Binuclear Alkoxide Complexes of Niobium and Tantalum in Lower Oxidation States

Sir:

Our knowledge of Nb and Ta complexes with RO^- and ROH ligands is almost exclusively limited to those in the highest oxidation state of the metals. Thus while extensive and multifaceted studies have been carried out for the M(V) species,[1-4] there have been only a few reports dealing with such compounds involving tetravalent metals[1,2,5,6] and none in lower oxidation states. In view of the very rich chemistry of Mo and W alkoxides[7,8] and recent developments in the chemistry of low-valent Nb and Ta complexes, where interesting novel complexes and remarkable reactivity patterns have been found,[9] there seems to be a considerable potential in the compounds of these two elements in oxidation states lower than +5 with alcohol-related ligands. Accordingly, we have explored the reaction of the confacial bioctahedral $Nb_2Cl_6(THT)_3$ (**1**), THT = tetrahydrothiophene, with alcohols, ROH, for R = Me, Et and *i*-Pr. Three different types of compounds have been isolated, and a representative compound from each group has been characterized by X-ray crystallography.[10,11] A purple solution of **1** in toluene changes to brown within several hours upon addition of excess alcohol. For R = Et and *i*-Pr the removal of solvent under vacuum affords a compound of the formula $Nb_2Cl_5(OR)(ROH)_4$ (**2**)[12] in the form of an orange or yellow-brown powder or a brown crystalline solid.[13] As can be seen in Figure 1 it is a Nb(III) edge-sharing bioctahedral complex resulting from substitution of one Cl^-, which is lost as HCl, by RO^- and replacement of the neutral ligands by the molecules of alcohol. The compound is diamagnetic as evidenced by the normal appearance of its NMR signals. The proton NMR spectra for both the Et and *i*-Pr derivatives in THF-d_8 are complex, and several peaks with different intensities are observed for a given type of proton. This is attributed to partial substitution of ROH by THF. We could not make unambiguous assignments even after running decoupling experiments, and the problem is still under study. Compound **2** is only moderately stable at room temperature, and the original brown solution changes to green and eventually becomes black-red. Layering of the THF solution containing **2** with hexane results in the formation of a green interface, and bubbles of gas are evolved. Eventually a red solution and a crystalline solid are obtained, in 40–50% yield. Crystallographic determination[14] showed that this new product is a Nb(IV) dimer of the formula $Nb_2OCl_4(OR)_2(THF)_2$ (**3**). It has one vacant coordination site, which in the solid state is occupied by the oxygen atom

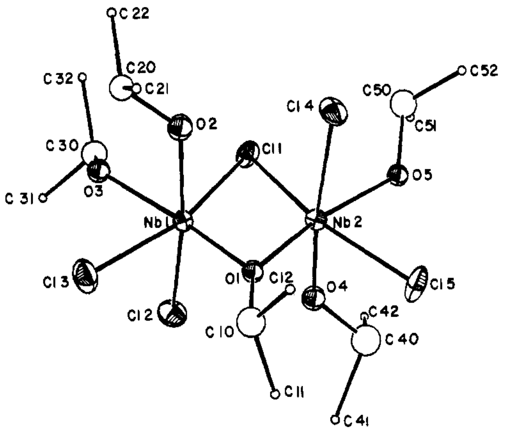

Figure 1. ORTEP drawing of $Nb_2Cl_5(O\text{-}i\text{-}Pr)(i\text{-}PrOH)_4$ (**2**). The ellipsoids enclose 30% of electron density. Methyl carbon atoms were assigned arbitrarily small thermal ellipsoids for the sake of clarity. Important interatomic dimensions (averaged): Nb(1)–Nb(2) = 2.611 (3) Å, Nb–O(1) = 2.03 [1] Å, Nb–Cl(1) = 2.473 [8] Å, Nb–Cl(trans Cl) = 2.49 [2] Å, Nb–Cl(trans O) = 2.437 [1] Å, Nb–O(trans Cl) = 2.11 [2] Å, Nb–O (trans O) = 2.25 [3] Å, Nb(1)–O(1)–Nb(2) = 80.2 (6)°, Nb(1)–Cl(1)–Nb(2) = 63.7 (2)°, Nb–O–C = 131 [2]°.

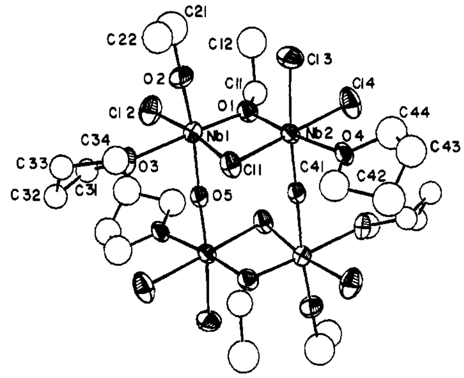

Figure 2. ORTEP drawing of $Nb_2OCl_4(OEt)_2(THF)_2$ (**3**). The ellipsoids enclose 30% of electron density. The crystallographic inversion center related halves of the tetramer. Important interatomic dimensions (averaged): Nb(1)–Nb(2) = 2.891 (1) Å, Nb–O(1) = 2.025 [7] Å, Nb–Cl(1) = 2.490 [8] Å, Nb–Cl_t = 2.423 [1] Å, Nb(2)–Cl(3) = 2.435 (3) Å, Nb(1)–O(2) = 1.794(8) Å, Nb(1)–O(5) = 2.008 (7) Å, Nb(2)′–O(5) = 1.816 (7) Å, Nb–O_{THF} = 2.229 [2] Å; Nb(1)–O(1)–Nb(2) = 91.1 (3)°, Nb(1)–Cl(1)–Nb(2) = 70.98(8)°, Nb(1)–O(5)–Nb(2)′ = 177.7 (4)°, Nb(1)–O(2)–C(21) = 175 (1)°.

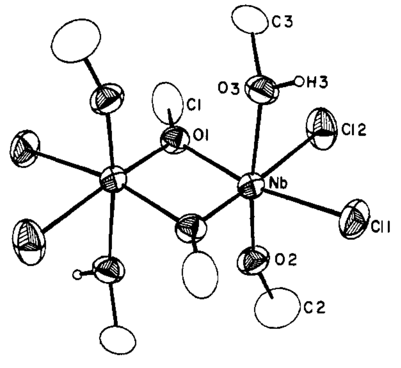

Figure 3. ORTEP drawing of the $Nb_2Cl_4(OMe)_4(MeOH)_2$ (**4**) molecule. The ellipsoids enclose 40% of electron density. The crystallographic inversion center relates halves of the molecule. Important interatomic dimensions (averaged): Nb–Nb = 2.781 (1) Å, Nb–Cl = 2.451 [15] Å, Nb–O(1) = 2.047 [1] Å, Nb–O(2) = 1.811 (4) Å, Nb–O(3) = 2.147 (4) Å, Nb–O(1)–Nb′ = 85.6 (1)°, Nb–O(2)–C(2) = 159.6 (5)°, Nb–O(3)–C(3) = 129.5 (4)°.

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(10) Crystal structure determinations were carried out by standard methods, which have been described previously: (a) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558. (b) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227.

(11) Calculations were done on the VAX-11/780 computer at the Department of Chemistry, Texas A&M University, College Station, TX, with the VAX-SDP software package. Tables of positional and isotropic equivalent thermal parameters are provided as supplementary material.

(12) Yields are above 60%. Anal. for R = *i*-Pr. Calcd for $Nb_2Cl_5O_5C_{15}H_{31}$: C, 27.53; H, 4.77. Found: C, 27.87; H, 5.78.

(13) Compound **2** with R = *i*-Pr: space group $P2_1/c$ with $a = 9.647$ (4) Å, $b = 15.964$ (5) Å, $c = 18.286$ (5) Å, $\beta = 91.43$ (3)°, $V = 2815$ (3) Å^3, $Z = 4$, and $d_{calcd} = 1.563$ g/cm^3 for fw = 662.55. Refinement of 144 parameters using 955 reflections with $F^2 > 3\sigma(F^2)$ produced residuals R and R_w equal to 0.064 and 0.071, respectively.

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from another dimer thus forming a tetramer as shown in Figure 2. Disregarding the neutral ligands, **3** is formally related to **2** by the loss of chloride, two hydrogen atoms and C_2H_5 (two ROH giving O and RO^-). At this point it is not possible to say whether this apparent decomposition is spontaneous and how the three moieties combine. The conversion may be mediated by impurities or some other adventitiously introduced contaminants. However, we would like to stress that **3** was consistently obtained in considerable quantity when the Nb(III) alcoholate was treated as described.

While the reaction of **1** with MeOH appears to give a compound of type **2**, we have not been able to isolate the product. If the reaction mixture is kept at +5 °C, a microcrystalline solid resembling the other Nb(III) alcoholates is formed. In addition a blue oil, which converts to dark blue crystals within several days, deposits at the bottom. This product, obtained in about 25% yield, is another dimeric Nb(IV) species, $Nb_2Cl_4(OMe)_4(MeOH)_2\cdot 2MeOH$ (**4**).[15] This outcome can probably be attributed to the higher acidity of methanol relative to other alcohols. The isolation of **4** (a d^1–d^1 species) is especially interesting since a tungsten dimer (a d^2–d^2 species) of identical stoichiometry has already been described.[16]

The three compounds reported here reveal some interesting bonding patterns, especially with respect to metal–metal bond lengths. On the basis of formal oxidation state and the fact that all distances between metal atoms are relatively short, a double Nb═Nb bond is assigned in **2** and a single one in **3** and **4**. The former is considerably shorter than typical M═M, (M = Nb and Ta) bonds[17] (usually 2.7 ± 0.3 Å). With the exception of the Ta═Ta bond in the hydrogen-bridged $Ta_2(\mu\text{-}H)_2Cl_4(PMe_3)_4$,[18] it is the shortest known M═M bond for either metal. It can be only partially attributed to the OR bridge since in **3**, which has the same type of bridging, one finds the longest single M–M bond in discrete Nb and Ta dimers. In **4** the single metal–metal bond is about 0.05 Å shorter than a typical metal–metal distance in dimeric Nb or Ta complexes in oxidation state +4.[19] The $Nb–O_b$ bonds are all within a narrow range from 2.025 [7] to 2.047 [1] Å. The terminal alkoxides form a very strong bond to the metal (Nb–O distances around 1.8 Å) due to considerable π interactions evidenced by nearly linear Nb–O–C angles. The Nb–O(alcohol) bonds are above 2.1 Å in length, and the Nb–O–C unit is bent.

Apparently all hydroxyl protons in **2** are involved in some sort of hydrogen bonding. The corresponding Cl–O distances are around 3 Å, and in the IR spectrum only a broad band about 3200 cm^{-1} is observed. No peaks due to an unhindered O–H stretch are present. Although **4** is an analogue of the W(IV) alkoxide $W_2Cl_4(OR)_4(ROH)_2$, it does not exhibit the same type of internal hydrogen bonding. Instead the proton from the axial alcohol ligand interacts with a molecule of MeOH in the lattice and the O(3)–O(4) distance is equal to 2.913 Å.

While we clearly have much still to learn about these and related compounds, the fact that such a class of compounds exists, and that they are rather easy to make, seems to us to warrant this preliminary note.

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Supplementary Material Available: Tables of positional and isotropic equivalent displacement parameters for **2**, **3**, and **4** (3 pages). Ordering information is given on any current masthead page.

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(14) Compound **3** with R = Et: space group *C2/c* with $a = 21.148$ (5) Å, $b = 12.034$ (3) Å, $c = 17.586$ (5) Å, $\beta = 107.53$ (2)°, $V = 4267$ (4) $Å^3$, $Z = 8$ (dimers), and $d_{calcd} = 1.779$ g/cm^3 for fw = 577.96. Refinement of 168 parameters (including disordered THF ligands) using 1529 reflections with $F^2 > 3\sigma(F^2)$ produced residuals R and R_w equal to 0.048 and 0.062, respectively.

(15) Compound **4** crystallizes with two molecules of the solvent per dimer in monoclinic space group $P2_1/n$ with $a = 9.231$ (2) Å, $b = 8.961$ (2) Å, $c = 13.236$ (1) Å, $\beta = 91.75$ (1)°, $V = 1094.4$ (6) $Å^3$, $Z = 2$ (dimers), and $d_{calcd} = 1.760$ g/cm^3 for fw = 579.93. Refinement of 100 parameters (H atoms located in a difference Fourier map and included without refinement in the structure factor calculations) using 1290 reflections with $F^2 > 3\sigma(F^2)$ produced reliability indices of $R = 0.033$ and $R_w = 0.044$.

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