Calix[4]arene as a Polyoxo Matrix for Functionalizable and Reducible Niobium(v) and Tantalum(v) Chlorides and Oxochlorides

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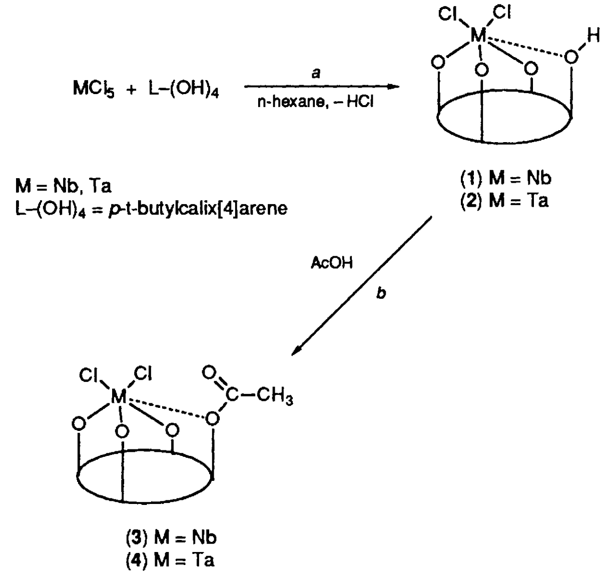
Reaction of MCl_5 (M = Nb or Ta) with *p*-butylcalix[4]arene, L-(OH)$_4$, led, depending on the reaction conditions, either to mononuclear complexes [(AcO)–L–(O)$_3$MCl$_2$], or, in the case of niobium only, to the tetranuclear complex [{μ-L-(O)$_4$}$_2$Nb$_4$O$_2$Cl$_8$], characterized by *X*-ray analysis.

Appropriate metal derivatization of calix[*n*]arenes[1] should provide reducible and functionalizable metal aggregates bonded to an oxo-matrix. However, such compounds so far have been only a curiosity in transition metal chemistry,[2] despite the fact that they may provide remarkable novel examples in polynuclear chemistry of alkoxo-type ligands, which are currently of great interest in mononuclear organometallic chemistry for early transition metals.[3] This report deals with the reaction of MCl_5 (M = Nb or Ta) with *p*-t-butylcalix[4]arene.

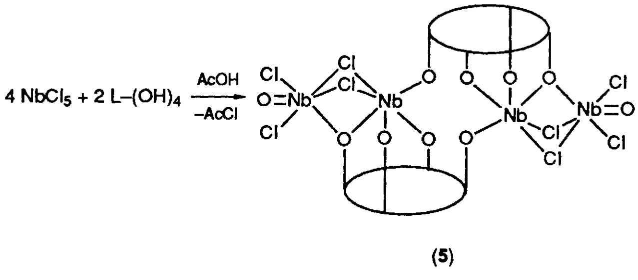
Complexes (**1**)† and (**3**),† which are crystalline solids, have been isolated and characterized (Scheme 1), while in case of tantalum the reaction was carried out in a single step leading to (**4**),† a yellow crystalline solid, without attempts being made to isolate (**2**). There are significant differences, however, between niobium and tantalum. $NbCl_5$ has to be used in a 2 : 1 metal : ligand molar ratio, while $TaCl_5$ gave the same result independently of the stoicheiometric ratio. The reaction has to be carried out in two separate steps in case of niobium; when it was carried out in a single step, in n-hexane containing AcOH or a small amount of H_2O, (**5**)† was the product (Scheme 2).

AcOH or H_2O control the introduction of a second metal centre in the form of an oxochloride fragment.[4] The results reported above suggest the intermediacy of (**1**) in the formation of (**5**).

The structure of (**5**) is shown in Figure 1,‡ with some bond distances and angles. The overall molecule is centrosymmetric. In the two dinuclear units the hexa-co-ordination environment of each niobium is significantly different. The Nb(1) · · · Nb(2) separation is rather long [3.346(2) Å]. The relatively long Nb(2)–Cl(1) distance seems to be affected by the oxo group [Nb(2)–O(5), 1.673(7) Å] *trans* to it. This distance is rather close to that in the few niobyl complexes so far structurally characterized.[5] The topology of the complex structure can be described through those parameters identifying the *p*-t-butylcalix[4]arene fragment which is present in the cone conformation.[6] The four oxygens deviate significantly [from −0.275(4) to 0.257(4) Å] from the mean plane, as do the bridging methylenes [from −0.111(6) to 0.119(7) Å] from their average plane. These two planes are nearly parallel [0.8(1)°]. Dihedral angles between opposite benzene ring planes range from 177.7(1)° to 72.4(1)°. Such parameters



Scheme 1



Scheme 2

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† Satisfactory analytical, IR, and ^{1}H NMR data have been obtained for (**1**), (**3**), (**4**), and (**5**). Complexes (**3**) and (**5**) crystallize with one and two molecules of benzene respectively. An *X*-ray analysis on (**4**) is in progress. Selected spectroscopic data for (**4**): ^{1}H NMR (200 MHz, CD_2Cl_2): δ 7.26 (q, 4H), 6.91 (s, 2H), 6.28 (s, 2H), 4.62 (d, 2H), 3.82 (d, 2H), 3.56 (d, 2H), 3.38 (d, 2H), 2.77 (s, 3H), 1.38 (s, 18H), 1.11 (s, 9H), and 0.55 (s, 9H); IR (Nujol): ν(C=O ester), 1672 cm^{-1}; for (**5**): ^{1}H NMR (200 MHz, CD_2Cl_2): δ 7.28 (s, 4H), 6.97 (s, 2H), 6.32 (s, 2H), 4.95 (d, 4H), 3.76 (d, 2H), 3.46 (d, 2H), 1.36 (s, 18H), 1.13 (s, 9H), and 0.65 (s, 9H); J_{HH} (CH2, Hz), 14.48; IR (Nujol): ν(Nb=O), 970 cm^{-1}.

‡ *Crystal data* for (**5**): $C_{100}H_{116}Cl_8Nb_4O_{10}$, M_r = 2133.3, triclinic, space group $P\bar{1}$, a = 15.193(1), b = 14.722(1), c = 13.633(1) Å, α = 113.47(1), β = 113.22(1), γ = 85.35(1)°, U = 2560.0(4) Å^3, Z = 1, D_c = 1.384 g cm^{-3}, Mo-K_α radiation (λ = 0.71069 Å), μ(Mo-K_α) = 6.80 cm^{-1}; crystal dimensions 0.38 × 0.4 × 0.54 mm^3. The structure was solved by the heavy-atom method (Patterson and Fourier synthesis) and anisotropically refined (except for the benzene solvent molecules) by full-matrix least-squares. For 5688 unique observed structure amplitudes [$I > 2\sigma(I)$] collected at room temperature on a Siemens AED diffractometer in the range $6 < 2\theta < 48°$, the R value is 0.046 (unit weights). The hydrogen atoms, either located or put in calculated positions, were introduced as fixed contributors in the final stage of refinement. All calculations were carried out using SHELX86 and SHELX76. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

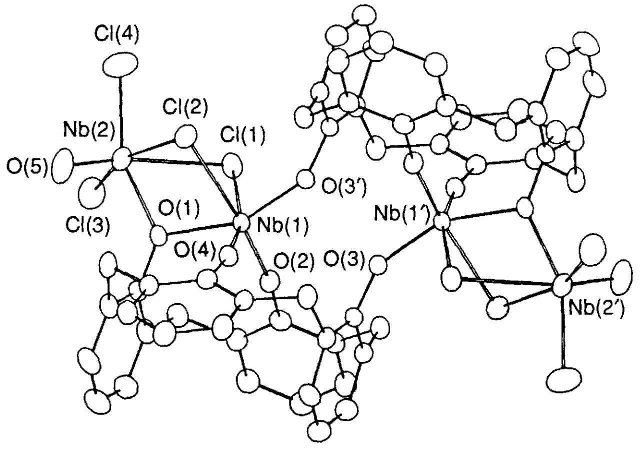

Figure 1. An ORTEP drawing of complex (**5**). Bond distances (Å): Nb(1)–Cl(1), 2.520(2); Nb(1)–Cl(2), 2.574(2); Nb(1)–O(1), 2.083(4); Nb(1)–O(2), 1.842(4); Nb(1)–O(3'), 1.866(3); Nb(1)–O(4), 1.859(5); Nb(2)–Cl(1), 2.793(2); Nb(2)–Cl(2), 2.548(2); Nb(2)–Cl(3), 2.302(3); Nb(2)–Cl(4), 2.296(2); Nb(2)–O(1), 2.111(4); Nb(2)–O(5), 1.673(7).

indicate a significant distortion of the *p*-t-butylcalix[4]arene unit from that in its free state.

Complex (**5**) has some of the peculiar properties for which the use of calix[*n*]arenes in transition metal chemistry is particularly attractive, *e.g.* the presence of a functionalizable and reducible dimetallic unit. Complexes (**1**)—(**4**) which have an additional functionalizable site can be used for introducing a different metal site or for a different donor atom.[7]

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