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# Synthesis, Structural and Spectroscopic Characterization, Catalytic Properties, and Thermal Transformations of New Cyclic Di- and Trisiloxanediolato Tantalum Complexes

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The reaction between $Ta(OEt)_5$ and 1,1,3,3-tetramethyl-1,3-disiloxanediol, ($HOSiMe_2OSiMe_2OH$), leads to new siloxy complexes in which the dimeric nature of $Ta(OEt)_5$ is maintained with both bridging ethoxide and disiloxanediolato bridges. With equal amounts of the reagents, two terminal OEt groups are replaced to form $[Ta(OEt)_2]_2(\mu\text{-}OEt)_2(\mu\text{-}OSiMe_2OSiMe_2O)_2$, **1**, whereas with an excess of diol, the remaining terminal OEt groups are also replaced but with a trisiloxanediolato unit to form $[Ta(OSiMe_2OSiMe_2OSiMe_2O)]_2(\mu\text{-}OEt)_2(\mu\text{-}OSiMe_2OSiMe_2O)_2$, **2**. Complexes **1** and **2** catalyze the transformation of $HOSiMe_2OSiMe_2OH$ to polysiloxanes. Thermal treatment of **1** results in the formation of a 1:2 mixture of $Ta_2O_5/SiO_2$; no new phases are observed. The molecular structures of **1** and **2** are confirmed by X-ray crystallography.

## Introduction

The synthesis and characterization of metallasiloxanes is an area that has been extensively studied and has included both main group and transition metal systems.[1] The inclusion of metal centers into the siloxane structures has the potential for interesting new materials with unusual magnetic and conducting properties plus providing insight into possible catalytic metal oxide surfaces. In general, metallasiloxanes can be formed by the reaction of alkali metal salts of the corresponding $[O-(SiR_2)_n-O]^{2-}$ siloxanediolato species with metal halides or, less frequently, via the use of $\alpha,\omega$-siloxane diols with amides or alkoxides.

The use of such silanols or siloxanediolates sometimes results in oligomerization of the silyl species, and for example, the reaction of $Ph_2Si(OH)_2$ with $Ti(O\text{-}{}^iPr)_4$ results in the formation of a bis-(tetrasiloxanediolato)titanium product, $Ti\{(OSiPh_2)_4O\}_2$.[2a,2b] On the other hand, the related disilanol $({}^tBu)_2Si(OH)_2$ results in nonoligomerized products, suggesting that the bulk of the R substituent on silicon is a determining factor.[2c]

In the few examples where disiloxane diols that are reported to react with metal complexes, products with both the disiloxanediolato and its oligomers have been observed. For example, the so-called "intact transfer" occurred from the reaction of $HOSiPh_2OSiPh_2OH$ with bis-(*tert*-butylamido)molybdenum chloride in the presence of pyridine to form $({}^tBuN)Mo\{O(Ph_2SiO)_2\}_2 \cdot py$ with the disiloxanediolato group acting as a bidentate chelate ligand.[3a] On the other hand, the reaction of the same diol with $[{}^tBuOGaH_2]_2$, in a 2:1 ratio, resulted in the formation of trisiloxanediolato ($OSiPh_2OSiPh_2OSiPh_2O$) and tetrasiloxanediolato ($OSiPh_2OSiPh_2OSiPh_2OSiPh_2O$) oligomerized derivatives.[3b] A similar pyridine-stabilized bis-trisiloxanediolato chelate complex $Py_2Ti(OSiPh_2OSiPh_2OSiPh_2O)_2$ was formed from the reaction of $[OSiPh_2OSiPh_2OSiPh_2O]^{2-}\ 2Li^+$ with titanium tetrachloride in the presence of pyridine.[3c] The reaction of $HOSiPh_2OSiPh_2OH$ with $KO^t$-

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Bu also led to ring-expanded products.[3d] A search of the literature did not find any related complexes with simple alkyl substituents on silicon.

Tantalum is a refractory metal, and we have a recent interest in the formation of new siloxanediolato complexes and their possible use as single-source molecular precursors to new Ta/Si oxide materials. A scattering of tantalum monosiloxy compounds have appeared in the literature, for example, $Ta(OSiMe_3)_5$,[4a] $Cl_2Ta\{OSi(^tBu)_3\}_3$,[4b] and $Cl_3Ta\{OSi(^tBu)_3\}_2$.[4c] Also using a bulky silanetriol, Roesky et al. have reported the formation of a tantalum siloxane cage compound containing the condensed disiloxanediolato unit.[4d] A more direct way into the disiloxanediolato tantalum complexes was reported by Sullivan et al. by the reaction between $[OPh_2SiOSiPh_2O]^{2-}\ 2Li^+$ and $TaCl_5$.[4e] Finally, reactions between incompletely condensed silsesquioxanes and $Ta(NMe_2)_5$ produced tantalum silsesquioxanes which can be viewed as model compounds for silica-immobilized heterogeneous catalysts[5a−c]

There appear to be no significant studies on the interactions of siloxanediols with tantalum alkoxides or amides and no reports of the utility of alkyl siloxanediols to form metallasiloxane materials. Thus, we have initiated such a study and report the results of the reactions of tantalum ethoxide with 1,1,3,3-tetramethyl-1,3-disiloxanediol.

## Experimental Section

Since the tantalum alkoxides hydrolyze readily, all operations were conducted in dry, oxygen-free nitrogen or argon. Solvents were dried over Na/benzophenone and freshly distilled under nitrogen prior to use. Tantalum pentaethoxide was purchased from Gelest and was distilled immediately prior to use; 1,1,3,3-tetramethyl-1,3-disiloxanediol, $(HOMe_2Si)_2O$, was prepared according to literature procedure.[6] Since the siloxanediol condenses easily in acidic medium, all the glass apparatus used was washed with water and dried in an oven prior to use. NMR spectra of all compounds were recorded on a Bruker 300 MHz spectrometer, and elemental analyses were performed by Galbraith Laboratories.

**Reaction of Tantalum Pentaethoxide with 1,1,3,3-Tetramethyl-1,3-siloxanediol, (1:1).** To a solution of tantalum pentaethoxide (1.9 g, 4.7 mmol) in benzene (50 mL) was added 1,1,3,3-tetramethyl-1,3-disiloxanediol (siloxanediol) (0.78 g, 4.7 mmol). The mixture was stirred until a clear solution was obtained, the mixture was refluxed for 1 h under a fractionating column, and the liberated ethanol was removed as the ethanol−benzene azeotrope. Final removal of the solvent, in vacuo, yielded a white solid that was recrystallized from hexane to yield $[Ta(OEt)_3(OSiMe_2OSiMe_2O)]_2$, **1**, 80%. mp = 178−179 °C.; Anal. Calcd for $C_{10}H_{27}O_6Si_2Ta$. C, 25.00; H, 5.66. Found: C, 24.24; H, 5.16. NMR Data ($C_6D_6$, ppm ): $^1H$ NMR: 0.14 (12 H; $SiMe_2$); 1.26 (3 H, t, $J$ = 6.9 Hz, terminal $OCH_2\mathit{CH_3}$); 1.34 (3H, t, $J$ = 6.9 Hz, bridging $OCH_2\mathit{CH_3}$); 4.42(2H, q, $J$ = 6.9 Hz, bridging $O\mathit{CH_2}CH_3$); 4.55 (2H, q, $J$ = 6.9 Hz, terminal $O\mathit{CH_2}CH_3$). $^{13}C$ NMR: 2.16 (Si−$CH_3$); 19.56; 18.02 ($CH_2CH_3$); 70.17, 68.71 ($CH_2CH_3$). $^{29}Si$ NMR: −18.2.

**Reaction of Tantalum Pentaethoxide with 1,1,3,3-Tetramethyl-1,3-siloxanediol, (1:3).** To a solution of tantalum pentaethoxide (3.89 g, 9.6 mmol) in benzene (60 mL) was added the siloxane diol (4.8 g, 28.8 mmol). The mixture was refluxed for 1 h under a fractionating column, and the liberated ethanol was removed as the ethanol−benzene azeotrope. Final removal of excess of the solvent, in vacuo, produced a viscous oily/solid material. Recrystallization using acetone yielded a white material in low yield, $[Ta(OEt)(SiMe_2)_5O_7]_2$, **2**, 15%. mp = 178 °C.; Anal. Calcd for $C_{12}H_{35}O_8Si_5Ta$: C, 22.91; H, 5.61. Found: C, 22.53; H, 5.64. NMR Data ($C_6D_6$, ppm ): $^1H$ NMR: 0.37 (30 H Si−$CH_3$); 1.24 (3H, t, $J$ = 6.9 Hz, $OCH_2\mathit{CH_3}$); 4.01 (2H, q, $J$ = 6.9 Hz, $O\mathit{CH_2}CH_3$); $^{13}C$ NMR: 0.89, 1.07, 1.42, (Si−$CH_3$); 17.03 ($CH_2\mathit{CH_3}$); 69.04 ($\mathit{CH_2}$-$CH_3$). $^9Si$ NMR: −15.7; −17.6; −20.6.

The same product **2** was obtained when the reaction was carried out with a 1:2 ratio of Ta/Si starting reagents with a yield of 20%. Crystals suitable for an X-ray crystal structure determination were obtained after recrystallization from hexane.

The viscous oily/solid residue, obtained in addition to the crystalline product **2**, was slightly soluble in THF. The $^{29}Si$ NMR shows a single resonance at −21 ppm, indicating siloxane polymer and a GPC analysis recorded a $M_w$ of 4100. Upon storage over several weeks, the viscous solid becomes a glassy insoluble material.

**Crystal Structure Determination.** A colorless irregular fragment of approximate dimensions 0.26 × 0.26 × 0.13 $mm^3$ was used for the X-ray crystallographic analysis of compound **2**. The X-ray intensity data were measured at 100(2) K on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and Mo Kα fine-focus sealed tube ($\lambda$ = 0.71073 Å) operated at 1.5 KW power (50 KV, 30 mA). The detector was placed at a distance of 4.957 cm from the crystal.

A total of 2400 frames was collected with a scan width of 0.3° in $\omega$ and an exposure time of 10 s/frame. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The integration of the data using an orthorhombic cell yielded a total of 63 757 reflections to a maximum $\theta$ angle of 27.50°, of which 6000 were independent with a $R_{int}$ = 0.033. The unit cell constants $a$ = 12.6917(4) Å, $b$ = 17.1502(5) Å, $c$ = 23.9634(7) Å, and $\alpha = \beta = \gamma = 90°$ are based upon refinement of 8470 reflections above $20\sigma(I)$ with $4.7° < 2\theta < 66.7°$. Analysis of the data showed no significant decay during the 10.2 h of data collection. Data were corrected for absorption effects using the multiscan technique (Bruker SADABS program V2.03),[7] with minimum and maximum transmission coefficients of 0.3892 and 0.5939, respectively.

The structure was solved and refined using the Bruker SHELXTL software package V6.1012.[7] The final anisotropic full-matrix least-squares refinement on $F^2$ with 281 variables converged at R1 = 0.0282 for the observed data and wR2 = 0.0845 for all data. The GOF was 1.355. The largest peak on the final difference electron density synthesis was 1.705 e/Å$^3$.

For compound **1**, a colorless plate of approximate dimensions 0.27 × 0.26 × 0.13 $mm^3$, was used in a data collection similar to

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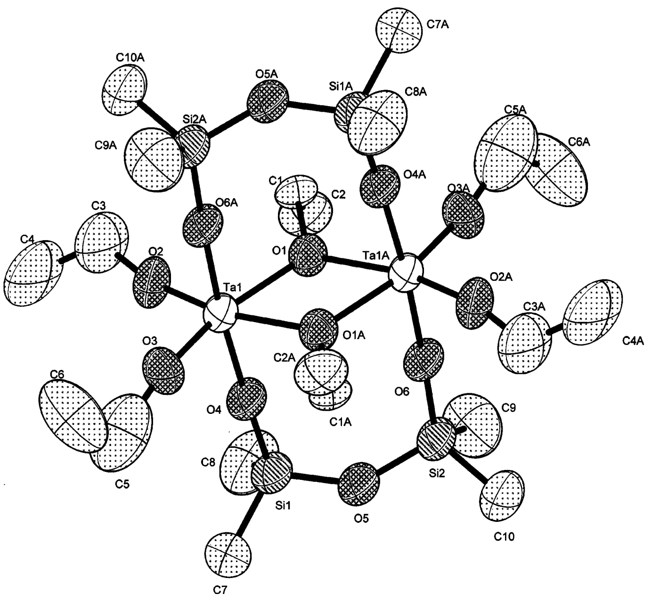


**Figure 1.** Structure of **1**.

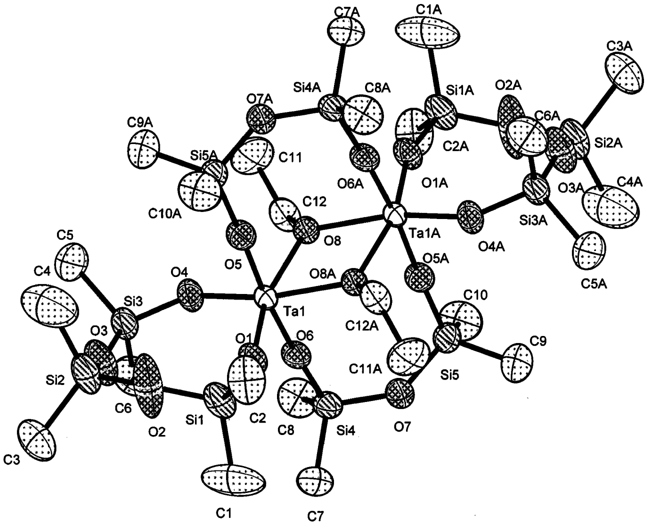


**Figure 2.** Structure of **2**.

that of **2** in the same Bruker SMART APEX system. The 2400 frames collected were also integrated with the Bruker SAINT software. Integration using a triclinic cell yielded 8805 reflections to a maximum $\theta$ angle of 23.25°, of which 2825 were independent with a $R_{\text{int}} = 0.040$. The cell constants $a = 9.2043(8)$ Å, $b = 10.7671(10)$ Å, $c = 11.8911(11)$ Å and $\alpha = 103.649(2)$, $\beta = 111.626(2)$, and $\gamma = 105.234(2)°$ were obtained from least-squares refinement of 995 reflections above $20\sigma(I)$ with $5.2° < 2\theta < 58.21°$. The Bruker SADABS program was also used for absorption correction, yielding minimum and maximum transmission coefficients of 0.3066 and 0.5227, respectively. Structure refinement on $F^2$ produced an $R1 = 0.0378$ for observed data and $wR2 = 0.0978$ for all data and a GOF of 1.083. All the ethoxy groups in **1** are disordered, the bond distances in all of them were constrained to keep them similar, and the site occupancy factors of corresponding parts left to refine as free variables adding up to 1.00 for the two disordered parts in each one of the ethoxy groups.

In Figures 1 and 2, the structures of **1** and **2** have been drawn at a probability level of 50% for the thermal ellipsoids with only one of the disordered parts shown in the case of **1** for the sake of clarity.

**Table 1.** Crystal Data for **1** and **2**

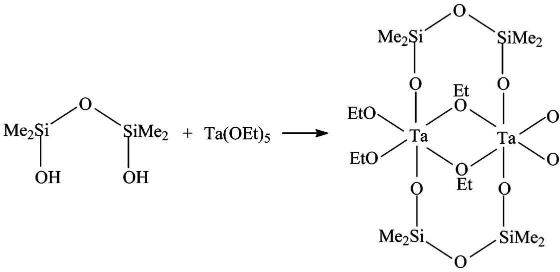
| | **1** | **2** |
|---|---|---|
| source | synthesis | synthesis |
| cryst color | colorless | colorless |
| cryst habit | thin plate | prism |
| cryst size/mm$^3$ | 0.27 × 0.26 × 0.13 | 0.26 × 0.26 × 0.13 |
| $a$/Å | 9.2043(8) | 12.6917(4) |
| $b$/Å | 10.7671(10) | 17.1502(5) |
| $c$/Å | 11.8911(11) | 23.9634(7) |
| $\alpha$/deg | 103.649(2) | 90 |
| $\beta$/deg | 111.626(2) | 90 |
| $\gamma$/deg | 105.234(2) | 90 |
| $V$/Å$^3$ | 981.55(15) | 5216.0(3) |
| cryst syst | triclinic | orthorhombic |
| space group | $P\bar{1}$ | $Pbca$ |
| Z | 1 | 8 |
| $D_{\text{calcd}}$/g cm$^{-3}$ | 1.626 | 1.601 |
| $\mu$/mm$^{-1}$ | 5.735 | 4.474 |
| absorption correction | Bruker SADABS program | Bruker SADABS program |
| temp/°C | 23(2) | −173(2) |
| wavelength | 0.71073 Å | 0.71073 Å |
| monochromator | graphite | graphite |
| diffractometer | Bruker SMART with Apex CCD | Bruker SMART with Apex CCD |
| reflns collected | 8805 | 63757 |
| independent reflns | 2825 [$R_{\text{int}} = 0.0397$] | 6000 [$R_{\text{int}} = 0.0331$] |
| structure solution technique | direct methods | direct methods |
| structure solution program | SHELXS-97 (Sheldrick, 1990) | SHELXS-97 (Sheldrick, 1990) |
| refinement technique | full-matrix least-squares on $F^2$ | full-matrix least-squares on $F^2$ |
| refinement program | SHELXS-97 (Sheldrick, 1997) | SHELXS-97 (Sheldrick, 1997) |
| function minimized | $\sum w(F_o^2 - F_c^2)^2$ | $\sum w(F_o^2 - F_c^2)^2$ |
| GOF on $F^2$ | 1.082 | 1.032 |
| R1,[a] wR2[b] [$I > 2\sigma(I)$] | 0.0376, 0.0926 | 0.0276, 0.0695 |
| R1,[a] wR2[b] (all data) | 0.0449, 0.0986 | 0.0373, 0.0790 |

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum [w(F_o^2 - F_c^2)^2]/\sum [w(F_o^2)^2]\}^{1/2}$.

Relevant crystal and refinement parameters are given in Table 1; selected bond lengths and angles are provided in Table 2.

## Results and Discussion

**Synthesis and Characterization of 1 and 2.** The reaction between tantalum ethoxide and 1,1,3,3-tetramethyl-1,3-disiloxanediol in stoichiometric amounts was rapid and led to high yields of the 1:1 complex, **1**, eq 1.



(1)

**1**

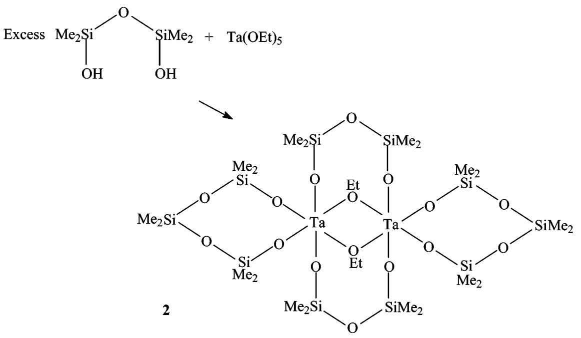
The $^1$H, $^{13}$C, and $^{29}$Si NMR spectral data are in all accord with the proposed structure. Thus, the $^{29}$Si resonance at −18.2 ppm is typical of such a grouping, and distinct $^{13}$C resonances for both the bridging and terminal ethoxide groups can be observed. The structure of **1** is presented in Figure 1 and confirms the spectroscopic data. It clearly indicates that the siloxanediol has formed a pair of bridges between the two tantalum atoms maintaining the dimeric nature of the starting $Ta(OEt)_5$.[8]

**Table 2.** Selected Bond Lengths and Angles for **1** and **2**

| | | | | | |
|---|---|---|---|---|---|
| Compound **1**[a] | | | | | |
| Ta1−O2 | 1.866(7) | Ta1−O3 | 1.858(6) | Ta1−O6A | 1.918(5) |
| Ta1−O4 | 1.925(5) | Ta1−O1 | 2.098(5) | Ta1−O1A | 2.108(5) |
| Si1−O4 | 1.589(6) | Si1−O5 | 1.599(7) | Si2−O6 | 1.593(6) |
| Si2−O5 | 1.628(7) | O1−Ta1A | 2.108(5) | O6−Ta1A | 1.918(5) |
| O2−Ta1−O3 | 102.4(3) | O2−Ta1−O6A | 91.9(3) | O3−Ta1−O6A | 91.1(3) |
| O2−Ta1−O4 | 91.1(3) | O3−Ta1−O4 | 91.3(3) | O6A-Ta1−O4 | 175.6(2) |
| O2−Ta1−O1 | 93.5(3) | O3−Ta1−O1 | 164.1(3) | O6A-Ta1−O1 | 88.0(2) |
| O4−Ta1−O1 | 88.7(2) | O2−Ta1−O1A | 163.7(3) | O3−Ta1−O1A | 93.8(3) |
| O6A-Ta1−O1A | 88.4(2) | O4−Ta1−O1A | 87.8(2) | O1−Ta1−O1A | 70.3(2) |
| O4−Si1−O5 | 109.5(3) | O6−Si2−O5 | 109.6(3) | Ta1−O1−Ta1A | 109.7(2) |
| Si1−O4−Ta1 | 175.1(4) | Si1−O5−Si2 | 142.7(4) | Si2−O6−Ta1A | 172.0(5) |
| Compound **2**[b] | | | | | |
| Ta1−O1 | 1.880(2) | Ta1−O4 | 1.888(3) | Ta1−O6 | 1.911(3) |
| Ta1−O5 | 1.912(3) | Ta1−O8 | 2.106(2) | Ta1−O8A | 2.112(2) |
| Si1−O2 | 1.620(4) | Si1−O1 | 1.623(3) | Si2−O2 | 1.593(4) |
| Si2−O3 | 1.615(3) | Si3−O3 | 1.608(3) | Si3−O4 | 1.628(3) |
| Si4−O6 | 1.619(3) | Si4−O7 | 1.623(3) | Si5−O5A | 1.620(3) |
| Si5−O7 | 1.626(3) | | | | |
| O1−Ta1−O4 | 101.55(12) | O1−Ta1−O6 | 92.60(10) | O4−Ta1−O6 | 91.25(11) |
| O1−Ta1−O5 | 92.16(11) | O4−Ta1−O5 | 91.05(11) | O6−Ta1−O5 | 174.20(11) |
| O1−Ta1−O8 | 162.70(11) | O4−Ta1−O8 | 95.74(11) | O6−Ta1−O8 | 86.32(9) |
| O5−Ta1−O8 | 88.15(9) | O1−Ta1−O8A | 92.36(10) | O4−Ta1−O8A | 166.02(11) |
| O6−Ta1−O8A | 89.54(9) | O5−Ta1−O8A | 86.95(9) | O8−Ta1−O8A | 70.37(10) |
| O2−Si1−O1 | 107.96(18) | O2−Si2−O3 | 109.5(2) | O3−Si3−O4 | 108.12(17) |
| O6−Si4−O7 | 109.46(14) | O5A-Si5−O7 | 109.66(13) | Si1−O1−Ta1 | 160.66(18) |
| Si2−O2−Si1 | 152.3(3) | Si3−O3−Si2 | 154.0(2) | Ta1−O8−Ta1A | 109.63(10) |
| Si4−O6−Ta1 | 173.41(18) | Si4−O7−Si5 | 139.55(18) | Si3−O4−Ta1 | 152.80(18) |
| Si5A−O5−Ta1 | 166.15(18) | | | | |

[a] Symmetry transformation used to generate equivalent atoms A: $-x + 1, -y + 1, -z + 1$. [b] Symmetry transformation used to generate equivalent atoms A: $-x, -y + 1, -z + 1$.

The reaction between $Ta(OEt)_5$ and $(HO)Me_2SiOSiMe_2(OH)$ with a stoichiometric ratio of 1:2, or higher, leads to a mixture of siloxane polymer and a new molecular species, **2**, the latter being recovered in ∼15−20% yields, eq 2.



(2)

**2**

Spectroscopic analysis of **2** indicated the presence of only bridging ethoxide groups, i.e., the complete absence of terminal ethoxide groups. Furthermore, the $^{29}$Si spectrum indicated the presence of three types of $O-Me_2Si-O$ structural unit, −15.7, −17.6, and −20.6 ppm. This suggested that in addition to the bridging disiloxane unit noted in **1**, the terminal OEt groups had also been replaced by siloxane units but with the possible incorporation of one or more dimethylsilyl units in manner reminiscent of those oligomerizations noted in the Introduction. This latter suggestion is also in accord with a third $^{13}$C resonance associated with another $Me_2Si$ group.

X-ray-quality crystals of **2** were obtained by recrystallization from hexane, and the molecular structure is shown in Figure 2. The structure illustrates that, as with **1**, a disiloxanediolato bridge between the two Ta atoms maintains the dimeric nature of the tantalum complex along with a pair of ethoxide bridging units. In place of the terminal ethoxide ligands of **1**, we now have a trisiloxanediolato unit acting as a bidentate chelating ligand, in agreement with the $^{13}$C and $^{29}$Si NMR data.

As noted above, similar ring enlargements have been observed for metallasiloxane systems derived from the aryl disiloxanediol $HOSiPh_2OSiPh_2OH$ in the form of the alkali metal (K) salt[3d] and a titanium complex obtained by reacting such alkali metal salts (Li) with $TiCl_4$.[3c] Mechanisms involving nucleophilic attack by $[R_3Si-O]-M^+$ at the silicon of a prior coordinated metallasiloxane, where by implication this atom is activated by the metal, were proposed. In the present case, where no alkali metal salts are present, the Ta coordination may be sufficient to suggest a strong polarization of the Si−O−Ta linkage, permitting a related nucleophilic attack at this Si atom by the diol. However, we have not examined this process in any detail with the exception of noting the capacity of the complex **1**, and to a lesser extent **2**, to act as catalysts for the oligomerization of the starting diol, vide infra.

**Discussion of Structures.** In both structures, each molecule consists of two asymmetric units related by a center of symmetry resulting in a distorted octahedral coordination of oxygen around each of the tantalum atoms as shown in Figures 1 and 2. In **1**, the two axial Ta−OSi distances of 1.918(5) and 1.925(5) Å are shorter than the data reported

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(8) (a) Bradley, D. C.; Chakravarti, B. N.; Wardlaw, W. *J. Chem. Soc.* **1956**, 4439; 2381. (b) Bradley, D. C.; Wardlaw, W.; Whitley, A. *J. Chem. Soc.* **1956**, 1139; **1955**, 726.

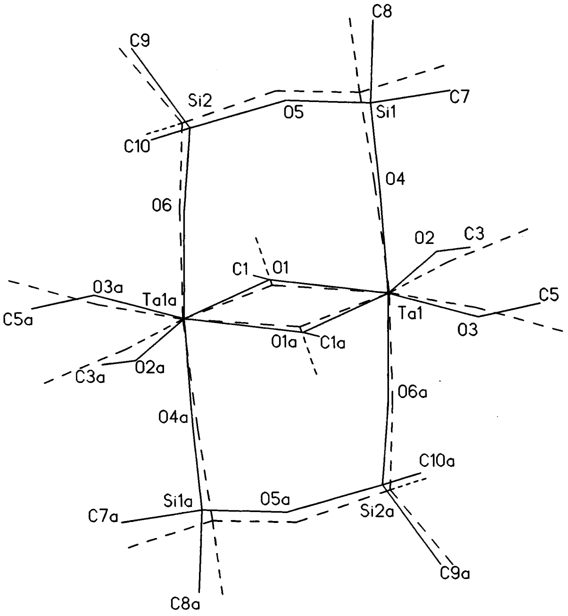

**Figure 3.** Superpositioning of the core sections of **1** and **2**.

for the axial Ta−OSi bonds in Ta(OSiPh$_2$OSiPh$_2$O)$_3$, 1.951(4) and 1.974(3) Å, but similar to the equatorial bond lengths in that compound, 1.918((4) and 1.945(3) Å.[4e] The alkoxide O−Ta bond lengths are in accord with expectations where the bridging Ta−O lengths are significantly longer than the terminal analogues, e.g., 2.098(5) and 2.108(5) Å versus 1.866(7) and 1.858(6) Å, respectively. The bond angles are typical of a distorted octahedral structure of a dimeric material. The bridging O1−Ta1−O1A angle is small, 70.3°, while the related angle between the two terminal ethoxide groups O3−Ta1−O2 has expanded beyond the normal 90° due to the angular constriction of the bridging units, 102°. The various Si−O bond lengths are statistically similar and exhibit no significant unsymmetrical polarization as reported for the Ta complex noted above.[4e]

In terms of the local structure at Ta, complex **2** is almost identical with that of **1**, as can be seen in the superposition of these parts in Figure 3. Also, the Si−O bond lengths are all similar within experimental error.

A search in the Cambridge Crystallographic Data Base, including the February, May, and August 2005 updates, yielded no examples of O−SiMe$_2$−O−SiMe$_2$−O groups forming a metallacycles. However, there are several structures reported with phenyl or other groups attached to silicon in the bridging siloxanes. The gallium systems by Veith et al.,[3b] the tantalum cage complex by Roesky et al.,[4d] the tantalum,[4e] hafnium,[9a] and sodium[9b] complexes of Sullivan et al., and aluminum complexes by Gun'ko et al. may be cited as examples.[9c] None of these, as well as other examples, consist of two symmetrically related parts forming the axial double ring exhibited by **1** and **2**. Furthermore, in the above-mentioned references, only a single tantalum siloxanediolato example was found that contains Ta−O−Ta bridges similar to those in **1** and **2**. However, in that case, two of the three Ta-bridging oxygens belong also to the disiloxanediolato bridge, forming a cage complex.[4d] In the cases of the gallium di- and trisiloxanediolato[3b] and aluminosiloxanediolato,[9c] similar chelate rings to those in **1** and **2** are present but with the corresponding gallium and aluminum atoms possessing tetrahedral coordination as opposed to the octahedrally coordinated tantalum atoms found in **1** and **2**. Complex **2** is the first example of a tantalum complex with di- and trisiloxane moieties in the same molecule formed as a result of 2:1 and greater disiloxanediol/Ta(OEt)$_5$ ratios. A similar effect occurs in the case of the gallium reactions where increasing the amount of disiloxanediol yielded products resulting from oligomeric forms of the diol. However, in this example, no di- and trisiloxanediolato groups are both present in the same molecule in either of the products.

**Thermal Treatment of 1 and 2.** Su and Tilley have reported that thermal decomposition of siloxy derivatives of molybdenum provided a potentially interesting route to new materials with significant catalytic interest.[10] We have studied the thermal decomposition of the new complexes, and the resulting material obtained at 900 °C analytically represented a residue of Ta$_2$O$_5$/2SiO$_2$. This material was shown to be essentially amorphous by powder XRD measurements; however, after further thermal treatment at 1100 °C for 4.5 h, it was transformed to a crystalline material whose powder XRD indicated it was $\delta$-Ta$_2$O$_5$.[11] The SiO$_2$ present is still amorphous, and no new forms of material were observed.

**Catalytic Properties of 1 and 2.** The transformation of **1** to **2** by excess disiloxanediol suggested that it was responsible for the transformation of a disiloxane unit to a trisiloxane unit. We therefore investigated the catalytic properties of **1** in the presence of an excess of the starting 1,1,3,3-tetramethyl-1,3-disiloxanediol. The reaction was monitored by $^{29}$Si NMR spectroscopy. From this spectral monitoring, we observed that complex **1** is indeed a catalyst for the transformation of the starting disiloxanediol to the dimethylsiloxanes. For example, a mixture containing 35 mg (0.03 mmol) of complex **1** and 0.165 g (1.0 mmol) of the siloxanediol led to the complete loss of diol within 24 h to form a series of siloxane materials that included small amounts of D3 and D4. The analogous process using complex **2** as catalyst was much slower and, for example, complete loss of the diol took 6 days. A distribution of higher siloxanes was formed that progressively changed to a final distribution after several days to result in the $^{29}$Si spectrum recorded in Figure 4. We have not made a detailed effort to characterize the various siloxanes, but from GC/MS analysis and comparison with other reported mixtures of cyclic dimethylsiloxanes, the product distribution ranged from D3 to D15 along with other materials that are probably acyclic analogues. A mixture of either pure D3 or D4 with either **1**

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(9) (a) Motevalli, M.; Shah, D.; Sullivan, A. C. *J. Chem. Soc., Dalton Trans.* **1993**, 2849. (b) Abrahams, I.; Lazell, M.; Motevalli, M.; Shah, S. A. A.; Sullivan, A. C. *J. Organomet. Chem.* **1998**, *553*, 23. (c) Gun'ko, Y. K.; Reilly, R.; Kessler, V. G. *New J. Chem.* **2001**, *25*, 528.

(10) Su, K.; Tilley, T. D. *Chem. Mater.* **1997**, *9*, 588.

(11) Gonzalez, J.; Ruiz, M. Del C.; Riverola, J. B.; Pasquevich, D. *J. Mater. Sci.* **1998**, *33*, 4173.

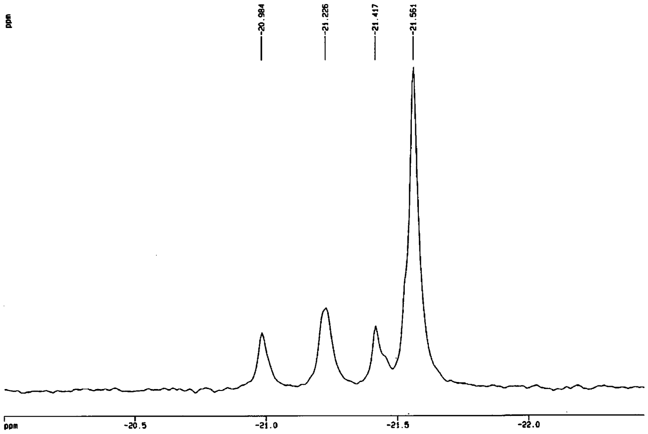

**Figure 4.** $^{29}$Si NMR spectrum of final polymerized product from the catalytic reaction of $HOMe_2SiOSiMe_2OH$ with complexes **1** or **2**.

or **2** resulted in no reaction as monitored by $^{29}$Si NMR. This indicates that the SiOH functionality is required for the oligomerization process to occur and suggests that a nucleophilic attack by the oxygen atom of the $Si-O^{\delta-}-H^{\delta+}$ group on a silicon atom of a coordinated siloxanedioloato Ta intermediate is a key step, similar to the suggestion of Sullivan noted above for the formation of ring enlarged metallasiloxanes.[3c]

Interestingly, HCl acid-catalyzed condensation of 1,3-tetramethyl-1,3-disiloxanediol by itself led to eventual formation of a mixture of mainly D3 and D4 with only trace amounts of higher D*n* materials.[12]

## Summary

We have demonstrated the capacity of the alkyl 1,3-disiloxanediol, $(HO)Me_2SiOSiMe_2(OH)$, to form both disiloxanediolato (**1**) and mixed disiloxanediolato/trisiloxanediolato (**2**) complexes of tantalum derived from $Ta(OEt)_5$. The complexes are dimeric in nature, maintaining the ethoxide bridges and involving both bridging disiloxanediolato (**1** and **2**) and terminal trisiloxandiolato (**2**) bidentate ligand groupings. Complex **2** appears to represent the first example of a ring-enlarged alkyl siloxanediolato complex, and both **1** and **2** are active catalysts in transforming the diol into oligomeric siloxanes.

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**Supporting Information Available:** X-ray crystallographic data in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

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[12] Recrystallized diol was dissolved in $C_6D_6$, and $^{29}$Si NMR spectroscopy indicated a single peak at −10.6 ppm. Addition of a single drop of 6 N HCl resulted in the formation of resonances at −8.5, −10.5, −11.4, −19.5, and −20.5 ppm; after 48 h, only resonances at −8.5, −11.33, −18.7, and −20.5 ppm remained, and after 15 days, two resonances at −8.5 and −18.9 ppm representing D3 and D4, respectively, were present. This conclusion was confirmed by GC/MS and comparison with authentic materials.