A, 6) 88.1(2), 111.7(1), 57.8(1), O(1Me)–K(1)–O(4A, 6) 158.6(2), 133.2(2), O(4A)–K(1)–O(6) 59.1(1), O(1B)–K(2)–O(2B, 4B, 5B, 1T1) 73.1(1), 142.4(1), 71.8(1), 118.3(2), O(2B)–K(2)–O(4B, 5B, 1T1) 119.9(1), 137.5(1), 107.6(2), O(4B)–K(2)–O(5B, 1T1) 78.1(1), 92.5(2), O(5B)–K(2)–O(1T1), 109.7(2), Ti(1)–O(1)–Ti(2) 151.5(2).

more symmetrical calix[5]arene binds K2 at its periphery through four O-centres, the uncomplexed fifth oxygen centre (O3B) residing at 3.052 Å from K(2). The open topography of this calix[5]arene also allows for the inclusion and complexation of a larger THF molecule rather than the methanol, as in the pinched calix[5]arene. Thus, K2 takes on five-fold coordination.

The origin of the oxo-group in **1**, which is reproducibly found, presumably comes from adventitious water or some metal oxide present on the surface of the potassium metal. This reiterates behaviour we have seen in bimetallic BaTi(iv) complexes based on calix[4]arenes.<sup>8</sup>

The new findings, on a less extensively studied calixarene, has implications in building up other mixed metal systems based on the same calixarene, or even higher oligomers. The presence of protonated O-centres for each calixarene suggests the possibility of replacing the potassium ions by divalent and even trivalent metal ions, which is an area we are actively pursuing.

## Notes and references

† Synthesis: **1** To a suspension of *p*-Bu-calix[5]arene (0.25 g, 0.308 mmol) in methanol (25 ml) was added potassium metal (0.015 g, 0.375 mmol). The mixture was stirred and, on complete consumption of the potassium metal, THF (25 ml) was added to form a clear solution. [Ti(acac)<sub>2</sub>(OPr<sup>i</sup>)<sub>2</sub>] (0.15 ml, 75%, 0.310 mmol) was then added and the mixture was evaporated by boiling until precipitation occurred. The solid material was then redissolved by addition of dichloromethane, additional methanol was added (~5 ml) and the solution was left to crystallise over three days, yielding **1** as orange prisms, 76%. X-ray crystal data: **1** was collected at 150(2) K on a Bruker-AXS SMART 1000 CCD diffractometer, and solved by direct methods (SIR92) and refined with a full matrix least-squares refinement on *F* (RAELS). **1** C<sub>120</sub>H<sub>144</sub>K<sub>2</sub>O<sub>15</sub>Ti<sub>2</sub>·4(CH<sub>2</sub>Cl-2)·1.5(C<sub>4</sub>H<sub>8</sub>O)·CH<sub>3</sub>OH·H<sub>2</sub>O, *M* = 2498.4, triclinic, *a* = 17.118(2), *b* = 18.018(2), *c* = 25.197(4) Å, *α* = 85.914(2), *β* = 70.719(2), *γ* = 74.888(2)°, *U* = 7081(3) Å<sup>3</sup>, *T* = 150(2) K, space group *P* $\bar{1}$ , *Z* = 2, *μ*(Mo–K<sub>α</sub>) = 0.377 mm<sup>−1</sup>, 70005 reflections measured, 30702 unique (*R*<sub>int</sub> =

0.036). The final *R* = 0.110, and *wR* = 0.174 (observed data). CCDC 211012. See <http://www.rsc.org/suppdata/cc/b3/b304449a/> for crystallographic data in .cif or other electronic format.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, 298K): **1** δ 7.48 (d, 2 H, *J* = 3 Hz, aryl), 7.23 (d, 2 H, *J* = 3 Hz, aryl), 7.16 (d, 2 H, *J* = 3 Hz, aryl), 7.09 (d, 4 H, *J* = 3 Hz, aryl), 7.04 (s, 4 H, aryl), 7.00 (d, 2 H, *J* = 3 Hz, aryl), 6.94 (d, 2 H, *J* = 3 Hz, aryl), 6.48 (s, 2 H, aryl), 5.54 (d, 2 H, *J* = 15 Hz, CH<sub>2</sub>), 5.29 (8 H, s, CH<sub>2</sub>Cl<sub>2</sub>), 5.18 (d, 2 H, *J* = 15 Hz, CH<sub>2</sub>), 4.93 (s, 2H, CH, acac), 4.36 (d, 2 H, *J* = 15 Hz, CH<sub>2</sub>), 4.24 (d, 2 H, *J* = 15 Hz, CH<sub>2</sub>), 3.73 (br, 4 H, CH<sub>2</sub>), 3.73 (br, 6 H, THF), 3.34 (s, 3 H, MeOH), 3.25 (d, 4 H, *J* = 15 Hz, CH<sub>2</sub>), 3.14 (d, 2 H, *J* = 15 Hz, CH<sub>2</sub>), 2.96 (d, 2 H, *J* = 15 Hz, CH<sub>2</sub>), 2.15 (s, 6 H, acac), 1.87 (m, 6 H, THF), 1.45 (s, 6 H, acac), 1.33 (s, 18 H, 'Bu), 1.22 (s, 18 H, 'Bu), 1.19 (s, br, 36 H, 'Bu), 1.12 (s, 9 H, 'Bu), 0.78 (s, 9 H, 'Bu).

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