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Novel tungsten calix[8]arene complexes†

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***p-tert*-Butylcalix[8]areneH_8 reacts with WCl_6 forming a number of new metallocalix[8]arenes, one of which is reduced to give the first example of a metal-metal triple bond supported by a large calixarene ligand; the degree of metallation and conformations adopted by the newly generated metallocalix[8]arene systems are determined by single crystal X-ray diffraction.**

Whilst the coordination chemistry of calix[4]arenes is enjoying much attention, there is a paucity of information concerning the larger ring systems, *viz* calix[5], [6] and [8].[1,2] This is particularly surprising in view of the ability of such rings to undergo conformational change and is highlighted by the calixarene chemistry of metal–metal bonds which is restricted to only a handful of reported calix[4]arene derivatives.[3] In this context, we report the first example of such a system based on a tungsten–tungsten triple bond supported by a *p-tert*-butylcalix[8]arene ligand. Furthermore, transition metal calix[4]arene chemistry is dominated by monometallic and bridged dimeric species, whilst the handful of structurally characterised calix[8]arene-derived complexes, including those of the lanthanides, are bimetallic. We, on the other hand, have embarked upon a programme of study aimed at accessing polymetallic calix[*n*]arene species.[4] Here, we describe our preliminary finding on the reaction of WCl_6 with *p-tert*-butylcalix[8]arene, which results in a series of novel tungsten calix[8]arene complexes bearing either two, three or four tungsten centres. The highest degree of metallation reported to-date is five for an aluminium *p-tert*-butylcalix[6]arene complex.[5]

Treatment of WCl_6 (1.98 equiv.) with the ligand *p-tert*-butylcalix[8]areneH_8 (H_8L) in toluene readily gives multigram quantities of $[(WCl_2)_2L]$ (**1**). Attempts to obtain meaningful NMR data were unsuccessful; the spectra are complex with a large number of doublets/multiplets appearing in the regions δ 6.37–4.38 and 3.68–2.69 for the *endo* and *exo* CH_2 groups (overall integration 8 : 8), respectively. This is thought to be due to the presence of mixtures of both *cis-* and *trans*-WCl_2 isomers;[3b] the sensitivity of the system is also problematic.‡ The former was confirmed when, following successive extractions of this crude product from acetonitrile, the *cis, trans*-isomer (**1**) was selectively crystallised and characterised by X-ray crystallography.§ Interestingly, in the related reaction of WCl_6 (0.99 equiv.) with *p-tert*-butylcalix[4]areneH_4, the kinetic product is the *cis*-isomer {*cis*-Cl_2W(*p-tert*-butylcalix[4]arene)} with a ^1H NMR spectrum indicative of a C_{2v}-symmetric species, which is converted into the *trans*-isomer (a C_{4v} species by NMR) upon reaction with Lewis acidic metal chlorides (typically $AlCl_3$ or WCl_6).[3a,b]

Reduction of **1** with sodium amalgam in toluene affords, after work-up, the orange–brown complex $\{[W_2(L)]Na_2(MeCN)_5\}\cdot 5MeCN$ (**2**) (yield *ca.* 60%). Crystals suitable for an X-ray determination were grown from acetonitrile at −20 °C; they incorporate five sodium-bound and five uncoordinated molecules of acetonitrile per molecule of the complex. A view of the molecule is shown in Fig. 1 and reveals the novel conformation adopted by the macrocycle; two back-to-back cups are formed each comprising three of the phenoxide subunits [O(2), O(3) and O(4) on W(1); O(6), O(7) and O(8) on W(2)]. The phenoxide subunits containing O(1) and O(5) form the links between the cups. The four phenoxide oxygens bound to each tungsten are somewhat staggered; the torsion angle O(4)W(1)W(2)O(6) = 39.4°. The overall result is a cleft between O(7), O(2) and O(3), with the geometry at each five-coordinate tungsten best described as square-based pyramidal with the metal–metal triple bond at the apex. The bridging atom Na(1) [to O(2) and O(8)] is coordinated by three MeCN ligands, whilst Na(2) [bridges O(4) and O(6)] coordinates two MeCN ligands—a situation reminiscent of that observed for the sodium/pyridine moieties of $[W_2(\text{calix[4]arene})_2\{\mu\text{-Na(pyridine)}_2\{\mu\text{-Na(pyridine)}_3\}]$.[3f] For the latter, the tungsten–tungsten distance is 2.313(1) Å, which compares favourably with that found for **2** [2.2976(6) Å] and is well within the range previously observed for tungsten–tungsten triple bonds [2.255(2)–2.3678(6) Å].[4]

In extending our studies on the *p-tert*-butylcalix[8]arene/WCl_6 system, H_8L was treated with an excess of WCl_6 (3 equiv.) generating on work-up, $[(WCl_3)_2WCl_4)L]$ (**3**) in *ca.* 55% yield as well as $[(WCl_4)_4L]$ (**4**) in *ca.* 15% isolated yield. Crystals of **3** were weakly diffracting requiring the use of synchrotron radiation,[6] but showed no disorder. A view of **3** is shown in Fig. 2 and reveals the way in which the macrocyclic ring twists considerably to accommodate the three tungsten centres, two of which [*i.e.* W(2) and W(3)] are facially bound to the calix[8]arene and possess three chloride ligands. The remaining tungsten centre has a *cis*-O_2Cl_4 geometry. There are local '3 phenolate' cups at each of the WCl_3 moieties [*i.e.* W(1) and W(2)]. For the former, a *tert*-butyl group resides over the cavity. Overall the W–O bond distances [1.799(12)–1.875(12) Å] are shorter than those observed in related calix[4]arene complexes of tungsten(VI),[3a,b] which is an indication of the

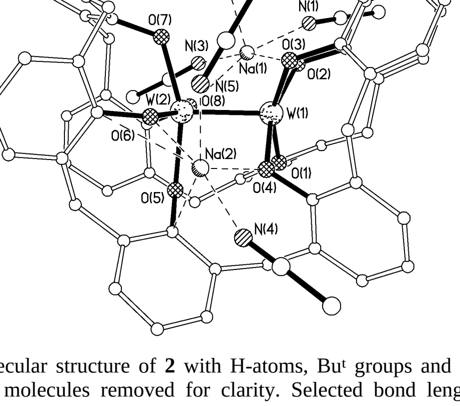

Fig. 1 Molecular structure of **2** with H-atoms, Bu^t groups and unbound acetonitrile molecules removed for clarity. Selected bond lengths (Å): W(1)–O(1) 1.986(7), W(1)–O(2) 2.008(6), W(1)–O(3) 1.965(6), W(1)–O(4) 1.995(7), W(1)–W(2) 2.2976(6), W(2)–O(5) 2.012(7), W(2)–O(6) 2.002(7), W(2)–O(7) 1.977(7), W(2)–O(8) 1.996(6).

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† Electronic supplementary information (ESI) available: selected spectroscopic data. See http://www.rsc.org/suppdata/cc/b2/b201777f/

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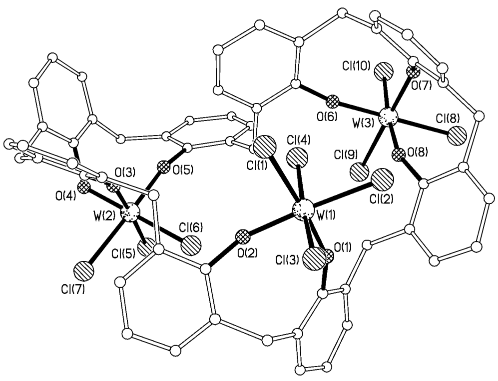

Fig. 2 Molecular structure of **3** with H-atoms, Bu^t groups and solvent molecules removed for clarity. Selected bond lengths (Å): W(1)–O range 1.824–1.856(11), W(1)–Cl range 2.286–2.352(5), W(2)–O range 1.830–1.858(12), W(2)–Cl range 2.321–2.332(5), W(3)–O range 1.799–1.875(12), W(3)–Cl range 2.321–2.370(5).

increased double bond character. The latter is also reflected in the majority of the W–O–C angles, only two of which are less than 150°. Indeed, two at W(3) are near linear. The W–Cl distances [2.286(5)–2.370(5) Å] are consistent with minimal W–Cl π-bonding [*cf.* WCl_6, W–Cl(av) 2.24 Å].

As for **3**, crystallographic data for **4** was obtained using synchrotron radiation.[6] The asymmetric unit comprises $\{[WCl_4]_2\text{calix[8]arene}\}_{1/2}$ with 2.5 molecules of 1,2-dichloroethane and a water molecule. The disorder in one of the WCl_4 groups and overall quality of the data precludes detailed geometric discussions, however, the general identity and connectivity is clear (Fig. 3). Each of the four WCl_4O_2 units is bound to the calix[8]arene framework *via cis*-oxygens.

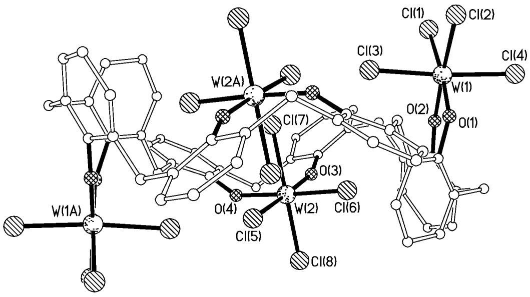

Fig. 3 Molecular structure of **4** with H-atoms, Bu^t groups and acetonitrile molecules removed for clarity.

We have demonstrated that the *p-tert*-calix[8]arene/WCl_6 system is complex and that subtle changes in reaction stoichiometry can lead to quite different products. Indeed, the calix[8]arene ligand is flexible enough to accommodate either two, three or four tungsten centres. Such systems should allow entry into multi-metallic chemistry supported by a diverse array of calix[8]arene conformations. Here, for example, we have shown that the calix[8]arene ligand is capable of supporting a tungsten–tungsten [W≡W] triple bond by encapsulation within a new 'channel' or cleft. Work is in progress to generate more highly functionalised tungstocalix[8]arenes and related metal complexes.

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Notes and references

‡ We have isolated and structurally characterised mixed tungsten oxo/tungsten chloro calix[8]arene species of the form $\{[WO][WCl_2](p\text{-}tert\text{-butylcalix[8]arene})\}$.

§ *Crystal data*: for **1**·3M$\underline{e}$CN: $C_{88}H_{104}Cl_4O_8W_2\cdot 3CH_3CN$, $M = 1922.37$, triclinic, space group $P1$, $a = 12.6346(8)$, $b = 17.6171(11)$, $c = 21.8873(14)$ Å, $\alpha = 85.711(2)$, $\beta = 83.857(2)$, $\gamma = 87.482(2)°$, $V = 4827.1(5)$ Å^3, $T = 150$ K, $Z = 2$, μ(Mo-Kα, $\lambda = 0.71073$ Å) = 2.543 mm^{-1}, 45995 data measured, 16910 unique, $R_{int} = 0.0450$, all data used in refinement against F^2 values to give $wR = 0.2675$, $R = 0.0997$ {for 13580 data with $F^2 > 4\sigma(F^2)$}.[7] Two-fold disorder modelled with restraints in five ^{t}Bu groups.

For **2**: $C_{88}H_{104}Na_2O_8W_2\cdot 10CH_3CN$, $M = 2113.93$, triclinic, $P\bar{1}$, $a = 13.8499(9)$, $b = 14.8714(10)$, $c = 28.9308(19)$ Å, $\alpha = 78.519(2)$, $\beta = 77.455(2)$, $\gamma = 65.342(2)°$, $V = 5246.5(6)$ Å^3, $T = 173$ K, $Z = 2$, μ(Mo-Kα, $\lambda = 0.71073$ Å) = 2.257 mm^{-1}, 39366 data measured, 23757 unique, $R_{int} = 0.1002$, all data used in refinement against F^2, $wR = 0.1788$, $R = 0.0835$ {11723 data with $F^2 > 4\sigma(F^2)$}.[7] Two-fold disorder modelled with restraints in two ^{t}Bu groups.

For **3**·4MeCN: $C_{88}H_{104}Cl_{10}O_8W_3\cdot 4CH_3CN$, $M = 2359.98$, monoclinic, $P2_1/c$, $a = 15.880(2)$, $b = 32.197(5)$, $c = 20.141(3)$ Å, $\beta = 99.955(3)°$, $V = 10143(3)$ Å^3, $T = 160$ K, $Z = 4$, μ(silicon 111 monochromated synchrotron radiation, $\lambda = 0.6928$ Å) = 3.711 mm^{-1}, 56311 data measured, 14555 unique, $R_{int} = 0.1414$, all data used in refinement against F^2, $wR = 0.2416$, $R = 0.0957$ {9795 data with $F^2 > 4\sigma(F^2)$}.[6,7]

For **4**·$4C_2H_4Cl_2\cdot 2H_2O$: $C_{88}H_{104}Cl_{16}O_8W_4\cdot 4C_2H_4Cl_2\cdot 2H_2O$, $M = 3024.15$, monoclinic, $P2_1/n$, $a = 13.9255(8)$, $b = 24.9463(14)$, $c = 18.0215(10)$ Å, $\beta = 107.937(2)°$, $V = 5956.2(6)$ Å^3, $T = 160$ K, $Z = 2$, μ(silicon 111 monochromated synchrotron radiation, $\lambda = 0.6884$ Å) = 4.438 mm^{-1}, 36959 data measured, 8539 unique, $R_{int} = 0.0943$, all data used in refinement against F^2, $wR = 0.3744$, $R = 0.1256$ {6438 data with $F^2 > 4\sigma(F^2)$}.[6,7] Two-fold disorder modelled with restraints in one WCl_4 and three ^{t}Bu groups.

In each of the above compounds, the largest residual peaks are close to the tungsten atoms.

CCDC reference numbers 181731–181734. See http://www.rsc.org/suppdata/cc/b2/b201777f/ for crystallographic data in CIF or other electronic format.

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