Heterobimetallic Calix[4]arene Complexes: Interconversion of Dimeric (Ca, Sr or Ba)/Ti^{IV} Complexes with a Monomeric K/Ti^{IV} Complex

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Reaction of calix[4]arene with alkaline earth metals (Ca/Sr/Ba) in methanol followed by the addition of various titanium(IV) sources afforded novel dimeric 1:1 alkaline earth/titanium(IV) calix[4]arene complexes. In each complex the central core of the crystallographically imposed centrosymmetric dimer consists of a rhombus of alternating alkaline earth metals and μ_3-oxo-centres. Five terminal methanol ligands form seven-coordinate calcium and strontium centres, while the barium centres are bridged by two additional methanol ligands, making them nine-coordinate. Each oxo centre is the apical ligand of a square-pyramidal titanium(IV) centre, whose basal plane ligands are the four phenolate oxygens from a calix[4]arene in the symmetrical cone-conformation. Deprotonation of calix[4]arene with potassium metal, followed by the addition of a titanium(IV) source containing at least one acetylacetonate ligand, formed a mixed potassium/titanium complex based on one calix[4]arene. The potassium cation in this complex binds within the π-basic calix[4]arene cavity, whilst titanium is octahedrally complexed in the *exo*-position, by four phenolates and one acetylacetonate. The alkaline earth titanium dimers and potassium/titanium monomers could be interconverted merely by changing the solvent, with the appropriate cations and ligands present in solution.

Introduction

There is currently much interest in the formation and characterisation of heterobimetallic alkoxide species with well-defined stoichiometries.[1] Such complexes have potential as single source precursors to ultra-pure oxide ceramics,[2] or as molecular catalysts.[3] The synthesis and structural characterisation of heterobimetallic alkoxides has typically required the use of inert atmosphere techniques, owing to the inherent instability of such complexes towards hydrolysis and/or facile redistribution reactions.[1] We sought to explore alternative synthetic approaches, using macrocyclic calix[n]arenes as multidentate alkoxy ligands to circumvent the above decomposition reactions, and to impart high thermal stability.

Calix[4]arenes provide a set of four contiguous phenolic oxygen centres poised for metal ion chelation, and their complexes show a wide range of structural types, usually with the macrocycle in the bowl-shaped conformation.[4] While there are many structurally authenticated calix[4]arene transition metal complexes, those for the main group metals are limited. In the case of alkali and alkaline earth metals there are few examples of complexes of calix[*n*]arenes, the main focus of the chemistry concerned with ion extraction processes. In the case of calix[4]arenes there are a few examples of alkali metal[5] and alkaline earth metal[6] complexes, and a few examples of mixed transition-alkali metal complexes,[4,7] yet there are no examples of mixed transition metal alkaline earth complexes.

Herein we report a simple route to the preparation of dimeric alkaline earth/titanium(IV) calix[4]arene complexes, **1−3**, and the formation of a monomeric potassium/titanium(IV) calix[4]arene complex, **4** (Scheme 1). The complexes are formed rapidly in good yield, and do not require the use of an inert atmosphere, or dry solvents, although the yield of the dimeric calcium/titanium(IV) complex is higher in dry solvent. We also show that the alkaline earth/titanium(IV) dimers may be inter-converted into the potassium/titanium(IV) monomers by merely changing the solvent, with the appropriate cations and ligands present in solution. Seemingly the relative disposition of the alkoxide groups in the calix[4]arene stabilises these novel structures, with their formation also depending on the nature of the alkali/alkaline earth metal as well as the choice of solvent.

Addition of one equivalent of alkaline earth metal (Ca, Sr or Ba) to a suspension of *p*-*t*Bu-calix[4]arene, *p*-*t*Bu-

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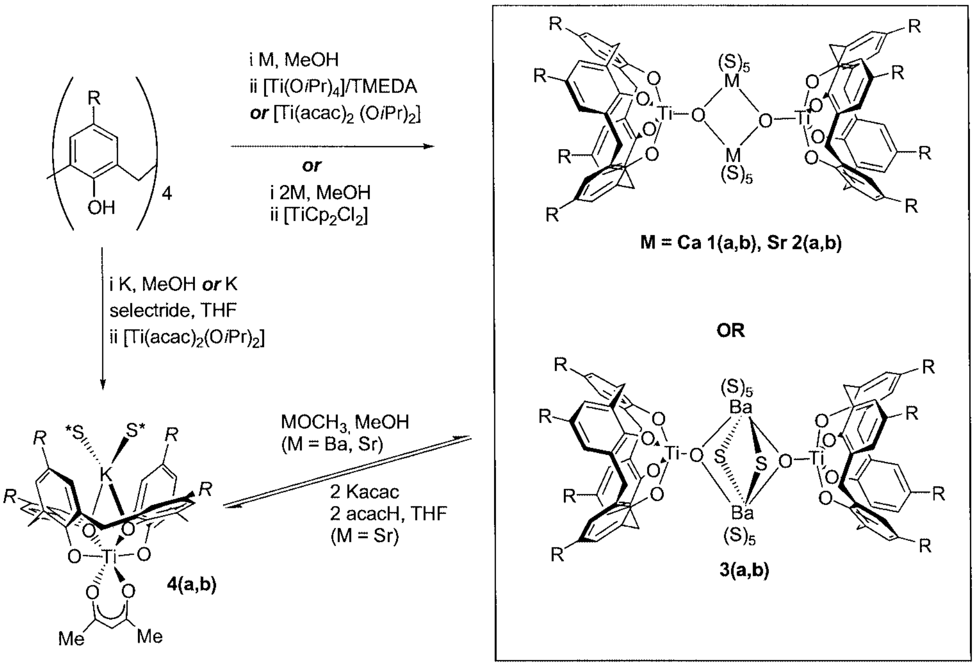

Scheme 1. S = MeOH, S* = MeOH or THF; (a) R = *t*Bu, (b) R = H

$L[OH]_4$, or calix[4]arene, $L[OH]_4$, in methanol, followed by addition of a 1:1 solution of $[Ti(OiPr)_4]$ and TMEDA (*N*,*N*,*N′*,*N′*-tetramethylethylenediamine) in methanol afforded complexes **1−3** (Scheme 1). In the case of reactions involving calcium metal, dry methanol was used (see below). Premixing the $[Ti(OiPr)_4]$ and TMEDA before addition of methanol avoids the precipitation of titanium hydroxides/methoxides.

Alternative preparations of **1−3** were also established, where $[Ti(acac)_2(OiPr)_2]$ (acac = acetylacetonate) or $[TiCp_2Cl_2]$ (Cp = cyclopentadienyl) and an extra equivalent of alkaline earth metal were used in place of $[Ti(OiPr)_4]$/TMEDA. Base cleavage of both Cp ligands from $[TiCp_2Cl_2]$ is consistent with previous reports that Cp groups are cleaved from titanocene reagents under basic conditions.[8] The success of this synthetic route suggests that the relatively slow reaction of $[TiCp_2Cl_2]$ provides a synthetically engineered pathway for gradually delivering labile titanium(IV) into the reaction mixture, which presumably allows ligation with calix[4]arene to compete successfully against hydrolysis/methanolysis. Similarly, the successful use of $[Ti(OiPr)_4]$/TMEDA or $[Ti(acac)_2(OiPr)_2]$ reagents appears to rely on the chelation of titanium(IV) by TMEDA or acetylacetonate ligand to provide the same slow delivery of titanium(IV).

When TMEDA was omitted from the reaction of $[Ti(OiPr)_4]$ with calix[4]arene deprotonated by strontium or barium, the respective yields of **2(a,b)** and **3(a,b)** were low (< 20%, identified by ^1H NMR spectroscopy) and the complexes were contaminated by insoluble titanium hydrolysis/alcoholysis products. For calcium metal, under the same conditions, some dimer products **1(a,b)** precipitated, ca. 50% yield, along with unchanged calix[4]arene. The same modest yield results for calcium, even in the presence of TMEDA, in contrast to the good yields, ca. 80%, for the strontium and barium analogues. However, the yield of the Ca/Ti dimers **1(a,b)** can be improved to ca. 70% by using dry methanol. These findings can be rationalised by the poor solubility of calcium hydroxide in wet methanol, compared to strontium and barium hydroxides. Thus, whereas solutions containing strontium and barium ions and calix[4]arenes in wet methanol remain clear, the corresponding calcium solutions deposit considerable amounts of white material. However, when the latter mixture is formed in dry methanol the solution remains clear. For all three structures oxo-bridges are possibly derived from adventitious water; alternatively they could result from the presence of oxides/hydroxides on the surface of the metal.

The dimeric structures of **1b**, **2b** and **3a** were established using single-crystal X-ray diffraction data. Complexes **1b** and **2b** crystallise in the space group $P2_1/n$ having similar cell dimensions and are strictly isomophous, with the cell volume of the calcium complex slightly smaller than that of the strontium analogue, as expected. Major differences in the molecular structures of **1b** and **2b** (Figure 1, Table 1),[9] relative to that of **3a** (Figure 2, Table 2),[9] other than those associated with the substituents on the calixarene, include two additional methanol ligands which bridge the two barium centres in **3a** and the resulting coordination environment of the alkaline earth metal centres. The ^1H NMR spectra of **1b**, **2b** and **3a** are consistent with the persistence of the solid-state structures in solution.

The central cores of the crystallographically imposed centrosymmetric dimers in **1b** and **2b** consist of a rhombus of alternating alkaline earth metals and μ_3 oxo-centres, with each oxygen atom forming the apical ligand to a square-pyramidal titanium(IV) centre. The basal plane ligands are the four phenolate oxygen centres from a calix[4]arene in a

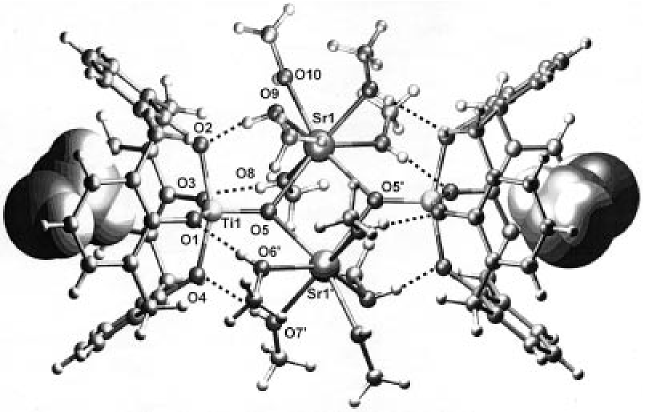

Figure 1. Molecular projection of the strontium/titanium(IV) complex, **2b**, showing included methanol (space filling) and intramolecular H-bonds

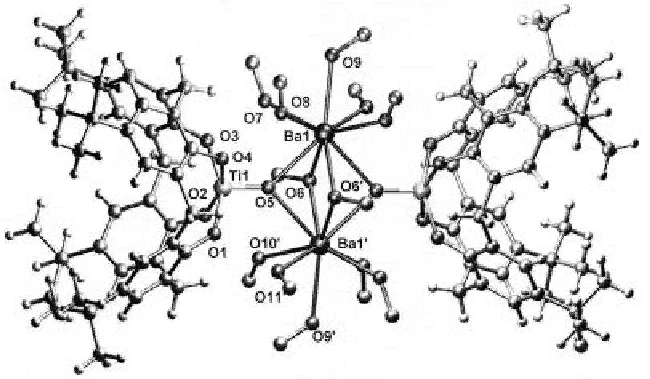

Figure 2. Molecular projection of the barium/titanium(IV) complex, **3a**, excluding methanol hydrogen atoms.

Table 1. Selected bond lengths (Å) and angles (°) for **2b**, values in parentheses are for the isomorphous calcium complex **1b**

Ti(1)−O(1, 2, 3, 4, 5)	1.9706(19), 1.9548(19), 1.9413(19), 1.9481(19), 1.7056(18), [1.9707(15), 1.9459(16), 1.9359(15), 1.9433(16),1.7078(14)]
Sr(1)−O(5, 5′, 6, 7, 8, 9, 10)	2.6019(18), 2.5426(17), 2.510(2), 2.549(2), 2.533(2), 2.578(2), 2.509(2), [2.5358(15), 2.4066(15), 2.3747(17), 2.4231(18), 2.4036(17), 2.4177(16), 2.3724(17)]
O(1)−Ti(1)−O(2, 3, 4, 5)	86.90(8), 156.36(8), 87.14(8), 102.07(8), [86.62(6), 155.18(6), 86.67(7), 102.87(7)]
O(2)−Ti(1)-(3, 4, 5)	87.86(8), 156.15(8), 100.50(8), [87.72(7), 154.40(6), 101.57(7)]
O(3)−Ti(1)−O(4, 5)	88.41(8), 101.55(8), [88.09(7), 101.94(7)]
O(4)−Ti(1)−O(5)	103.33(8), [104.00(7)]
O(5)−Sr(1)−O(5′, 6, 7, 8, 9, 10)	77.61(6), 133.63(7), 130.93(8), 75.46(7), 72.80(6), 120.02(7), [77.76(5), 134.70(6), 134.43(6), 75.32(6), 73.14(5), 116.97(6)]
O(5′)−Sr(1)−O(6, 7, 8, 9, 10)	78.41(6), 78.19(7), 111.67(7), 103.04(6), 162.30(7), [80.52(5), 81.32(6), 112.24(6), 104.45(7), 165.14(6)]
O(6)−Sr(1)−O(7, 8, 9, 10)	80.91(8), 77.47(7), 151.83(8), 88.85(7), [79.54(7), 76.98(6), 151.47(6), 89.28(6)]
O(7)−Sr(1)−O(8, 9, 10)	153.59(8), 72.06(8), 87.79(8), [150.21(7), 73.64(6), 86.23(7)]
O(8)−Sr(1)−O(9, 10)	125.72(7), 76.86(8), [124.21(6), 75.46(6)]
O(9)−Sr(1)−O(10)	82.46(7), [79.57(6)]

Table 2. Selected bond lengths (Å) and angles (°) for **3a**

Ti(1)−O(1, 2, 3, 4, 5)	1.961(4), 1.977(4), 1.938(4), 2.035(4), 1.680(4)
Ba(1)−O(5, 5′, 6, 6′ 7, 8, 9, 10, 11)	2.816(4), 2.861(4), 2.907(4), 2.889(4), 2.751(4), 2.742(4), 2.799(5), 2.743(4), 2.704(4)
O(1)−Ti(1)−O(2, 3, 4, 5)	87.7(2), 153.3(2), 87.3(2), 104.0(2)
O(2)−Ti(1)-(3, 4, 5)	88.2(2), 159.6(2), 101.5(2)
O(3)−Ti(1)−O(4, 5)	87.5(2), 102.7(2)
O(4)−Ti(1)−O(5)	98.9(2)
O(5)−Ba(1)−O(5′, 6, 6′, 7, 8, 9, 10, 11)	91.7(1), 61.0(71), 62.8(1), 72.1(1), 75.1(1), 137.0(1), 135.2(1), 132.6(1)
O(5′)−Ba(1)−O(6, 6′, 7, 8, 9, 10, 11)	62.1(1), 60.7(1), 140.2(1), 134.5(1), 131.3(1), 70.9(1), 73.6(1)
O(6)−Ba(1)−O(6′, 7, 8, 9, 10, 11)	94.0(1), 78.5(1), 134.5(1), 132.0(2), 131.3(1), 72.6(1)
O(6′)−Ba(1)−O(7, 8, 9, 10, 11)	131.6(1), 74.8(1), 133.8(2), 72.8(1), 133.0(1)
O(7)−Ba(1)−O(8, 9, 10, 11)	77.3(2), 72.2(2), 144.5(1), 90.7(1)
O(8)−Ba(1)−O(9, 10, 11)	7304 (2), 88.1(1), 144.9(1)
O(9)−Ba(1)−O(10, 11)	72.7(2), 70.7(2)
O(10)−Ba(1)−O(11)	82.9(1)

symmetrical cone-conformation, as shown in Figure 1, along with key bond lengths and angles, which are unexceptional. Deviation of the titanium centres from the plane defined by the four phenolate oxygen centres is 0.4016 and 0.4250 Å for **2b** and **1b** respectively. The calcium/strontium centres are seven-coordinate, having a distorted pentagonal bipyramidal geometry with two bridging oxo- and five terminal methanol ligands. An oxo group and one methanol ligand are in apical positions, with the other methanol ligands associated with hydrogen bonding to the oxygen atoms of the calix[4]arene, this presumably contributes to the stability and favourable formation/crystallisation of the complexes from methanol. The calixarene-methanol O···O distances and corresponding O···HO distances (in parentheses) are 2.676, (2.006), 2.645, (1.759), 2.649, (1.881), 2.603, (1.889) for **1b**; and 2.684, (1.920), 2.649, (1.769), 2.648, (1.910) 2.689, (2.026) for **2b**. There are 15 methanol solvates per dimer, of which 10 are coordinated to the strontium metal centres, two are located within the cavities of the calixarenes, and the remainder are found at interstitial sites in the structure.

Complex **3a** crystallises in the space group *Pbca*. The molecular structure of the complex is essentially the same as in **1b** and **2b**, being also comprised of centrosymmetric dimers. The titanium centres are in a similar environment, the metal centres deviating from the basal plane of four oxygen centres by 0.4021 Å. The expanded coordination sphere of the barium centres, each now with nine ligands, two bridging oxo, two bridging methanol and five terminal methanol solvates, is best described as capped square antiprismatic (Figure 2). The square face opposite the unique capping methanol is comprised of two *trans*-μ_3-oxo groups and two *trans*-μ_2-methanol ligands, which is common to both barium centres, and replaces the rhombus oxo-Ca/Sr core in **1b** and **2b**. Intramolecular hydrogen bonding is also prevalent, with calixarene-methanol O···O distances 2.688, 2.723, 2.631, 2.667Å, and additional interactions between bridging oxo and bridging methanol ligands, O5···O1, O1′ 2.904, 2.974 Å. Overall there are 24 methanol solvent molecules per dimer: 12 are coordinated to barium centres, two are located in the cavities of the calix[4]arenes, and the remaining 10 are located in the interstitial sites in the structure, along with one molecule of water. The titanium(IV) centres have similar geometries to those in **1b** and **2b**.

Previous examples of mixed-metal M/Ti species (M = Ba, Sr, Ca) based on simple alkoxide ligands do not generally have 1:1 stoichiometry,[10] but this is the case for complexes based on β-diketonates (M = Sr, Ba),[11] catecholate (M = Sr, Ba),[12] and aryloxy ligands [M = Ba].[13] The structures of such complexes are similar to the present structures in being dimeric, but are dissimilar in that the titanium centres are octahedrally coordinated. Also, whilst there are several examples of larger M/Ti aggregates displaying oxo-bridging between alkaline earth and titanium(IV) centres,[14] examples of oxo-bridged 2:2 complexes (as in the present structures) have the oxo groups between the titanium centres. Thus our structures are unique in the interplay of the oxo groups with the two different metal centres. This, and the lower coordination number of the titanium centres, possibly relates to the steric constraints imposed by the four phenolato groups of the calixarene, and also the intramolecular hydrogen bonds between the coordinated methanol molecules and the calixarene oxygens.

The monomeric heterobimetallic K/Ti calix[4]arene complexes, **4(a,b)**, were prepared by addition of one equivalent of potassium metal to *p*-*t*Bu-L[OH]$_4$ in either methanol, for **4a**, or THF for **4b**, followed by the addition of one equivalent of [Ti(acac)$_2$(O*i*Pr)$_2$]. The complexes were structurally authenticated using X-ray diffraction data. They crystallise in the space groups *C*2/*c* and *P*2$_1$/*n*, respectively, **4a** having half a molecule in the asymmetric unit, the other half being generated by a twofold rotation operation, whereas **4b** has a full molecule as the asymmetric unit. A molecular projection of **4a** is shown in Figure 3.[9] For both complexes the titanium(IV) centres are octahedral, bound by a bidentate β-diketonate and four phenolato oxygen atoms of a pinched cone conformation calix[4]arene (the pitch of the phenol planes relative to the plane through the oxygens of the calixarene being 18.2° and 70.1° for **4a** and 12.0°, 13.2°, 67.7°, 66.1° for **4b**; see also Table 3). The potassium is accommodated within the cavity of the calix[4]arene, interacting with two of the phenolate oxygen atoms and forming π-interactions to two opposite aromatic rings. Additionally two terminal methanol or THF ligands result in six-coordinate potassium centres. The K^+-η^6-arene(centroid) distances in **4a** and **4b** are 3.142 and 3.180, 3.253 Å, respectively, which are similar to previously reported values for a mixed *endo*-*exo*-potassium *exo* titanium dimeric calix[4]arene complex (3.217 Å).[7b]

The formation of the monomeric species **4(a,b)** is favoured by the incorporation of a chelating β-diketonate ligand, which provides steric protection against the formation of metallo-bridged structures, and predisposes titanium to chelate to only one calix[4]arene. In addition, the potassium ion is bound within the calix[4]arene cavity. Analogous monomeric alkaline earth/titanium calix[4]arene complexes could not be obtained, the dimers **1(a,b)−3(a,b)** being formed instead, even in the presence of acetylacetonate. This difference is consistent with the more polarising divalent alkaline earth cations preferring *exo*-cavity coordination, where they can obtain higher coordination numbers relative to the coordination available in the *endo*-cavity.

Dimers **1a−3a** possessing the *p*-*t*Bu substituents are sparingly soluble in methanol, and they precipitate from solution in good yield when prepared in this solvent. In contrast, these same dimers are highly soluble in solvents such

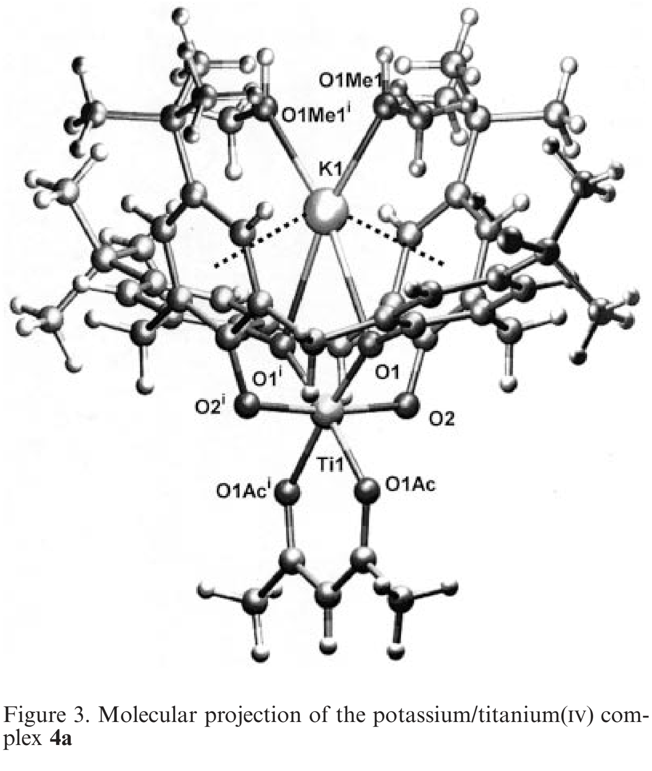

Figure 3. Molecular projection of the potassium/titanium(IV) complex **4a**

Table 3. Selected bond lengths (Å) and angles (°) for **4a** and **4b**

	4a
Ti(1)−O(1, 1Ac, 2)	1.8307(19), 1.999(2), 1.9907(18)
K(1)−O(1, 1Me)	2.833(2), 2.68(3)
O(2)−Ti(1)−O(1Ac, 1Ac[i], 2[i])	94.24(13), 86.51(8), 88.75(8), 91.45(9), 173.76(9)
O(1Ac)−Ti(1)−O(1Ac^{i})	82.99(14)
O(1)−K(1)−O(1[i], 1Me, 1Me^{i})	56.53(8), 108.78(8), 165.29(8)
O(1Me)−K(1)−O(1Me^{i})	85.91(15)
	4b
Ti(1)−O(1, 2, 3, 4, 7, 8)	1.8593(16), 1.9503(17), 1.8547(16), 1.9622(17), 1.9989(17), 2.0130(17)
K(1)−O(1, 3, 5, 6)	2.7476(17), 2.7479(17), 2.706(2), 2.693(2)
O(1)−Ti(1)−O(2, 3, 4, 7, 8)	87.89(7), 90.86(7), 87.44(7), 173.94(7), 91.04(7)
O(2)−Ti(1)−O(3, 4, 7, 8)	87.81(7), 172.90(7), 94.79(7), 92.04(7)
O(3)−Ti(1)−O(4, 7, 8)	86.91(7), 94.66(7), 178.09(7)
O(4)−Ti(1)−O(7, 8)	90.37(7), 93.40(7),
O(7)−Ti(1)−O(8)	83.45(7)
O(1)−K(1)−O(3, 5, 6)	57.56(5), 110.84(6), 162.04(6),
O(3)−K(1)−O(5, 6)	168.40(7), 104.62(6)
O(5)−K(1)−O(6)	86.98(7)

as toluene, dichloromethane or THF. We utilised solubility differences to devise methods to interconvert the dimers, in general, with the corresponding K/Ti monomers, **4(a,b)**, the latter being readily recrystallised from a variety of solvents. Thus, the K/Ti monomer **4a** crystallises from THF on addition of two equivalents of K(acetylacetonate) and acetylacetone to the alkaline earth/Ti dimers **2a** or **3a** (Scheme 1). No conversion into monomer could be effected in methanol. In THF, both the K/Ti monomer and Ba/Ti, Sr/Ti dimers are soluble, hence both monomeric and dimeric species can be present in equilibrium in solution. The K/Ti monomer can then be isolated from the mixture by selective crystallisation in the presence of additional ligand, since the Ba/Ti and Sr/Ti dimers cannot be crystallised from THF. Dissolution of the dimers in THF presumably results in ligand solvent displacement with disruption of the tightly coordinated methanol-calix[4]arene hydrogen bonding array (Figure 1).

Conversely the K/Ti monomer **4b** can be converted simply to the dimers by addition of methanolic solutions of Ba/Sr methoxides (>90%). Evidently the insolubility of the Ba/Ti and Sr/Ti dimers in methanol drives their formation. Attempts to interconvert the Ca/Ti dimers with monomers were thwarted by the precipitation of $Ca(OH)_2$.

Dimers **1−3** have been tested for application as single source precursors for CVD of perovskite titanate films. Preliminary results indicate that the compounds sublime under high vacuum and that annealing of this sublimate indeed gives a crystalline perovskite phase, and further investigations are underway. This aspect aside, the significance of the above results include (i) the simplicity and versatility of the synthetic approach in gaining access to heterobimetallic complexes, which should have a profound impact on synthetic strategies for gaining access to a wide range of mixed metal complexes, (ii) the novelty of the structures, and (iii) the remarkable control of the interconversion of monomeric and dimeric complexes.

Experimental Section

Synthesis of 1(a,b) 2(a,b) and 3(a,b): Full experimental details are given for **3a**, the synthesis of **1**, **2** and **3b** being very similar. Barium (0.12 g, 0.87 mmol) was added to a suspension of *p*-*t*Bu-calix[4]arene (0.50 g, 0.77 mmol) in methanol (30 mL). The mixture was stirred, affording a clear pale yellow solution on complete reaction of the metal. $[Ti(OiPr)_4]$ (0.25 mL, 97%, 0.84 mmol) and TMEDA (0.15 mL, 1 mmol) were mixed together and then diluted in approximately 5 mL methanol and this solution was added to the barium calix[4]arene complex. A fine white solid formed, which was collected after 15 min and recrystallised from 10 mL dichloromethane by the addition of 15 mL of boiling methanol, yielding colorless prisms of **3a** (0.7 g, 80%). The analogous Sr/Ti **2a** (85% yield) and Ca/Ti (**1a**, 51% yield), were prepared as for **3a**. For **1a**, the solution formed by reaction of calcium with *p*-*t*Bu-calix[4]arene required filtering. Also, the solution of crude **1a** in dichloromethane required filtering to remove some precipitated *p*-*t*Bu-calix[4]arene. Crystals of **3a** suitable for X-ray crystallography were grown by layering methanol onto a dichloromethane solution of the complex. Compounds **1b**, **2b**, and **3b** were prepared similarly, calix[4]arene being used in place of *p*-*t*Bu-calix[4]arene, except that recrystallisation was performed directly from hot methanol,[15] yield 71% **1b**,[16] 80% **2b**, 82% **3b**. ^1H NMR ($CDCl_3$, 300 MHz, 298 K): δ = **1a**: 6.90 (s, 16 H, aryl), 4.73 (br., 8 H, CH_2), 3.40, (s, 66 H, methanol), 2.88 (br., 8 H, CH_2), 1.15 (s, 72 H, *t*Bu); **2a**: 6.92 (s, 16 H, aryl), 4.64 (d, J = 12 Hz, 8 H, CH_2), 3.33 (s, 66 H, methanol), 2.94 (d, J = 12 Hz, 8 H, CH_2), 1.15 (s, 72 H, *t*Bu); **3a**: 6.94 (s, 16 H, aryl), 4.63 (d, J = 12 Hz, 8 H, CH_2), 3.35 (s, 72 H, methanol), 3.00 (d, J = 12 Hz, 8 H, CH_2), 1.15 (s, 72 H, *t*Bu); **1b**: 6.98 (d, 16 H, J = 6 Hz, aryl), 6.49 (t, J = 6 Hz, 8 H, aryl), 4.79 (d, J = 12 Hz, 8 H, CH_2), 3.40 (s, 45 H, methanol), 3.16 (d, J = 12 Hz, 8 H, CH_2); **2b**: 6.96 (d, 16 H, J = 6 Hz, aryl), 6.51 (t, J = 6 Hz, 8 H, aryl), 4.74 (d, J = 12 Hz, 8 H, CH_2), 3.40 (s, 45 H, methanol), 3.03 (d, J = 12 Hz, 8 H, CH_2); **3b**: 6.96 (d, 16 H, J = 6 Hz, aryl), 6.50 (t, J = 6 Hz, 8 H, aryl), 4.74 (d, J = 12 Hz, 8 H, CH_2), 3.40 (s, 51 H, methanol), 3.06 (d, J = 12 Hz, 8 H, CH_2) ppm.

Synthesis of 4a and 4b: Potassium was added (0.04 g, 1.0 mmol) to a suspension of *p*-*t*Bu-calix[4]arene (0.50 g, 0.77 mmol) in methanol (20 mL). The mixture was stirred, resulting in a clear pale yellow solution on complete reaction of the metal. The addition of $[Ti(acac)_2(OiPr)_2]$ (0.40 mL, 75%, 0.82 mmol) gave an orange solution, which was concentrated by boiling to incipient crystallisation. On slow cooling to 0 °C orange prisms of **4a** formed[15] (0.6 g, 72%). **4b**: This THF adduct was prepared using dry THF and K-selectride (1 M in THF) in place of methanol and potassium metal, giving **4b** (0.45, 56%). ^1H NMR ($CDCl_3$, 300 MHz, 298 K): δ = **4a** 7.13 (s, 4 H, aryl), 6.91 (s, 4 H, aryl), 5.94 (s, 1 H, CH), 4.53 (d, J = 15 Hz, 4 H, CH_2), 3.45 (s, 24 H, methanol), 3.12 (d, J = 15 Hz, 4 H, CH_2), 2.00 (s, 6 H, CH_3), 1.37 (s, 18 H, *t*Bu), 1.10 (s, 18 H, *t*Bu); **4b:** 7.13 (s, 4 H, aryl), 6.93 (s, 4 H, aryl), 5.93 (s, 1 H, CH), 4.52 (d, J = 15 Hz, 4 H, CH_2), 3.69 (m, 12 H, THF), 3.14 (d, J = 15 Hz, 4 H, CH_2), 1.98 (s, 6 H, CH_3), 1.83 (m, 12 H, THF), 1.37 (s, 18 H, *t*Bu), 1.10 (s, 18 H, *t*Bu) ppm.

Conversion of Ba/Ti Dimers to K/Ti Monomers: Acetylacetone (0.12 mL, 1.2 mmol) in methanol (ca. 2 mL) was treated with potassium metal (0.025 g, 0.64 mmol) and the solution was added to a solution of the Ba/Ti dimer **3a** (0.7 g 0.30 mmol) dissolved in THF (20 mL). The orange solution was concentrated by heating until incipient crystallisation. On cooling slowly to room temperature, crystals of **4b** formed (0.22 g, 36%). The Sr/Ti dimer **2a** could be converted into **4b** analogously (38% yield).

Conversion of K/Ti Monomer to Ba/Ti or Sr/Ti Dimer: A solution of **4b** (0.5 g, 0.48 mmol) in methanol (50 mL) was treated with a solution of Ba in methanol (0.07 g, 0.50 mmol) to give a white precipitate of **1a** (0.49 g, 96%); **4b** could be similarly converted into **1b** using Sr in place of Ba (94%).

Crystal Data: The intensity data was collected at 150(1)K on an Enraf−Nonius Kappa CCD diffractometer with Mo-K_α (λ = 0.71073Å) radiation. Structures **1b**, **2b**, **4a** and **4b** were solved by direct methods (SHELXL-97) and refined with a full-matrix least-squares fit refinement on F^2 (SHELXL-97). Structure **3a** was solved by direct methods (SIR92) and refined with a full-matrix least-squares fit on F (RAELS).

1b: $C_{28}H_{20}O_5CaTi{\cdot}7.5(CH_3OH)$ M_r = 764.74, monoclinic, space group $P2_1/n$, a = 11.4550(2), b = 17.2957(2), c = 18.9410(3) Å, β = 94.497(2), V = 3741.08(11) Å^3, Z = 4, $\rho_{\text{calcd.}}$ = 1.358 Mg/m^3, μ(Mo-K_α) = 0.427 mm^{-1}, F(000) = 1620, 32671 reflections collected, 7344 independent reflections, GooF = 1.041, R_1 = 0.0416, wR_2 = 0.1061 (observed data).

2b: $C_{28}H_{20}O_5SrTi{\cdot}7.5(CH_3OH)$, M_r = 812.28, monoclinic, space group $P2_1/n$, a = 11.5578(2), b = 17.3628(2), c = 19.0148(3) Å, β = 94.253(2), V = 3805.30(10) Å^3, Z = 4, $\rho_{\text{calcd.}}$ = 1.418 Mg/m^3, μ(Mo-K_α) = 1.672 mm^{-1}, F(000) = 1692, 14265 reflections collected, 7476 independent reflections, GooF = 1.053, R_1 = 0.038, wR_2 = 0.0998 (observed data).

3a: $C_{44}H_{52}BaO_5Ti{\cdot}12(CH_3OH){\cdot}H_2O$, M_r = 1248.7, orthorhombic, space group $Pbca$, a = 21.3817(2), b = 22.4084(2), c = 27.7100(3) Å, V = 13277(1) Å^3, Z = 8, $\rho_{\text{calcd.}}$ = 1.25 Mg/m^3, μ(Mo-K_α) = 0.766 mm^{-1}, F(000) = 5280.0, 121528 reflections collected, 15053 independent reflections, GooF = 1.37, R_1 = 0.077, wR_2 = 0.109 (observed data).

4a: $C_{49}H_{59}KO_6Ti{\cdot}8(CH_3OH)$, M = 1087.3, monoclinic, space group $C2/c$, a = 14.2018(5), b = 21.9002(9), c = 21.1284(8) Å, β = 106.461(2)°, V = 6302.1(4) Å^3, T = 150(2) K, Z = 4, μ(Mo-K_α) = 0.259mm^{-1}, 12718 reflections collected, 4209 independent reflections, GooF = 1.112, R_1 = 0.0503, wR_2 = 0.1324 (observed data).

4b: $C_{49}H_{59}KO_6Ti{\cdot}3(THF)$, M = 1047.27, monoclinic, space group $P2_1/n$, a = 13.8800(2), b = 20.3074(3) c = 21.3492(3) Å, β = 96.309(2)°, V = 5981.18(15) Å^3, T = 150(2) K, Z = 4, μ(Mo-K_α) = 0.265mm^{-1}, 66468 reflections collected, 11731 independent reflections, GooF = 1.058, R_1 = 0.0562, wR_2 = 0.1455 (observed data).

CCDC-208110−208114 (for **2b**, **1b**, **4a**, **4b** and **3a** respectively) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[15] Crystals suitable for X-ray structural analysis were obtained from this sample.

[16] Dry methanol was used in this synthesis.

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