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FULL PAPER

A novel titanium–oxygen ladder structure supported by calix[4]arene ligands, characterised by synchrotron crystallography

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Reaction of an excess of $TiCl_4$ with *p-tert*-butylcalix[4]arene (H_4L^1) in toluene led to [{$Ti_2(\mu_3$-O)Cl_2L^1}$_2$] **1**, presumably *via* a fortuitous oxidation reaction. The crystal structure of the toluene disolvate, determined using synchrotron radiation single-crystal diffraction facilities, revealed a four-runged Ti_4O_4 planar ladder core terminated by chloro ligands on the outer titanium atoms. Each of the two calix[4]arene ligands is involved in co-ordination to three of the four titanium atoms, with one oxygen atom in a bridging mode between two metal atoms. This co-ordination enforces an unusual conformation on the ligand, with two opposite aromatic rings almost parallel and the other two splayed widely apart.

Recent years have witnessed increased interest in the co-ordination chemistry and potential applications of transition metal complexes containing calixarene ligands. In particular, metallocalix[4]arenes have been the focus of attention due to their availability, crystallinity and conformational rigidity; the majority exist as mononuclear complexes retaining a cone-like conformation for the ligand. After the work of Atwood (Ti),[1] Power (Ti, Fe, Co)[2] and Pedersen (Ti, V, calix[8]arene)[3] and their co-workers, calix[4]arenes have been applied by Floriani and co-workers[4] as quasi-oxo supports for Zr, Ta and W. Reviews dealing with aspects of the chemistry of metallocalixarenes have also recently been published.[5,6]

As a continuation of our work in the field of early transition metal calixarene chemistry,[7–9] we have studied the reaction of $TiCl_4$ with *p-tert*-butylcalix[4]arene (H_4L^1). On the basis of analytical and spectroscopic data, the nature of the product was unclear. Small orange-red platelets grown from toluene–pentane (1 : 1) proved to be unsuitable for conventional X-ray diffraction techniques. As a consequence, data collection was carried out on a recently commissioned single-crystal diffraction facility at the Synchrotron Radiation Source (SRS) at CLRC Daresbury Laboratory, which has been specially developed for dealing with such cases, where normal X-ray diffraction intensities are weak.

Results and discussion

Reaction of an excess of $TiCl_4$ (4 equivalents) with *p-tert*-butylcalix[4]arene in refluxing toluene afforded, after work-up, small but diffraction quality orange-red single crystals. The asymmetric unit of the crystal structure comprises half a molecule of the complex **1** and one molecule of toluene. The molecule of **1** is an exactly centrosymmetric dimer containing four Ti^{IV} and two triply bridging O atoms which form a central planar (root-mean-square deviation 0.018 Å) ladder motif (Figs. 1 and 2) reminiscent of that found in the *p-tert*-butylcalix[6]arene complex [$Ti_2(\mu_3$-O)L^2] (H_6L^2 = *p-tert*-butylcalix[6]arene).[10] As in the latter complex, the Ti^{IV} centres in **1** exhibit distorted trigonal bipyramidal geometry.

Each of the two calixarene ligands binds to three different Ti atoms. Two oxygen atoms [O(2) and O(4)] are terminally bonded to the same Ti(2) atom; O(3) acts as a bridge between Ti(1) and Ti(2), while the fourth oxygen atom O(5) is terminally bonded to Ti(1A) at the other end of the ladder. This mode of co-ordination imposes an unusual extreme conformation on the calixarene ligand. Two opposite aromatic rings [those bonded

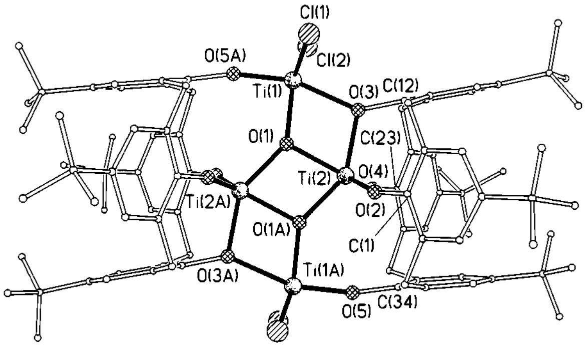

Fig. 1 Molecular structure of complex **1** with partial atom numbering scheme (including some symmetry-equivalent atoms), showing the planar Ti–O ladder and approximate parallel arrangement of two aromatic rings of the calixarene ligand.

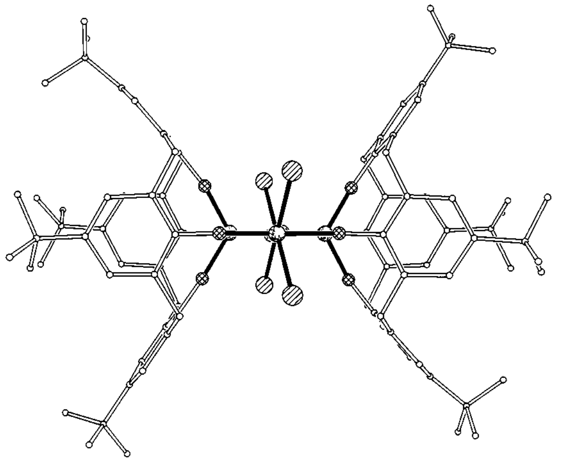

Fig. 2 An alternative view of the structure of complex **1** end-on to the ladder, showing two of the calixarene aromatic rings widely splayed.

Table 1 Selected bond lengths (Å) and angles (°) for complex **1**

Ti(1)–Cl(1)	2.2342(10)	Ti(1)–Cl(2)	2.2334(12)
Ti(1)–O(1)	1.884(2)	Ti(1)–O(3)	2.124(2)
Ti(1)–O(5A)	1.769(2)	Ti(2)–O(1)	1.987(2)
Ti(2)–O(2)	1.777(2)	Ti(2)–O(3)	1.975(2)
Ti(2)–O(4)	1.778(2)	Ti(2)–O(1A)	1.951(2)
O(2)–C(1)	1.378(4)	O(3)–C(12)	1.387(4)
O(4)–C(23)	1.371(4)	O(5)–C(34)	1.362(4)
Cl(1)–Ti(1)–Cl(2)	111.72(4)	O(1)–Ti(1)–O(3)	71.48(9)
O(1)–Ti(2)–O(3)	72.75(9)	O(1)–Ti(2)–O(1A)	73.71(10)
O(2)–Ti(2)–O(4)	116.10(10)	Ti(1)–O(1)–Ti(2)	112.41(11)
Ti(1)–O(1)–Ti(2A)	140.99(12)	Ti(2)–O(1)–Ti(2A)	106.29(10)
C(1)–O(2)–Ti(2)	163.0(2)	Ti(1)–O(3)–Ti(2)	103.33(10)
C(12)–O(3)–Ti(1)	144.44(19)	C(12)–O(3)–Ti(2)	112.16(18)
C(23)–O(4)–Ti(2)	168.2(2)	C(34)–O(5)–Ti(1A)	116.7(2)

Symmetry transformation used to generate equivalent atoms:
A $-x + 2, -y + 1, -z + 1$.

to O(3) and O(5)] are approximately parallel, with a dihedral angle of 5.6° between their mean planes (Fig. 1). The other two opposite rings [bonded to O(2) and O(4)] have a dihedral angle of 103.9° (Fig. 2).

As expected, there are significant variations in the Ti–O bond lengths (see Table 1). The crystal structure of **1** highlights an imprecision in the description of Ti–O bonds as either single or double. The bond lengths Ti(1)–O(5A), Ti(2)–O(2) and Ti(2)–O(4) [1.769(2)–1.778(2) Å] for the non-bridging calixarene oxygen atoms are reasonable for double bonds, but this would result in formal oxidation states for the titanium centres greater than IV. In the literature,[1,2] Ti–O bond lengths of 1.77–1.79 Å have been attributed to both single and double bonds for titanium calixarene complexes. It is clear that intermediate bonding descriptions must apply in **1**. The bond Ti(1)–O(1) [1.884(2) Å] can then be considered single. The bonds Ti(2)–O(1), Ti(2)–O(3) and Ti(2)–O(1A) [1.951(2)–1.987(2) Å] are somewhat longer, reflecting both the bridging (Ti–O–Ti) nature of the oxygen atoms and the 'competition' for bonding at Ti(2). The long Ti(1)–O(3) bond [2.124(2) Å] is formally dative, whilst the Ti···Ti distances [3.1507(11) and 3.2170(8) Å] preclude any significant direct bonding interaction.

The Ti–Cl bonds are short [2.2334(12) and 2.2342(10) Å], but are similar to those observed in the titanium(IV) bis(phenoxy) complexes [$TiCl_2$(mbp)] (2.21 Å)[11] and [$TiCl_2$(mbp)(thf)] (2.26 Å)[12] [mbp = 2,2′-methylenebis(6-*tert*-butyl-4-methylphenolate)].

Experimental

Synthesis of complex 1

The compound $TiCl_4$ (2.0 cm^3, 18.24 mmol) was added to *p*-*tert*-butylcalix[4]arene (3.0 g, 4.62 mmol) in toluene (*ca.* 50 cm^3). After refluxing for 12 h the solution was filtered and allowed to cool to ambient temperature. On standing (1–2 d) small orange-red blocks of complex **1** formed. Yield 1.19 g, 28% (Found: C, 66.1; H, 6.4. $C_{44}H_{52}Cl_2O_5Ti_2\cdot C_6H_5CH_3$ requires C, 66.6; H, 6.6%) IR: 1601m, 1301s, 1277m, 1242s, 1191vs, 1114s, 946s, 933s, 894s, 881s, 863s, 828s, 799s, 767s, 756s, 728s, 695m, 685m, 640s and 582s cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.28–6.44 (multiplets, 16 H, aryl + 2 toluene), 5.06 (d, 4 H, $^3J_{HH}$ 14.0, CH_2), 5.00 (d, 4 H, $^3J_{HH}$ 14.4, CH_2), 3.47 (d, 4 H, $^3J_{HH}$ 14.5, CH_2), 3.41 (d, 4 H, $^3J_{HH}$ 14.2 Hz, CH_2), 2.36 (s, 6 H, CH_3 of toluene), 1.34 (s, 36 H, Bu^t), 1.06 (s, 18 H, Bu^t) and 0.73 (s, 18 H, Bu^t).

X-Ray crystallography

Crystal data. $C_{88}H_{104}Cl_4O_{10}Ti_4\cdot 2C_7H_8$, $M = 1839.4$, triclinic, space group $P\bar{1}$, a = 12.5692(14), b = 13.4268(15), c = 15.4275(17) Å, $\alpha = 89.299(3)$, $\beta = 68.935(3)$, $\gamma = 85.043(3)°$, $U = 2420.0(5)$ Å^3, $Z = 1$, $D_c = 1.262$ g cm^{-3}, $T = 160$ K, $\lambda = 0.6879$ Å, $\mu = 0.484$ mm^{-1}.

Data collection and processing. All measurements were made on a Bruker AXS SMART CCD area-detector diffractometer at Station 9.8 of the CLRC Daresbury Laboratory SRS.[13] The crystal, of size 0.20 × 0.12 × 0.02 mm, was mounted on the end of a two-stage glass fibre (a short very fine section in the X-ray beam, glued to a stouter fibre for stability) with a perfluoropolyether oil, and cooled by a Cryostream nitrogen-gas stream.[14] The X-ray wavelength was calibrated by measurement of the unit cell parameters of a standard crystal of known structure. Data collection nominally covered more than a hemisphere of reciprocal space by three series of ω-rotation exposure frames with different crystal orientation φ angles, each frame having an ω range of 0.2° and an exposure time of 1 s; the frame width and exposure time are both smaller than for most experiments with similar equipment and conventional X-ray sources, because of the high degree of collimation and the high incident intensity of synchrotron radiation. Reflection intensities were integrated by standard procedures,[15] allowing for the plane-polarised nature of the primary synchrotron beam. Corrections were applied semiempirically for absorption and incident beam decay;[16] the range of overall correction factors was 0.564–0.978, combining a range of transmission of approximately 0.91–0.99 and an approximate 30% beam decay. Unit cell parameters were refined from the observed ω angles of all strong reflections in the complete data set (8219 observations).[17] With a single detector position, 11915 intensities were obtained ($\theta_{max} = 27.1°$), giving 9287 unique data ($R_{int} = 0.0424$), with 91% data completeness to $\theta = 25°$.

Structure solution and refinement. The structure was solved by routine automatic direct methods and refined by least-squares refinement on all unique measured F^2 values.[18] Two-fold disorder of orientation was resolved for one *tert*-butyl group, and refined with the aid of restraints. Constrained riding hydrogen atoms were included. Final conventional $R = 0.0595$ [F values of 6241 data with $F^2 > 2\sigma(F^2)$], $wR2 = 0.1498$ (F^2 values of all data), $S = 0.925$ (F^2, all data, 579 parameters). The major features in a final difference map (1.28 e Å^{-3}) were close to Ti atoms.

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See http://www.rsc.org/suppdata/dt/1998/3037/ for crystallographic files in .cif format.

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