New Chemistry of Oxo Trinuclear, Metal–Metal Bonded Niobium Compounds

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Reaction of Nb_2Cl_6(tetrahydrothiophene)$_3$ with aqueous acids provides a general route to oxo trinuclear, metal–metal bonded species such as $[Nb_3(\mu_3\text{-}O)_2(SO_4)_6(H_2O)_3]^{5-}$, $[Nb_3(\mu_3\text{-}O)_2(O_2CMe)_6(\text{tetrahydrofuran})_3]^+$, and $[Nb_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(NCS)_9]^{6-}$.

The chemistry of oxo trinuclear compounds of molybdenum and tungsten that contain metal–metal bonded equilateral triangular clusters is now extensively developed.[1—3] There have been indications that niobium (and possibly tantalum) can form similar species[4,5] but relatively little is yet known about them. Recent work in this laboratory has provided a possible general entry into this area and has suggested that it may have considerable scope.

The $[Nb_3(\mu_3\text{-}O)_2(SO_4)_6(H_2O)_3]^{5-}$ ion has previously been obtained only by electrochemical reduction of Nb_2O_5 in H_2SO_4.[4] We now find that $Nb_2Cl_6(THT)_3$, THT = tetrahydrothiophene, reacts with a mixture of 40—70% aqueous H_2SO_4 and tetrahydrofuran (THF) at 25 °C to give a solution from which the complex anion can be precipitated (60% yield) as red-brown $(NH_4)_3(H_3O)_2[Nb_3O_2(SO_4)_6(H_2O)_3]\cdot 3H_2O$ (**1**) after addition of $(NH_4)_2SO_4$. Both hexagonal ($P6_3/m$, a = 13.870, c = 9.886 Å) and monoclinic crystals can be obtained. The latter provided the best structural information†‡ and the following average distances (Å) that were found in the

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† *Crystal data* for (**1**): $Nb_3S_6O_{34}N_3H_{30}$, $a = 9.651(3)$, $b = 9.866(3)$, $c = 16.141(5)$ Å, $\beta = 94.07(3)°$, $U = 1533(2)$ Å^3, monoclinic, space group $P2_1/m$ (No. 11), $Z = 2$, $D_c = 2.355$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 15.70$ cm^{-1}. Data were collected on a Syntex P3 diffractometer over the range 4—50° in 2θ at 295 K. Lorentz and polarization corrections were applied but azimuthal scans showed that absorption corrections were unnecessary. From a total of 2491 reflections, 2329 $[I > 3\sigma(I)]$ were considered observed and used to solve (Patterson) and refine (difference Fouriers, full-matrix least squares) the structure. The refinement converged to $R = 0.052$ and $R_w = 0.079$ with the largest shift in any refined parameter equal to 0.07 times its e.s.d.

‡ Atomic co-ordinates, bond lengths and angles, and thermal parameters for (**2**) and (**4**) have been deposited at the Cambridge Crystallographic Data Centre and those for (**1**) at the University of Bonn. See Notice to Authors, Issue No. 1, 1986.

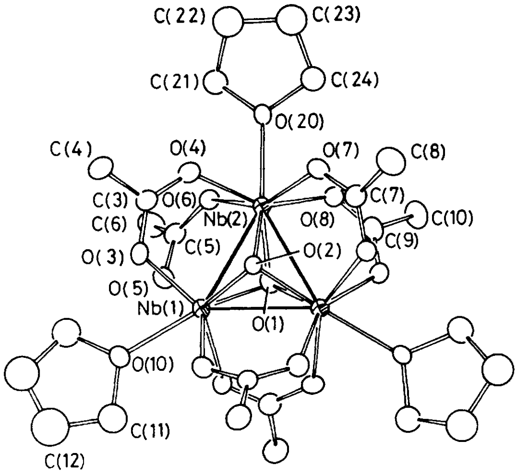

Figure 1. The structure of the $[Nb_3O_2(O_2CMe)_6(THF)_3]^+$ ion in compound (**2**). A crystallographic mirror plane passes through Nb(1),O(1),O(2),O(10), and C(7)—C(10).

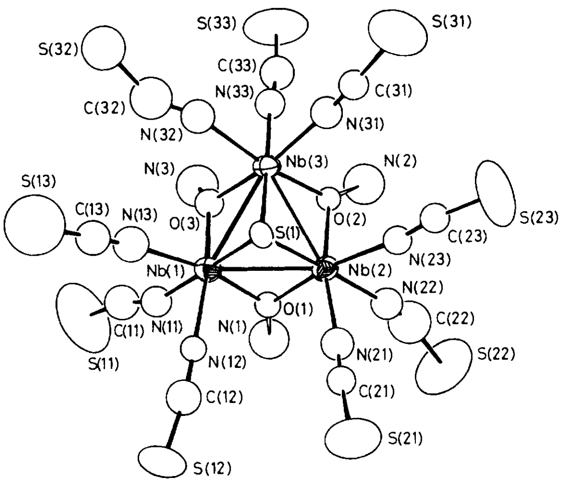

Figure 2. The structure of the $[Nb_3SO_3(NCS)_9]^{6-}$ anion in compound (**4**) together with the hydrogen bonded NH_4^+ cations.

complex anion agree well with those (in square brackets) found by Bino[4] in the potassium compound: Nb–Nb 2.870(6) [2.885(7)], Nb–(μ_3-O) 2.030(2) [2.051(7)], Nb–O(sulphate) 2.132(3) [2.134(4)], Nb–O(water) 2.257(7) [2.240(11)]. It is thus evident that the $Nb_2Cl_6(THF)_3$ starting material can be used to prepare the sulphato-bridged as well as carboxylato-bridged[5] Nb_3O_2 derivatives.

The previous preparations[5] of two $[Nb_3O_2(O_2CR)_6(THF)_3]^+$ ions with R = Ph and Bu^t were carried out with $Nb_2Cl_6(Me_2S)$, and the appropriate $NaRCO_2$ salts as reactants; with R = Me this method did not succeed. We now find that a 1 : 1 mixture of acetic acid and acetic anhydride reacts readily with $Nb_2Cl_6(THT)_3$ to give, after crystallization from THF, red-brown, crystalline $[Nb_3O_2(O_2CMe)_6(THF)_3][NbOCl_4(THF)]$, (**2**). The structure§‡ of the complex cation is shown in Figure 1. It has a mean Nb–Nb distance of 2.831(3) Å, which is not significantly different from that previously found for the pivalate complex, 2.843(3) Å.

In all of the Nb_3O_2 species now known, the number of core electrons available for Nb–Nb bonding is four, so that all of them have an Nb–Nb bond order of 2/3. The slightly shorter Nb–Nb distances for RCO_2-bridged species (*ca.* 2.83 Å) compared to those in the sulphato bridged species (*ca.* 2.87 Å) may be due to the slightly smaller 'bite' of the carboxy group. The results reported here, together with the previously known facts,[4,5] show that bioxo capped Nb_3 clusters with RCO_2^- or SO_4^{2-} bridges can be prepared systematically from the $Nb_2Cl_6(R_2S)_3$ starting materials.

From the reaction mixture used to prepare (**2**), by further workup, an unusual yellow compound $Nb_2Cl_2(OEt)(O_2CMe)_5$, (**3**), was also obtained (*ca.* 15% yield). The structure of this compound has been determined and will be reported elsewhere. Two $(MeCO_2)_2Nb^{IV}$ units are bridged by one EtO, two Cl, and a $MeCO_2$ group to give a Nb–Nb single bond [2.789(1) Å].

Given that bioxo capped Nb_3 clusters are now readily available and well characterized, it is natural to wonder if, by analogy with the chemistry of molybdenum and tungsten, where both $Mo_3(\mu_3\text{-}O)_2$ and $Mo_3(\mu_3\text{-}X)(\mu_2\text{-}Y)_3$ (X, Y = S, O) type clusters are well known, it is possible to obtain $Nb_3(\mu_3\text{-}X)(\mu_2\text{-}Y)_3$ species. We can report here the first proof of the existence of such species. When $Nb_2Cl_6(THT)_3$ dissolved in THF at 0 °C was treated with concentrated aqueous HCl (with O_2 rigorously excluded), a rapid reaction occurred. Evaporation to dryness followed by redissolution in water afforded a green solution which was then passed through a cation exchange column where a green band was formed. This green band can be eluted with >3 M HCl or with a solution of SCN^- or oxalate ion. In this respect the behaviour is very similar to that of the $Mo_3O_4^{4+}$ ion. This together with the structure of the thiocyanate derivative described below suggests that the green cation is of the type $[Nb_3O_4(H_2O)_9]^{n+}$ or it is an immediate precursor to such species.

No way has yet been found to obtain a really good crystalline compound, but crystals of what appears to be $(NH_4)_3(NMe_4)_3[Nb_3SO_3(NCS)_9]\cdot MeOH$, (**4**), have provided an adequate data set¶‡ from which the structure in Figure 2 has been obtained. These crystals were obtained by dissolving the green material, after removal of water, in methanol (where it assumed a dark red colour); solid NH_4SCN was added, followed by a saturated solution of NMe_4Br in MeOH. Black crystals of (**4**) were formed in over 60% yield. They were contaminated with a variable but usually small amount of

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§ *Crystal data* for (**2**): $Nb_4Cl_4O_{19}C_{28}H_{50}$, a = 14.425(5), b = 16.662(4), c = 19.423(8) Å, U = 4668(5) Å^3, orthorhombic, space group *Pmna* (No. 53), Z = 4, D_c = 1.713 g cm^{-3}, $\mu(Mo\text{-}K_\alpha)$ = 12.1 cm^{-1}. Data were collected on a CAD-4 diffractometer over the range 4—50° in 2θ at 295 K. Lorentz and polarization corrections were applied, but azimuthal scans showed that absorption corrections were negligible. From a total of 2948 reflections, 2178 [$I > 3\sigma(I)$] were considered observed and used to solve (Patterson) and refine (difference Fouriers, full-matrix least squares) the structure to final residuals of R = 0.048 and R_w = 0.061, with the largest parameter shift to e.s.d. ratio being 0.05.

¶ *Crystal data* for (**4**): $Nb_3S_{10}O_4N_{15}C_{22}H_{52}$, a = b = 30.11(1), c = 29.98(1) Å, U = 27 171(28) Å^3, tetragonal, space group $I\bar{4}c2$ (No. 120), Z = 16, D_c = 1.164 g cm^{-3}, $\mu(Mo\text{-}K_\alpha)$ = 8.0 cm^{-1}. Data were collected on a Syntex P$\bar{1}$ diffractometer over the range 4—37° in 2θ, at 278 K. Lorentz and polarization corrections were applied. From a total of 1953 reflections, 1618 [$I > 3\sigma(I)$] were considered observed and used to solve (direct methods, MULTAN) and refine (program SHELX, difference Fouriers, full-matrix least squares) the structure to final residuals of R = 0.076 and R_w = 0.098. The N–C and C–S distances were constrained at 1.15 and 1.65 Å, respectively, while NMe_4^+ ions were refined as rigid tetrahedral NC_4 groups, with a common thermal parameter for each group. The largest parameter shift to e.s.d. ratio in the final cycle was 0.08.

an orange Nb^{IV} complex $(NMe_4)_2[Nb(OMe)_2(NCS)_4]$, which has also been structurally characterized.

The $[Nb_3SO_3(NCS)_9]^{6-}$ ion resides on a general crystallographic position but has effectively C_{3v} symmetry, with the following average principal dimensions: Nb–Nb 2.763(3), Nb–S 2.51(1), Nb–O 2.03(1), Nb–N 2.14(2) Å; Nb–S–Nb 66.9(1), Nb–O–Nb 86(1)°. The determined charge of the trinuclear anion, namely 6−, which still requires an independent verification, indicates a d^4 electronic configuration for the Nb_3 core. The same number of d electrons is present in the Nb_3O_2 type species and this is consistent with the properties of molybdenum systems where the trimers with both the Mo_3O_2 and Mo_3O_4 units have identical number, *viz.* 6, electrons involved in metal–metal bonding. The introduction of μ_3-S into the trimer can occur *via* one of two most probable processes. It may originate from decomposition of thiocyanate ion, whereby a μ_3-O atom is replaced by S. A study of exchange rates for oxygen atoms in the $Mo_3O_4^{4+}$ (aq) ion[6] showed that μ_3-O atom is far more labile than the μ_2-O atoms. The second possibility is that the green species is a Nb^{III}-oxo compound which is oxidized by SCN^- with the formation of $Nb_3SO_3^{3+}$ species and CN^- ions.

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