Tungsten(VI) Complexes Derived from Calix[6]- and -[8]arenes: Oxo and Oxychloride Species

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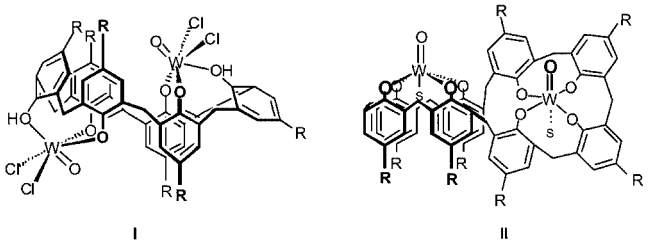
Treatment of *p-tert*-butylcalix[6]areneH_6 (H_6L) or *p-tert*-butylcalix[8]areneH_8 (H_8L^1) with 2 equiv. of [$WOCl_4$] in refluxing toluene affords, after workup, the complexes [$(WOCl_2)_2LH_2$] (**1**) and [{$WO(NCMe)$}$_2L^1$] (**2**), respectively. The molecular structures of **1** and **2** have been determined and reveal conformationally constrained macrocyclic rings.

Introduction

The coordination chemistry of the calix[*n*]arene ring systems has attracted considerable attention during the last decade.[1] Attention has focused primarily on calix[4]arene transition metal species, however despite this activity, only a limited number of oxometal species have been reported.[2] Such oxo species have attracted attention due, in part, to their tendency to self-assemble into columnar structures.[3] In certain cases, this has resulted in liquid crystalline properties. For the group-VI metals, the contributions of the groups of Floriani and Young are particularly relevant. Crystallographic studies of species derived from the oxychloride precursors [$MOCl_4$] (M = Mo, W) reveal monomeric complexes with octahedrally coordinated metal centres.[2c,2g] By contrast, oxometal species for the larger ring systems ($n > 4$) are extremely rare and no structural data have been reported.[4] As part of an ongoing programme[5] investigating the coordination environments afforded by the medium-sized calix[*n*]arene rings (n = 6, 8), we here describe the synthesis and molecular structures of novel tungsten(VI) complexes (see **I** and **II** in Scheme 1) bearing either oxo or both oxo and chloro ligands via the interaction of the parent calix[6 and 8]arene$H_{6,8}$ with the metal oxytetrachloride complex [$WOCl_4$]. The molecular structures of the two new calixarene tungsten species have been determined and reveal conformationally constrained macrocyclic rings.



Scheme 1. R = *t*Bu; S = solvent (CH_3CN)

Results and Discussion

Reaction of H_6L with 2 equiv. of [$WOCl_4$] in refluxing toluene affords, after workup, large red-purple prisms of the complex [$(WOCl_2)_2LH_2$] (**1**) in ca. 60% yield. Stoichiometrically, **1** is formed by loss of 2 equiv. of HCl per tungsten centre. In the IR spectrum of this compound, a band is observed for ν(W=O) at 941 cm^{-1} {cf. 999 and 1006 cm^{-1} reported for the 1,3-dialkoxy-*p-tert*-butylcalix[4]-areneH_2 (R_2calH_2) complexes [$Et_2calWOCl_2$] and [$Me_2calWOCl_2$], respectively},[2g] whilst a broad feature at 3181 cm^{-1} is assigned to ν(OH). The ^1H NMR spectrum is consistent with the solid-state structure: two singlets in the *tert*-butyl region in a 2:1 ratio. The methylene protons appear as two doublets and a singlet (each integrating to 4 H), for which the latter is assigned to the CH_2 groups on the "fold" of the pinch (see Figure1, b). A broad singlet (integrating to 2 H) appears at δ_{OH} = 9.28 ppm.

Crystals of **1**·8MeCN suitable for an X-ray determination were grown from a hot, saturated solution of acetonitrile on slow cooling to ambient temperature. The asymmetric unit comprises one molecule of **1** and eight molecules of acetonitrile, one of which is disordered, with two others H-bonded to the calix[6]arene oxygen atoms O(2) and O(5). The molecular structure is shown in Figure 1 (a and b) to-

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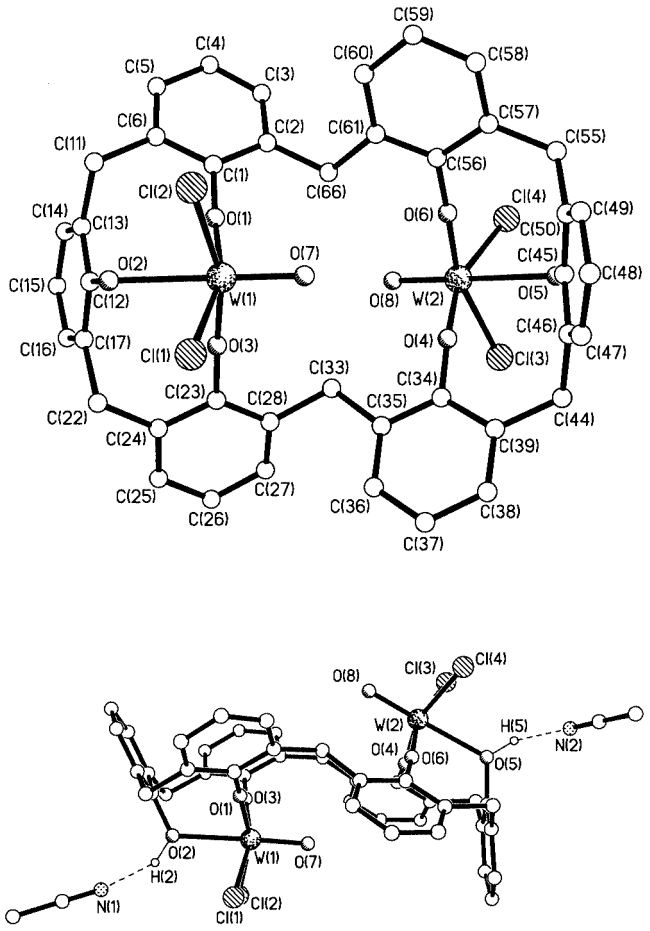

Figure 1. (a, top) Molecular structure of **1**; H atoms and calixarene *t*Bu groups omitted for clarity; (b, bottom) view of **1** emphasising pinched conformation; C*H* atoms and calixarene *t*Bu groups omitted for clarity; selected bond lengths [Å] and angles [°]: W(1)−Cl(1) 2.344(4), W(1)−Cl(2) 2.369(4), W(1)−O(1) 1.847(8), W(1)−O(2) 2.332(8), W(1)−O(3) 1.842(8), W(1)−O(7) 1.706(9), W(2)−Cl(3) 2.380(3), W(2)−Cl(4) 2.345(3), W(2)−O(4) 1.858(7), W(2)−O(5) 2.335(7), W(2)−O(6) 1.845(8), W(2)−O(8) 1.688(8); Cl(1)−W(1)−Cl(2) 85.95(18), O(7)−W(1) − Cl(1) 97.3(3), O(7)−W(1) − Cl(2) 96.6(3), O(1)−W(1)−O(7) 100.8(4), O(93) − W(1)−O(7) 100.0(4), W(1)−O(1)−C(1) 164.3(8), W(1)−O(2)−C(12) 119.0(6), W(1)−O(3)−C(23) 170.5(7)

gether with selected bond lengths and angles. The calix[6]arene ligand remains doubly protonated and adopts a pinched conformation to accommodate the two facially coordinated tungsten centres, one lying above and one below the plane of the macrocyclic ring (as emphasised in Figure 1, b). The geometry about each tungsten centre is best described as pseudo-octahedral with the oxo ligand lying *trans* to the elongated W−OH bond [W(1)−O(2) 2.332(8), cf. W(1)−O(1) 1.847(8); W(1)−O(3) 1.842(8) Å]. Interestingly, the OH binding site in **1** is equivalent to that occupied by the OR groups for the complexes [R_2calMOCl_2] (M = Mo, R = Et; M = W, R = Me) reported by Young et al.[2g] Furthermore, in these 1,3-dialkoxy-*p*-*tert*-butylcalix[4]arene systems, the W=O grouping leads to the adoption of an unusual nonconical conformation. Similarly, in **1** the W=O groups push other groups away (VSEPR) and this is thought to lead to the adoption of the pinched conformation. The W−O−C angles are also indicative of deprotonation at O(1) and O(3), viz. W(1)−O(1)−C(1) 164.3(8)°, W(1)−O(3)−C(23) 170.5(7)°, cf. W(1)−O(2)−C(12) 119.0(6)°. The W=O bond lengths (av. 1.70 Å) are typical of those observed in other oxotungsten(VI) complexes[6] and is in good agreement with that observed for the calix[4]areneH$_4$ (calH$_4$) complex [calWO(CH$_3$CO$_2$H)] [1.698(4) Å];[2c] that observed for [R_2calWOCl_2] is slightly longer [1.673(3) Å].[2g]

We then targeted the calix[8]arene (H_8L^1) species {[WO(NCMe)]$_2L^1$} (**2**), using a procedure similar to that for **1**. As expected, four molecules of HCl are lost per tungsten centre. The NMR signals/integrals are consistent with the expected target complex: eight distinct doublets for the *endo*- and *exo*-methylene groups together with four signals (each of 18 H) for the *tert*-butyl groups. In the IR spectrum of **2**, a strong band at 969 cm^{-1} is assigned to the ν(W=O) stretch. Crystals suitable for an X-ray determination were grown from an acetonitrile solution at room temperature; they incorporate two noncoordinated molecules of acetonitrile per molecule of the complex. The molecular structure is shown in Figure 2 together with selected bond lengths and angles. The calix[8]arene twists to accommodate the two [W=O] fragments in a manner similar to that observed previously for the organoimido complex {[Mo(NAr)(NCMe)]$_2L^1$} (Ar = C$_6$H$_3$*i*Pr$_2$-2,6).[5a] In **2**·2MeCN, each tungsten centre adopts a pseudo-octahedral geometry with the tungsten atoms an average of 0.30 Å out of the plane of the calixarene oxygen atoms. The W=O bond lengths (ca. 1.70 Å) are similar to those observed in **1** and elsewhere.[6] A molecule of acetonitrile binds to each tungsten centre *trans* to the oxo function and each is surrounded by three calixarene phenoxide sub-units.

The analogous reactions using [MoOCl_4] appear to be more sensitive to reduction, and deep blue solutions are readily formed. However, we note with interest that in the

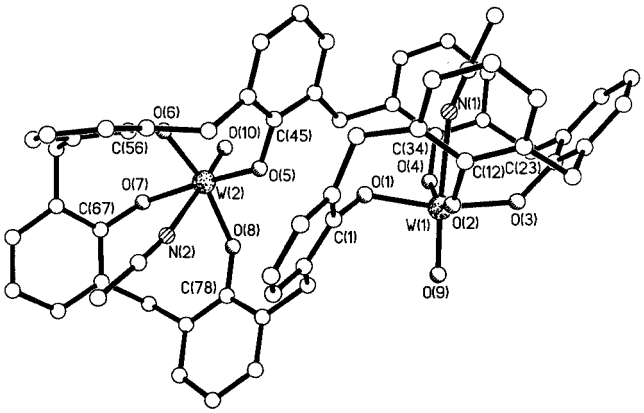

Figure 2. Molecular structure of **2**; H atoms and calixarene *t*Bu groups omitted for clarity; selected bond lengths [Å] and angles [°]: W(1)−O(1) 1.922(3), W(1)−O(2) 1.921(3), W(1)−O(3) 1.927(3), W(1)−O(4) 1.891(2), W(1)−O(9) 1.703(3), W(1)−N(1) 2.402(3), W(2)−O(5) 1.913(3), W(2)−O(6) 1.912(3), W(2)−O(7) 1.935(3), W(2)−O(8) 1.903(3), W(2)−O(10) 1.699(3), W(2)−N(2) 2.413(3); O(9)−W(1)−N(1) 176.15(12), O(9)−W(1)−O(1) 99.29(12), O(9)−W(1)−O(2) 99.74(12), O(9)−W(1)−O(3) 95.23(12), O(9)−W(1)−O(4) 103.24(12)

case of *p-tert*-butylcalix[4]areneH$_4$ (*t*BucalH$_4$), reaction with [MoOCl$_4$] affords a blue, diamagnetic complex of stoichiometry [(*t*BucalH$_4$)(*t*Bucal)MoO·2CH$_2$Cl$_2$].[2a]

In conclusion, we have demonstrated that the oxychloride complex [WOCl$_4$] readily reacts with medium-sized calix[*n*]arene ring systems (n = 6 or 8) to afford highly crystalline products. In each case, the calixarene ligands are flexible enough to accommodate two tungsten centres possessing oxo or chloro ligands or combinations thereof.

Experimental Section

General: All manipulations were carried out under nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove-box. Solvents were refluxed in the presence of an appropriate drying agent, and distilled and degassed prior to use. Elemental analyses were performed by the microanalytical services of the School of Chemical Sciences and Pharmacy at the University of East Anglia. NMR spectra were recorded with a Varian VXR 400 S spectrometer at 400 or a Gemini at 300 MHz (^{1}H) at 298 K; chemical shifts are referenced to the residual protio impurity of the deuterated solvent. IR spectra (nujol mulls, KBr windows), Perkin−Elmer 577 and 457 grating spectrophotometers. [WOCl$_4$] was prepared by the method of Gibson;[7] the ligands *p-tert*-butylcalix[6]arene H$_6$ (H$_6$L) and *p-tert*-butylcalix[8]arene (H$_8$L′) were prepared from *p-tert*-butylphenol and formaldehyde.[8] All other chemicals were obtained commercially and used as received, unless stated otherwise.

[(WOCl$_2$)$_2$L] (1): [WOCl$_4$] (1.0 g, 2.94 mmol) and H$_6$L (1.4 g, 1.44 mmol) were refluxed in toluene (40 mL) for 12 h. After cooling to room temperature, the volatiles were removed under reduced pressure and the residue extracted with MeCN (30 mL). Prolonged standing at ambient temperature afforded large red/purple prisms of **1**·8MeCN. (1.55 g, 58%). C$_{82}$H$_{104}$Cl$_4$N$_8$O$_8$W$_2$·CH$_3$CN (1880.3): calcd. C 52.6, H 5.4, N 0.9;[9]found C 52.3, H 5.3, N 1.1. IR: $\tilde{\nu}$ = 2359 w, 1608 m, 1302 m, 1268 m, 1205 s, 1122 m, 1096 w, 993 s, 941 m, 898 w, 881 m, 812 w, 806 w, 752 w, 730 w cm^{-1}. ^{1}H NMR (300 MHz, CD$_3$CN): δ = 9.28 (br. s, 2 H, OH), 7.60−7.14 (3 × m, 12 H, aryl H), 4.86 (d, $^2J_{H,H}$ = 13.5 Hz, 4 H, *endo*-CH$_2$), 4.66 (s, 4 H, *endo*/*exo*-CH$_2$), 3.66 (d, $^2J_{H,H}$ = 13.5 Hz, 4 H, *exo*-CH$_2$), 1.40 [s, 36 H, C(CH$_3$)$_3$], 1.29 [s, 18 H, C(CH$_3$)$_3$] ppm.

[{WO(NCMe)}$_2$L^1] (2): [WOCl$_4$] (1.0 g, 2.94 mmol) and H$_8$L^1 (1.86 g, 1.43 mmol) were refluxed in toluene (40 mL) for 12 h. After cooling to room temperature, the volatiles were removed under reduced pressure and the residue extracted with MeCN (30 mL). Prolonged standing at ambient temperature afforded orange prisms (1.13 g, 41%). C$_{92}$H$_{110}$N$_2$O$_{10}$W$_2$·4CH$_3$CN (1935.7): calcd. C 62.0, H 6.3, N 4.3; found C 61.6, H 6.3, N 4.1.[9] IR: $\tilde{\nu}$ = 2393 w, 2359 w, 2307 w, 2280 w, 2256 w, 1600 w, 1586 w, 1293 s, 1259 s, 1242 m, 1200 s, 1182 s, 1113 s, 1027 s, 968 s, 941 w, 916 m, 855 m, 838 s, 821 m, 795 s, 786 m, 760 w, 727 w, 675 w cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.45 (d, $^4J_{H,H}$ = 2.4 Hz, 2 H, aryl H), 7.31 (t, $^4J_{H,H}$ = 2.6 Hz, 4 H, aryl H), 7.18 (d, $^4J_{H,H}$ = 2.3 Hz, 2 H, aryl H), 7.09 (d, $^4J_{H,H}$ = 2.3 Hz, 2 H, aryl H), 6.96 (d, $^4J_{H,H}$ = 2.3 Hz, 2 H, aryl H), 6.87 (d, $^4J_{H,H}$ = 1.8 Hz, 2 H, aryl H), 6.70 (d, $^4J_{H,H}$ = 2.2 Hz, 2 H, aryl H), 5.44 (d, $^2J_{H,H}$ = 16.6 Hz, 2 H, *endo*-CH$_2$), 4.77 (d, $^2J_{H,H}$ = 12.9 Hz, 2 H, *endo*-CH$_2$), 4.61 (d, $^2J_{H,H}$ = 12.5 Hz, 2 H, *endo*-CH$_2$), 4.28 (d, $^2J_{H,H}$ = 16.7 Hz, 2 H, *endo*-CH$_2$), 3.43 (d, $^2J_{H,H}$ = 13.0 Hz, 2 H, *exo*-CH$_2$), 3.24 (d, $^2J_{H,H}$ = 12.6 Hz, 2 H, *exo*-CH$_2$), 2.58 (d, $^2J_{H,H}$ = 15.4 Hz, 2 H, *exo*-CH$_2$), 2.31 (d, $^2J_{H,H}$ = 15.1 Hz, 2 H, *exo*-CH$_2$), 1.95 (br. s, 9 H, 3 MeCN), 1.34 [s, 18 H, C(CH$_3$)$_3$], 1.27 [s, 18 H, C(CH$_3$)$_3$], 1.16 [s, 18 H, C(CH$_3$)$_3$], 1.02 [s, 18 H, C(CH$_3$)$_3$] ppm.

X-ray Crystallography: Measurements for **1**·8MeCN and **2**·2MeCN were carried out with a Bruker AXS SMART 1 K CCD area detector diffractometer equipped with Mo-K_α radiation (λ = 0.71073 Å) at 160 K. Narrow-frame exposures (0.3° in ω) were employed. Cell parameters were refined from all strong reflections in each data set. Intensities were corrected semiempirically for absorption, based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and refined by full-matrix least squares on F^2 values for all unique data. All non-hydrogen atoms were refined anisotropically. H atoms were included in a riding model with U_{iso} set to be 1.2 times (1.5 times for methyl-H) U_{eq} of the carrier atom. Crystal data for **1**·8MeCN: C$_{66}$H$_{80}$Cl$_4$O$_8$W$_2$·8CH$_3$CN, M = 1839.23, monoclinic, space group $P2_1/c$, a = 12.4800(6), b = 24.8091(12), c = 28.1016(14) Å, V = 8696.2(7) Å^3, Z = 4, F(000) = 3728, $D_{calcd.}$ = 1.405 g·cm^{-3}, μ (Mo-K_α) = 2.821 mm^{-1}, 60614 data measured of which 15280 were unique, R_{int} = 0.0358, wR = 0.1866 (on F^2), R = 0.0779 [for 14455 data with $F^2 > 2\sigma(F^2)$]. Largest difference map features within ±4.3 e·Å^{-3}. Two calixarene *t*Bu groups and one CH$_3$CN molecule of crystallisation were disordered over two sets of positions. Crystal Data for **2**·2MeCN: C$_{92}$H$_{110}$N$_2$O$_{10}$W$_2$·2CH$_3$CN, M = 1853.63, triclinic, space group $P\bar{1}$, a = 15.7724(6), b = 16.3034(6), c = 18.2020(6) Å, α = 101.005(2), β = 90.436(2), γ = 93.838(2)°, V = 4583.2(3) Å^3, Z = 2, F(000) = 1896, $D_{calcd.}$ = 1.343 g·cm^{-3}, μ (Mo-K_α) = 2.565 mm^{-1}, 34801 data measured of which 20907 were unique, R_{int} = 0.0273, wR = 0.0906 (on F^2), R = 0.0348 [for 15392 data with $F^2 > 2\sigma(F^2)$]. Largest difference map features within ±1.6 e·Å^{-3}. One calixarene *t*Bu group was disordered over two sets of positions and two CH$_3$CH molecules of crystallisation were refined at half occupancy. Programs used were Bruker AXS SHELXTL[10] for structure solution, refinement, and molecular graphics, Bruker AXS SMART (control) and SAINT (integration), and local programs.[11] CCDC-203411 and -203412 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/cont/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].

Acknowledgments

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