Inorg. Chem. **1998,** *37,* 5507−5511

Synthesis and Crystal Structure of a Self-Assembled, Octanuclear Oxo-Tantalum(V) Derivative Containing the First Example of a Transition Metal $M_8(\mu\text{-}O)_{12}$ Cage

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Received April 9, 1998

By reduction with $CoCp^*_2$ in THF or toluene, the tantalum(V) chlorocarbamato complex $TaCl_2(O_2CNEt_2)_3$, **1**, gives high yields of the tantalum(III) *N*,*N*-diethylcarbamate, $Ta(O_2CNEt_2)_3$, **2**. On the other hand, good yields of the octanuclear μ-oxo-*N*,*N*-diethylcarbamato cage compound $Ta_8(\mu\text{-}O)_{12}(O_2CNEt_2)_{16}$, **3**, were secured by reaction of **1** with sodium in THF. Compound **3** has been characterized by analytical and spectroscopic methods and by X-ray diffractometry. Crystal data for $C_{80}H_{160}N_{16}O_{44}Ta_8$: $M = 3497.84$, triclinic, space group = $P\bar{1}$ (no. 2), $\bar{1}a = 15.440(3)$ Å, $b = 15.710(1)$ Å, $c = 16.090(2)$ Å, $\alpha = 101.53(4)°$, $\beta = 107.51(5)°$, $\gamma = 118.79(3)°$, $V = 2971.4(3)$ Å^3, $Z = 1$, $D_c = 1.955$ Mg/m^3, $\mu = 7.416$ mm^{-1}, $F(000) = 1688$, R1 = 0.0350, wR2 = 0.0798, $T = 213$ K. The eight tantalum atoms are located at the vertexes of a cube whose edges are occupied by 12 bridging oxo groups. Hexacoordination at tantalum is completed by bridging and terminal *N*,*N*-diethylcarbamato ligands. Both THF and the carbon dioxide fragments of the carbamato groups are involved in the formation of the μ-oxo cage oxides.

Introduction

Recently, some of us reported the synthesis and reactivity of *N*,*N*-dialkylcarbamato derivatives of niobium and tantalum.[1] In agreement with the general observation that the stability of high oxidation states increases in descending a vertical sequence of transition metal ions, difficulties were encountered in the preparation of *N*,*N*-diethylcarbamates containing tantalum in the relatively low oxidation states IV and III.

In this paper, we wish to report that the mixed chloro/*N*,*N*-diethylcarbamato of tantalum(V), $TaCl_2(O_2CNEt_2)_3$, **1**, is expectedly reduced to $Ta(O_2CNEt_2)_3$, **2**, by $CoCp^*_2$ in toluene or THF. On the other hand, sodium reduction in tetrahydrofuran has been accompanied by the unexpected oxidation of the lower-valent intermediate under the combined action of THF and CO_2 (as such or as a constituting fragment of the *N*,*N*-diethylcarbamato ligand) to give high yields of an octanuclear μ-oxo derivative of tantalum(V), $Ta_8(\mu\text{-}O)_{12}(O_2CNEt_2)_{16}$, **3**. The properties of this cage compound, including the molecular structure, are presented in this paper.

Experimental Section

All the operations were carried out under an atmosphere of prepurified argon. Solvents were dried by conventional methods prior to use.

IR spectra were measured with an FT-1725X instrument on solutions or Nujol and/or polychlorotrifluoroethylene (PCTFE) mulls prepared under rigorous exclusion of moisture and air. ^1H (200 MHz) and ^{13}C NMR (50.3 MHz) spectra were measured at 20 °C with a Varian Gemini 200 instrument. The chemical shifts are referred to TMS. Magnetic susceptibility measurements were performed in the temperature range 80−290 K with a Faraday balance using $CuSO_4 \cdot 5H_2O$ as a standard. For the diamagnetic correction, Pascal contributions[2] were used. The carbon dioxide content of the products was determined gas-volumetrically by decomposition with diluted sulfuric acid.

Decamethylcobaltocene, $CoCp^*_2$,[3] and $TaCl_2(O_2CNEt_2)_3$, **1**,[1] were prepared according to literature methods.

Reaction of $TaCl_2(O_2CNEt_2)_3$ with decamethylcobaltocene. Preparation of $Ta(O_2CNEt_2)_3$, 2. When solid $TaCl_2(O_2CNEt_2)_3$ (1.11 g, 1.85 mmol) was added to a red-brown solution of $CoCp^*_2$ (1.22 g, 3.70 mmol) in toluene (30 mL), formation of the yellow insoluble $[CoCp^*_2]Cl$ occurred immediately. The suspension was stirred overnight at room temperature, filtered in order to separate the cobalticinium chloride (0.994 g, 74% yield), and characterized by IR, NMR, and elemental analysis. The volume of the solution was reduced to ca. 5 mL, and the residue was added of heptane (10 mL). The supernatant liquid was removed by suction, and the remaining solid was dissolved in toluene (5 mL). By addition of heptane (25 mL), a brown solid separated out, which was collected by filtration and dried in vacuo at room temperature, affording 0.81 g (83% yield) of **2** as a brown microcrystalline compound very sensitive to moisture and oxygen. Anal. Calcd for $Ta(O_2CNEt_2)_3 \cdot 2.5C_7H_{16}$, $C_{32.5}H_{70}N_3O_6Ta$: C, 50.0; H, 9.0; N, 5.4; Ta, 23.2; CO_2, 16.9. Found: C, 50.3; H, 8.8; N, 5.9; Ta, 23.4; CO_2, 16.8. IR: (*sym*-$C_2H_2Cl_4$, cm^{-1}) 1685 (mw), 1647 (m), 1543 (s), 1477 (s); (PCTFE, cm^{-1}) 2962 (m), 2927 (m), 1684 (w), 1646 (m), 1540 (m), 1507 (m), 1475 (m), 1426 (m), 1377 (m), 1262 (s), 1201 (ms). ^1H NMR (C_6D_6, 200 MHz): 3.0−3.2 (broad m, 2H, CH_2), 0.8−1.2 (broad m, 3H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 50.3 MHz): 167.89 ($O_2\mathbf{C}N$), 40.32 ($\mathbf{C}H_2$), 13.48 ($\mathbf{C}H_3$). Compound **2** was also obtained in a THF reaction medium.

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10.1021/ic980408l CCC: $15.00

Reaction of $TaCl_2(O_2CNEt_2)_3$ with Sodium in THF. (a) Preparation of $Ta_8(\mu\text{-}O)_{12}(O_2CNEt_2)_{16}$, 3. A pale yellow solution of $TaCl_2(O_2CNEt_2)_3$ (3.44 g, 5.7 mmol) in THF (50 mL) was treated with finely divided sodium (0.27 g, 11.7 mmol) at room temperature. The pale yellow suspension slowly changed to pale green and then to pale brown over 72 h. A qualitative test revealed the absence of chloride in the solution. The reaction mixture was filtered, and the filtrate was dried in vacuo at room temperature. The semisolid residue, after treatment with heptane (50 mL), was converted to a pale brown solid, which was separated by filtration and dried in vacuo at room temperature (1.89 g; 76% yield of **3**). Anal. Calcd for $Ta_8(\mu\text{-}O)_{12}(O_2CNEt_2)_{16}$, $C_{80}H_{160}N_{16}O_{44}Ta_8$: C, 27.5; H, 4.6; N, 6.4; Ta, 41.4; CO_2, 20.1. Found: C, 27.4; H, 5.1; N, 6.6; Ta, 40.2; CO_2, 19.2. IR (PCTE, cm^{-1}): 2972 (m), 2933 (m), 1684 (w), 1650 (w), 1540 (vs), 1507 (m), 1495 (s), 1465 (m), 1440 (m-s), 1383 (m), 1210 (m-w).

A GC−MS analysis of the filtrate from the recovery of **3** showed the presence of $HCONEt_2$ {MS, *m/z* %: 101 (100) [M^+], 86 (40) [$M^+ - CH_3$], 72 (20) [$M^+ - C_2H_5$], 58 (38) [$C_4H_{10}^+$], 30 (20) [$NH_2{=}CH_2^+$]}.

The crude material (0.442 g) was purified by slow evaporation of a toluene/heptane solution affording large pale yellow crystals (82% yield), which were used for the X-ray diffractometric experiment. Anal. Calcd for $C_{80}H_{160}N_{16}O_{44}Ta_8$: C, 27.5; H, 4.6; N, 6.4; Ta, 41.4; CO_2, 20.1. Found: C, 27.3; H, 4.5; N, 6.2; Ta, 40.9; CO_2, 20.0. IR (Nujol + PCTFE, cm^{-1}): 2973 (m), 2933 (m), 2873(m-w), 1651 (w), 1538 (vs), 1495 (s), 1460 (m), 1440 (m-s), 1382 (m), 1337 (m-s), 1217 (m-w), 1100 (m), 1076 (m), 981 (w), 940 (w), 837 (m-s), 794 (s), 646 (s), 446 (m), 406 (w). ^1H NMR (C_6D_6, 200 MHz): 3.47−3.40 (broad m, 2H, CH_2), 1.35−1.09 (broad m, 3H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 50.3 MHz): 162.17 ($O_2\mathbf{C}N$), 156.18 ($O_2\mathbf{C}N$), 42.20 (broad, $\mathbf{C}H_2$), 14.63 (broad, $\mathbf{C}H_3$).

(b) Crystal Structure of 3: Solution and Refinement. A crystal of approximate dimensions 0.2 × 0.2 × 0.3 mm^3 was sealed under argon in a Lindeman capillary and mounted at −60 °C on a Enraf Nonius CAD4 diffractometer equipped with a graphite monochromator using the Mo Kα radiation (λ= 0.710 73 Å). The cell parameters were obtained on the basis of 25 carefully centered reflections in the range $\theta = 8-13°$. Table 1 lists the crystal data and the structure refinement parameters.

In the range $3 \leq \theta \leq 27°$, 14 376 reflections were measured with a ω-scan. During data collection, the intensity of three control reflections was measured every hour; 10 132 reflections [$I \geq 2\sigma(I)$] were considered for the refinement. The tantalum atoms were located by the Patterson method; a Fourier difference synthesis allowed the localization of the oxygen, nitrogen, and carbon atoms. Hydrogen atoms were located in their ideal positions. In the first stage of the refinement of 297 parameters, by using isotropic thermal parameters and neglecting the hydrogen atoms, a value of $R = 0.1215$ was obtained. The final R value of 0.035 was obtained after an empirical absorption correction with the DIFABS[4] program, 667 parameters being refined with the full-matrix least-squares method and with anisotropic thermal parameters for the non-hydrogen atoms.

Results and Discussion

Under an atmosphere of argon, the tantalum(V) derivative $TaCl_2(O_2CNEt_2)_3$ promptly reacts with 2 equiv of $CoCp^*_2$[5] in toluene or THF according to eq 1.

$$\underset{\mathbf{1}}{TaCl_2(O_2CNEt_2)_3} + 2CoCp^*_2 \rightarrow \underset{\mathbf{2}}{Ta(O_2CNEt_2)_3} + 2[CoCp^*_2]Cl \quad (1)$$

Table 1. Crystal Data and Structure Refinement for $Ta_8(\mu\text{-}O)_{12}(O_2CNEt_2)_{16}$, **3**[a]

empirical formula	$C_{80}H_{160}N_{16}O_{44}Ta_8$
fw	3497.82
temp	213 K
λ (Å)	0.71073
cryst syst/space group	triclinic/$P\bar{1}$ (No. 2)
cryst size (mm^3)	0.2 × 0.2 × 0.3
unit cell dimens	$a = 15.440(3)$ Å; $\alpha = 101.53(4)°$ $b = 15.710(1)$ Å; $\beta = 107.51(5)°$ $c = 16.090(2)$ Å; $\gamma = 118.79(3)°$
vol ($Å^3$)	2971.4(3)
Z	1
D_c (Mg/m^3)	1.955
μ (mm^{-1})	7.416
$F(000)$	1688
no. of reflns (lattice)	25
θ range (lattice) (deg)	7.6−13
θ range for data collection (deg)	3.01−26.92
index ranges	$-1 \leq h \leq 19, -20 \leq k \leq 18, -20 \leq l \leq 19$
reflns collected	14376
indep reflns	12921 [$R_{int} = 0.0243$]
reflns obsd	10132
max and min transmission	1.301 and 0.728
refinement method	full-matrix least-squares on F^2
data/restraints/params	12921/0/667
goodness-of-fit on F^2	1.121
final R indices [$I > 2\sigma(I)$]	R1 = 0.0350, wR2 = 0.0798
R indices (all data)	R1 = 0.0523, wR2 = 0.0889
largest diff peak and hole	1.500 and −1.837 e A^{-3}

[a] Goodness-of-fit $= [\sum[w(F_o^2 - F_c^2)^2]/(N - P)]^{1/2}$, where N and P are the numbers of observations and parameters, respectively, $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o)^2 + (0.0376Q)^2 + 13.42Q]$, where $Q = [\mathrm{Max}(F_o^2,0) + 2F_c^2]/3$.

Compound **2** is a brown solid, soluble in aromatic hydrocarbons and THF and stable for days under rigorous exclusion of air and moisture. The IR spectrum shows absorptions above and below 1600 cm^{-1}, suggesting the presence of mono- and bidentate *N,N*-diethylcarbamato ligands, respectively.[1] A variable temperature magnetic study has shown the compound to be substantially diamagnetic between 80 and 293 K. The magnetic moment is almost constant with temperature (1.00 μ_B at 290 K and 0.87 μ_B at 80 K). The Curie law is obeyed in the range of temperature 100−293 K, with the magnetic moment slightly decreasing between 80 and 100 K. As a result of the fact that a spin-only value for a $5d^2$ system would be 2.87 μ_B, strongly interacting tantalum(III) centers are suggested to be present in this compound.[6] In the absence of a solid-state structure, we can only use infrared and magnetic data to suggest that **2** is dinuclear with four bridging[7] and two terminal carbamato ligands. The substantial diamagnetism of the compound at low temperature may suggest the presence of a

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(4) Walker, N.; Stuart, D. *Acta Crystallogr. Sect. A* **1983**, *39*, 159.

(5) No reaction was observed with $CoCp_2$, in agreement with the lower reducing power of the unsubstituted derivative with respect to $CoCp^*_2$; see: Calderazzo, F.; Pampaloni, G.; Zanazzi, P. F. *Chem. Ber.* **1986**, *119*, 2796. Biagini, P.; Calderazzo, F.; Pampaloni, G.; Zanazzi, P. F. *Gazz. Chim. Ital.* **1987**, *117*, 27 and references therein.

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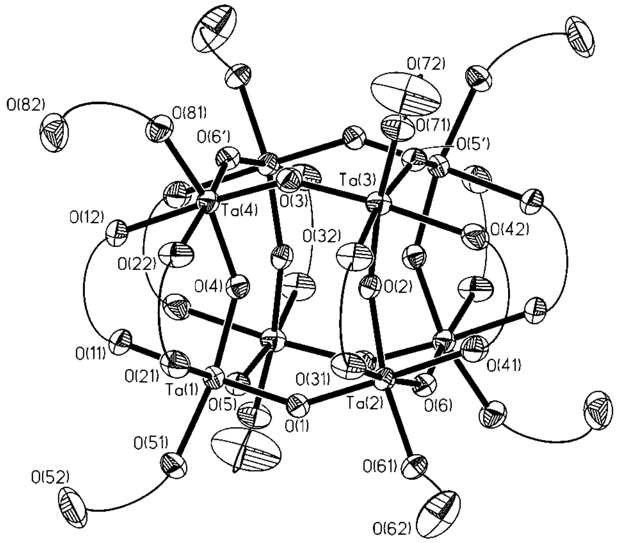

Figure 1. ORTEP[8] plot of the molecular structure of $Ta_8(\mu\text{-}O)_{12}(O_2CNEt_2)_{16}$, **3**. Thermal ellipsoids are drawn at 50% probability. For sake of clarity, only the oxygen atoms of the *N*,*N*-diethylcarbamato groups are represented.

tantalum−tantalum double bond. Most of the tantalum(III) complexes reported in the literature[6] are diamagnetic and dinuclear with tantalum−tantalum distances around 2.7 Å. The dinuclear $Mo_2(O_2CNEt)_4$, a derivative of molybdenum(II) of d^4 configuration, has been shown to contain a strong (probably quadruple) metal−metal bond at the short Mo−Mo distance of 2.067(2) Å[7a] and four bridging carbamato groups.

In search of a more readily available reducing system, we considered the reaction of $TaCl_2(O_2CNEt_2)_3$ with 2 equiv of sodium in THF (under an atmosphere of argon). At variance with the $CoCp^*_2$ case, a rather slow reaction was observed with formation of NaCl and a chloride-free solution from which crude **3** was isolated in high yields as a pale brown solid. Compound **3** is very soluble in THF and toluene and is practically insoluble in saturated hydrocarbons; it evolves CO_2 upon contact with acids and shows IR absorptions typical of both mono- and bidentate *N*,*N*-diethylcarbamato groups (1650 and 1540 cm^{-1}, respectively).[1] Much to our surprise, the new compound had analytical data compatible with a O_2CNEt_2/Ta molar ratio of 2 rather than 3, while the absence of strong absorptions in the visible region suggested the oxidation state of V for the central metal atom. The presence of μ-oxo ligands was therefore anticipated. Compound **3** was recrystallized from toluene/heptane to give well-formed, almost colorless single crystals. On the basis of an X-ray diffraction experiment, the compound has been identified (vide infra) as the μ-oxo-*N*,*N*-diethylcarbamato derivative of tantalum(V), $Ta_8(\mu\text{-}O)_{12}(O_2CNEt_2)_{16}$. A representation of the molecular structure is in Figure 1. Table 2 lists some selected bond distances and angles.

The point symmetry of **3** is $\bar{1}$ (C_s in the Schönflies notation), and the internal cage $Ta_8(\mu\text{-}O)_{12}$ possesses approximate $4/mmm$ (D_{4h}) symmetry. The eight tantalum atoms are located at the vertexes of a cube. The Ta···Ta nonbonding distances are similar and are between 3.60 and 3.67 Å; moreover, each set of four tantalum atoms deviate from their best plane by 0.002 Å (mean value) only. Thus, the eight tantalum atoms define an almost regular cubic cage. The edges of the cube are occupied by the 12 oxygen atoms [O(1)−O(6) and their symmetry-related ones], each bridging two tantalum centers [mean value of the Ta−O−Ta angle = 145.8(2)°]. The six faces of the cube can be divided into three sets differentiated by the different coordination of the ligands, as shown in Figure 2. The mean distance of the bridging oxygen atoms from the ideal plane defined, for example, by Ta(1), Ta(2), Ta(3), and Ta(4) is 0.416 Å for the atoms pointing inside this face [O(2), O(4)] and 0.177 Å for those directed outside [O(1), O(3)]. The tantalum−oxygen bond distance to the bridging oxides averages 1.902(4)

Table 2. A Selection of Bond Lengths (Å) and Bond Angles (deg) of $Ta_8(\mu\text{-}O)_{12}(O_2CNEt_2)_{16}$, **3**[a]

Ta(1)−O(5)	1.884(4)	Ta(3)−O(2)	1.906(4)
Ta(1)−O(4)	1.895(4)	Ta(3)−O(3)	1.893(4)
Ta(1)−O(1)	1.912(4)	Ta(3)−O(5′)	1.924(5)
Ta(2)−O(2)	1.892(4)	Ta(4)−O(4)	1.892(4)
Ta(2)−O(1)	1.894(4)	Ta(4)−O(6′)	1.897(5)
Ta(2)−O(6)	1.926(4)	Ta(4)−O(3)	1.910(4)
O(5)−Ta(1)−O(4)	94.7(2)	O(3)−Ta(3)−O(2)	92.9(2)
O(5)−Ta(1)−O(1)	95.5(2)	O(3)−Ta(3)−O(5′)	96.0(2)
O(4)−Ta(1)−O(1)	92.0(2)	O(2)−Ta(3)−O(5′)	93.2(2)
O(2)−Ta(2)−O(1)	96.4(2)	O(4)−Ta(4)−O(6′)	95.4(2)
O(2)−Ta(2)−O(6)	92.1(2)	O(4)−Ta(4)−O(3)	93.9(2)
O(1)−Ta(2)−O(6)	96.5(2)	O(6′)−Ta(4)−O(3)	96.3(2)
Ta(2)−O(1)−Ta(1)	145.9(2)	Ta(4)−O(4)−Ta(1)	144.2(2)
Ta(2)−O(2)−Ta(3)	143.4(2)	Ta(1)−O(5)−Ta(3′)	147.3(2)
Ta(3)−O(3)−Ta(4)	147.1(2)	Ta(4′)−O(6)−Ta(2)	147.0(2)

[a] Estimated standard deviations refer to the least significant digit. Primed atoms are generated by the symmetry transformation ‘ = −*x*, −*y*, −*z*.

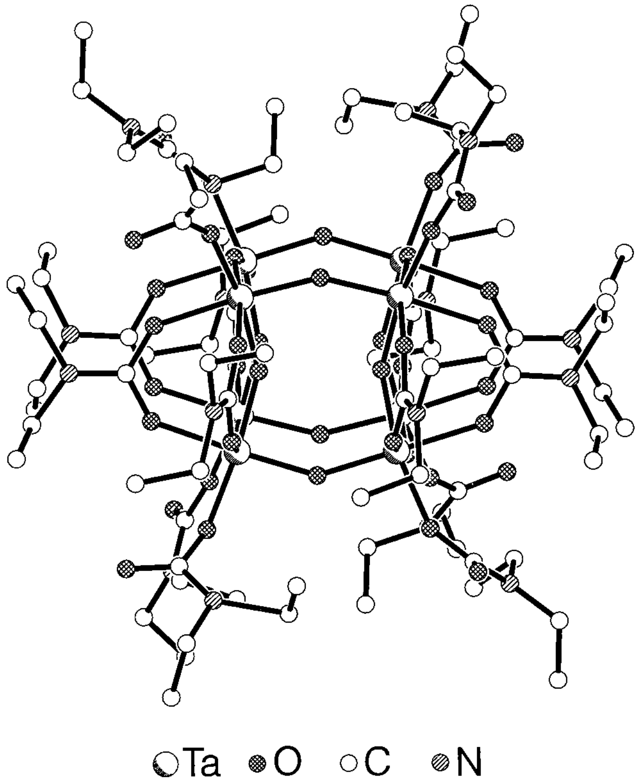

Figure 2. View of $Ta_8(\mu\text{-}O)_{12}(O_2CNEt_2)_{16}$, **3**, through to two opposite faces of the $Ta_8(\mu\text{-}O)_{12}$ polyhedron. Hydrogen atoms have been omitted.

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(7) For dinuclear complexes with bridging carbamato groups, see the following. (a) $Mo_2(\mu\text{-}O_2CNEt_2)_4$ and $Cr_2(\mu\text{-}O_2CNEt_2)_4(NHEt_2)_2$: Belforte, A.; Belli Dell'Amico, D.; Calderazzo, F.; Devillers, M.; Englert, U. *Inorg. Chem.* **1993**, *32*, 2282. (b) $Cu_2(\mu\text{-}O_2CNEt_2)_4(NHEt_2)_2$: Agostinelli, E.; Belli Dell'Amico, D.; Calderazzo, F.; Fiorani, D.; Pelizzi, G. *Gazz. Chim. Ital.* **1988**, *118*, 729. (c) $V_2Cp_2(\mu\text{-}O_2CNEt_2)_4$: Calderazzo, F.; Pampaloni, G.; Sperrle, M.; Englert, U. *Z. Naturforsch.* **1992**, *47B*, 389.

(8) Johnson, C. K. *ORTEPII*; Report ORNL-5138; Oak Ridge National Laboratory: Teneesee, 1976.

Å, comparable with the value found in compounds containing a Ta−O−Ta system.[9]

The 16 *N*,*N*-diethylcarbamato ligands are bonded in two fashions: 8 of them, i.e., those defined by O(11)−O(12), O(21)−O(22), O(31)−O(32), and O(41)−O(42), and the symmetry-related ones, act as bridging groups, and the others, bonded to tantalum through O(51), O(61), O(71), O(81), and the symmetry-related oxygen atoms, behave as monodentate ligands. Each tantalum atom is therefore surrounded by three μ-oxo ligands and by three oxygen atoms of three *N*,*N*-diethylcarbamato groups. The tantalum coordination polyhedron is a distorted octahedron (Figure 1), the mean O−Ta−O angles being 170.9(2)° and 91.8(2)° for the trans and cis oxygen atoms, respectively (the bite of the bridging *N*,*N*-diethylcarbamato group is 2.25 Å, mean value).[10]

The O_2CNEt_2 groups are substantially planar (mean deviation from the ideal plane = 0.053 Å), with the bridging ligands being almost perpendicular to each other [the mean value of the angle is 86.2(1)°]. The mean Ta−O bond distance (monodentate ligands) is 1.949(4) Å; the Ta−O distances within the bridging ligands are larger and average 2.093(4) Å. The bridging *N*,*N*-diethylcarbamates are almost symmetrically bonded to tantalum [for example, Ta(1)−O(21) = 2.110(4) Å; Ta(4)−O(22) = 2.114(4) Å; Ta(2)−O(31) = 2.080(5) Å; Ta(3)−O(32) = 2.081(4) Å]. The monodentate O_2CNEt_2 groups show C−O distances [mean values = 1.338(8) and 1.211(9) Å] comparable to those found in $Ta(O_2CNEt_2)_5$ [1.318(9) and 1.207(9) Å].[1] As expected, the C−O bond distances within the bridging *N*,*N*-diethylcarbamato groups do not show significant differences [mean value = 1.281(8) Å]. The O−C−O angle within the monodentate groups is 122.1(7)°, to be compared with 123.6(6)° observed in the case of the bidendate, bridging ligands; both values are similar to those observed in $Ta(O_2CNEt_2)_5$ [115.0(7) and 123.5°].[1]

To the best of our knowledge, the internal framework of **3** represents a rather peculiar structural situation. A tetranuclear derivative of oxo-tantalum(V), $[TaOCl_2(O_2CC_6H_4Me\text{-}p)]_4$ has recently been shown[9c] to have an arrangement of tantalum atoms and bridging oxides reminiscent of half the cage observed in compound **3**. Although topologically similar frameworks may be recognized as parts of both more extended ions such as $[M_xO_y]^{z-}$, M = V, Mo, W[11] and infinite structures such as ReO_3,[12] **3** represents the first example of a molecular $M_8(\mu\text{-}O)_{12}$ cage containing an element of the transition series such as tantalum. The oxide/tantalum molar ratio being 1.5, compound **3** belongs to the class of sesquioxides, which is well represented within nontransition elements. Similar cages have been observed in octanuclear octasubstituted sesquioxanes containing silicon.[13,14]

The formation of **3**, a derivative of tantalum(V), during the reduction of $TaCl_2(O_2CNEt_2)_3$ with 2 equiv of sodium requires some considerations. Compound **3** contains two carbamato groups and 1.5 oxides per tantalum atom. Particularly intriguing is the origin of the 12 bridging oxides, 8 of them corresponding to the oxidation of tantalum(III) (potentially arising from the treatment with 2 equiv of sodium) to tantalum(V). We have reported in the past the formation of bridging oxides by controlled hydrolysis of homoleptic *N*,*N*-dialkylcarbamato derivatives.[15] Obviously, a hydrolytic process does not alter the oxidation state of the metal, unless some concomitant redox process occurs, for example, formation of dihydrogen. Compound **3** was obtained in good yields special care was taken to avoid the presence of moisture, and no H_2 was found in the gas phase after the reaction; it was therefore concluded that (i) 8 of the 12 bridging oxides originate from a redox process not involving water, (ii) adventitious water (as such) was not the source of the 4 remaining μ-oxo ligands in **3**, and (iii) a dehydration process of some kind was involved in the formation of the four bridging oxides. The literature teaches that (a) dehydration of THF to 1,3-butadiene[16] occurs in the presence of titana or alumina and (b) deoxygenation of CO_2 has been found[17] in the $Zn/CO_2/NHEt_2$ system giving *N*,*N*-diethylformamide. Thus, the skeletal oxygen atoms of **3** must arise from carbon dioxide (as such or as a constituting fragment of the *N*,*N*-diethylcarbamato ligand) and THF.

The mother liquor after the isolation of **3** was found (by GC−MS) to contain *N*,*N*-diethylformamide. This leads us to suggest that **3** most likely self-assembles through both a tantalum-mediated dehydration of THF and CO_2-deoxygenation.[18] The formation of **3** from $TaCl_2(O_2CNEt_2)_3$ and sodium in THF may therefore be represented as described in eq 2.

$$8TaCl_2(O_2CNEt_2)_3 + 16Na + 4C_4H_8O \rightarrow Ta_8(\mu\text{-}O)_{12}(O_2CNEt_2)_{16} + 8HCONEt_2 + 16NaCl + 4\{C_4H_6\} \quad (2)$$

It has to be pointed out that the sodium cation must be involved in the process, since the $CoCp^*_2$/THF reducing system yields $Ta(O_2CNEt_2)_3$ only. Sodium coordination may be required for the dehydration of THF.

The formation of **3** has to be considered an example that adds to the still limited number of oxo-*N*,*N*-dialkylcarbamates[17,19] obtained by a route not involving the presence of water as such.

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(18) The experimentally observed lack of reactivity of **2** with THF (it is stable for months in this medium) excludes the possibility that $Ta(O_2CNEt_2)_3$ is responsible for the THF activation. On the other hand, all attempts to obtain **3** by controlled hydrolysis of $Ta(O_2CNEt_2)_3$, $Ta(O_2CNEt_2)_5$, or $TaCl_2(O_2CNEt_2)_3$ failed.

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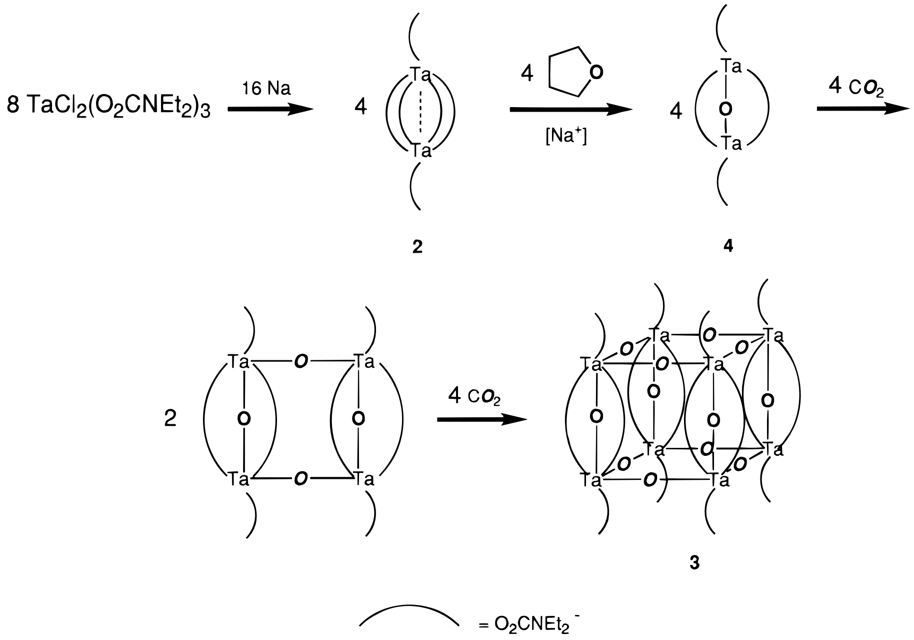
Scheme 1



Concluding Remarks

In the presence of sodium, $TaCl_2(O_2CNEt_2)_3$ undergoes a transformation mediated by THF and CO_2 (the latter as such or combined in the *N*,*N*-diethylcarbamato ligands through a concerted mechanism involving coordinated THF) to give the first example of an uncharged octanuclear oxo-tantalum cage of formula $Ta_8(\mu\text{-}O)_{12}(O_2CNEt_2)_{16}$. An important relation can be found between the structure we propose for **2** and the octanuclear cage of **3**; if **2** provided the building block $[Ta_2(\mu\text{-}O)(O_2CNEt_2)_4]$, **4**, by THF dehydration, **3** would be obtained by further deoxygenation of CO_2 and by stepwise fusion of the binuclear units via the oxide bridges; see Scheme 1.

The surprising selectivity of the process leading to the μ-oxo cage compound **3** suggests the possibility of using the THF/"CO_2" route for the synthesis of similar compounds within the transition d series.

Acknowledgment. Work was supported by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST), by the Consiglio Nazionale delle Ricerche (C. N. R., Roma), and by the Fonds der Chemischen Industrie. Part of the work has been carried out by P.B.A. at the Universität Tübingen, within the framework of an Erasmus program (Contract ICP-95-UK-2044/13). Thanks are due to Prof. Dr. H. P. Fritz, Technische Universität München, Germany, for providing the facilities to carry out the GC−MS measurements.

Supporting Information Available: Tables of structural data for **3**, which include positional parameters of non-hydrogen atoms, positional parameters of hydrogen atoms, full list of bond distances and angles, and thermal parameters, are available, in CIF format, on the Internet only. Access information is given on any current masthead page.

IC980408L