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Niobium and Tantalum Oxo Compounds: Synthesis and Crystal Structure of the Tetranuclear Tantalum(v) Oxo Cluster [{$TaOCl_2(O_2CC_6H_4Me$-*p*)}$_4$]

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Products from the reaction of MCl_5 (M = Nb or Ta) with acids RCO_2H (R = aryl) include the tetranuclear tantalum oxo cluster [{$TaCl_2(\mu$-O)($O_2CC_6H_4Me$-*p*)}$_4$] containing a Ta_4O_4 core, dinuclear [{$NbCl_3(O_2CR)$}$_2(\mu$-O)], and the monosubstituted [$TaCl_4(O_2CR)$].

Metal oxo cluster compounds continue to be of interest since they serve as catalysts in oxidation reactions, precursors for metal oxides, and provide useful intermediates with reactive metal centres, which can be substituted and reduced, within an oxo matrix.[1] For compounds, which contain both an organic group and an oxo ligand, there is only a restricted range available,[2] and for the early transition metals, niobium(v) and tantalum(v) in particular, the few known oxo clusters often contain the η^5-C_5R_5 (*e.g.* R_5 = Me_5 or H_4Me) group. These derivatives are typified by [{Nb(μ-Cl)(μ-O)(η-C_5Me_5)}$_3$],[2] [{$NbCl_3(H_2O)(C_5H_4Me)$}$_2(\mu$-O)],[3] [$Ta_3(\mu$-O)$_3(\mu_3$-O)(μ-Cl)$Cl_3(\eta$-$C_5Me_5)$][4] and [$Ta_4(\mu$-O)$_4(\mu_3$-O)$_2(\mu_4$-O)$(OH)_2(C_5Me_5)_4$][5a] the latter of which contains an interesting μ_4-oxo group, and the proposed dimer [{$TaOCl_2(C_5Me_5)$}$_2$].[5b] Apart from these organometallic derivatives two other dinuclear oxo compounds have been reported namely the ionic [PMe_3Ph][Ta_2OCl_{10}][6] and neutral [{$TaCl_2(NMe_2)_2$·$HNMe_2$}$_2$O],[7] both of which contain linear Ta–O–Ta linkages.

We now report a convenient route to a new range of metal oxo compounds including a tetranuclear tantalum(v) oxo cluster containing an asymmetric Ta_4O_4 ring system, and some dinuclear niobium(v) oxo species. Thus while investigating the interaction between $TaCl_5$ (1.86 g, 5.2 mmol) and RCO_2H (R = Ph, C_6H_4F-*p* or C_6H_4Me-*p*) we have found that *p*-$MeC_6H_4CO_2H$ (1.41 g, 10.4 mmol) reacts cleanly, when a 1 : 2 (Ta : acid) molar ratio is used in refluxing toluene (90 cm^3), to form the oxo cluster **1** as an air-reactive yellow powder (0.8 g, *ca.* 40%). The reaction appears to proceed according to equation (1). The presence of the aroyl chloride in the mother-liquor was detected using IR spectroscopy.

$$4TaCl_5 + 8\,p\text{-}MeC_6H_4CO_2H \longrightarrow \underset{\mathbf{1}}{[\{TaOCl_2(O_2CC_6H_4Me\text{-}p)\}_4]} + 8HCl + 4\,p\text{-}MeC_6H_4COCl \quad (1)$$

The X-ray crystal structure of **1**, Fig. 1, shows it to be a tetranuclear species with a central Ta_4O_4 unit.* The four Ta atoms are coplanar with two oxygen atoms O(13) and O(13a), whilst the other two oxygen atoms O(11) and O(11a) lie ≈0.5 Å above and below this plane. Within this metal oxo unit there are two different Ta–O–Ta angles of 141 and 152°. The larger Ta(1)–O(13)–Ta(1a) angle is associated with a shorter Ta(1)–O(13) distance of 1.869(4) Å [*cf.* Ta(1)–O(11), 1.909(4) Å] reflecting the expected greater degree of Ta–O π bonding in this less bent Ta(1)–O(13)–Ta(1a) bridge. The presence of the bridging carboxylate groups is consistent with the IR data for **1**† and these groups together with the terminal halogens result in a distorted octahedral environment for each metal centre.

The formation of **1** illustrates further the general utility of the reaction of a metal halide with a carboxylic acid at higher temperatures to prepare metal oxo derivatives. The reaction proceeds *via* the elimination of 1 mol of hydrogen halide per mol of acid, with the residual carboxyl (RCO_2) groups either co-ordinating to the metal, or being cleaved by oxygen

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* Crystal data for $C_{32}H_{28}Cl_8O_{12}Ta_4$ **1**: *M* = 1612.1, monoclinic, space group *C*2/*m*, *a* = 18.122(7), *b* = 14.566(6), *c* = 12.706(4) Å, β = 127.19(2)°, *U* = 2671.9 $Å^3$, *Z* = 2, D_c = 2.00 g cm^{-3}, Mo-Kα radiation, λ = 0.710 69 Å, μ(Mo-Kα) = 8.61 mm^{-1}, *F*(000) 1488, *T* = 290 K, *R* = 0.054, *R′* = 0.061; 2233 reflections measured, 2154 unique, 1531 observed [$I/\sigma(I) \geqslant 2.0$]. Crystal character: pale yellow irregular blocks (0.45 × 0.29 × 0.20 mm). Data were collected with a Siemens R3m four-circle diffractometer in the ω–2θ mode to maximum 2θ of 50°. A gaussian absorption correction was applied (*T* = 0.11–0.31). The structure was solved by Patterson methods. Anisotropic thermal factors were used for all non-H atoms. Hydrogen atoms were given fixed isotropic thermal factors, *U* = 0.08 $Å^2$, inserted at calculated positions and not refined. The molecule has precise crystallographic *C* (2/*m*) symmetry, with a mirror plane through O(11), O(11a) and all the bridging carboxylate oxygen atoms and a two-fold rotation axis through O(13) and O(13a). Final refinement was on *F* by cascaded least-squares methods refining 142 parameters. Large positive and negative peaks on a final Fourier difference synthesis were of height +1.7 and −0.9 e $Å^{-3}$. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with *g* = 0.0069 was used and shown to be satisfactory by a weight analysis. Maximum shift/error = 0.003. Computing with SHELXTL PLUS[8] on a DEC MicroVax-II. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

† All the compounds isolated exhibited satisfactory analytical and spectroscopic data. For compound **1**, isolated as a toluene solvate with 1.25 mol C_6H_5Me (Found: C, 28.55; H, 2.60; Ta, 39.95. $C_{32}H_{28}Cl_8O_{12}Ta_4$·1.25$C_6H_5CH_3$ requires C, 28.35; H, 2.20; Ta, 41.90%); yellow crystals, yield ≈40%. IR: ν_{max} 1580s, 1514s, 1500 (sh), 1400s, 800s, 620s, 475s, 460s, 430s, 370s, 320s and 280s cm^{-1}. For [$TaCl_4$ ($O_2CC_6H_4F$-*p*)] (Found: C, 18.85; H, 0.95. $C_7H_4Cl_4FO_2Ta$ requires C, 18.20; H, 0.85%). IR: ν_{max} 1489s and 1397s [$\nu(CO_2^-)$], 410s, 380s, 350s and 265s (Ta-Cl) cm^{-1}. For [{$NbCl_3(O_2CC_6H_4F$-*p*)}$_2(\mu$-O)] (Found: C, 24.15; H, 1.30. $C_{14}H_8Cl_6F_2Nb_2O_5$ requires C, 24.25; H, 1.15%); yellow solid, yield ≈40%. IR: ν_{max} 1480s, 1320s, 1272s, 1098s, 692s, 456s, 390s, 340s and 290s cm^{-1}.

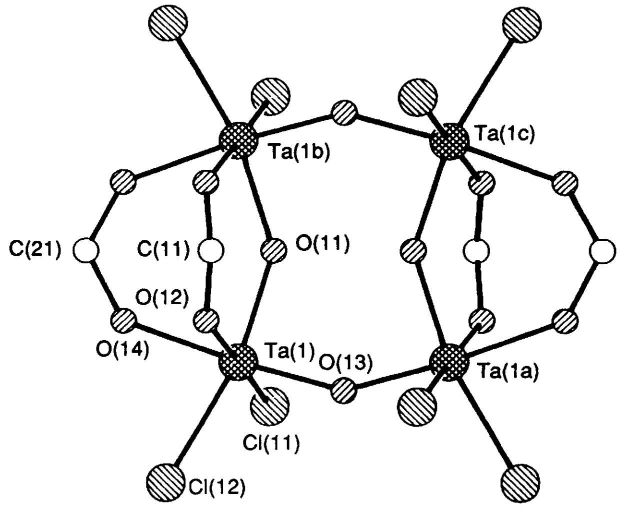

Fig. 1 Molecular structure of $[\{TaOCl_2(O_2CC_6H_4Me\text{-}p)\}_4]$ with the p-MeC_6H_4 carboxylate groups omitted for clarity. Selected bond lengths (Å) and angles (°): Ta(1)–O(11) 1.909(4), Ta(1)–O(13) 1.869(4), Ta(1)–Cl(11) 2.263(7), Ta(1)–Cl(12) 2.322(4), Ta(1)–O(12) 2.031(13); Cl(11)–Ta(1)–Cl(12) 95.6(2), Cl(12)–Ta(1)–O(12) 84.9(3), Cl(11)–Ta(1)–O(13) 95.4(2), O(11)–Ta(1)–O(13) 91.9(7), Cl(11)–Ta(1)–O(14) 90.4(6), O(11)–Ta(1)–O(14) 84.1(6), Cl(11)–Ta(1)–O(11) 95.1(6), O(11)–Ta(1)–O(12) 84.1(6), Cl(12)–Ta(1)–O(13) 96.9(4), O(12)–Ta(1)–O(13) 86.7(4), Cl(12)–Ta(1)–O(14) 86.0(4), O(12)–Ta(1)–O(14) 87.4(7), Ta(1)–O(11)–Ta(1b) 141.3(7), Ta(1)–O(13)–Ta(1a) 151.9(9)

abstraction to form an M – O fragment with the remaining aroyl group appearing as an aroyl chloride by using a halide from the metal. As has been observed for titanium[9] the molar ratio of reactants (Ta : acid) and the reaction temperatures are clearly important, since under the above conditions using a 1 : 2 molar ratio both $PhCO_2H$ and p-$FC_6H_4CO_2H$ react differently from p-$MeC_6H_4CO_2H$ in that some unreacted acid remains, and different metal-containing products are obtained which we have not yet fully identified.

When a 1 : 1 (MCl_5 : acid, M = Nb or Ta) molar ratio is used, and the reactions carried out at 25 °C, $TaCl_5$ reacts cleanly with $PhCO_2H$ or p-$FC_6H_4CO_2H$ to form $[TaCl_4(O_2CR)]$ (R = Ph or C_6H_4F-p) species which appear to contain bridging carboxylate groups from their IR spectra. However, with p-$MeC_6H_4CO_2H$ using a 1 : 1 molar ratio the products contain some unreacted acid together with a mixture of unidentified solids. We have also found for a 1 : 1 ratio that $NbCl_5$ affords only a complex mixture of products with RCO_2H (R = Ph, C_6H_4F-p or C_6H_4Me-p), although other reports[10,11] have claimed that both metals form $[MCl_4(O_2CR)]$ (M = Nb or Ta) compounds when R = alkyl, and that tantalum also forms $[TaOCl_2(O_2CR)]$ but no structural information is available on any of these derivatives. The optimum reaction conditions for niobium consist of using a molar ratio of 1 : 1.5 ($NbCl_5$: acid) and a temperature of 60 °C when the major product is now the dinuclear oxo species $[\{NbCl_3(O_2CR)\}_2O]$ (R = Ph, C_6H_4-Me-p or C_6H_4F-p). The presence of bands near 1500 and 1400 cm^{-1} in the IR spectra, arising from stretching modes of bridging carboxylate groups, together with absorptions between 400 and 250 cm^{-1} from terminal Nb–Cl bonds, indicates that these species are probably best formulated as oxo/carboxylate-bridged dinuclear niobium(v) derivatives. It is possible that there is a relationship between this type of compound and the tetranuclear tantalum species **1**, since the latter could be formed from two such dinuclear units with two oxo bridges in **1** formally replacing four terminally bound chlorine atoms in the niobium compound. We are currently attempting to define such relationships more closely in order to extend the available range of polynuclear oxo compounds for these Group 5 elements.

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