The synthesis and structure of $\{[\eta^4\text{-Me}_8\text{taa}]\text{Sn}(\mu\text{-O})\}_2$: a bridging oxo complex in a system that yields terminal sulfido and selenido counterparts

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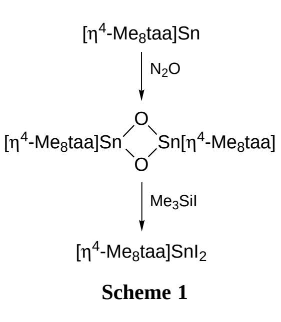
Oxo transfer from N_2O to divalent $[\eta^4\text{-Me}_8\text{taa}]\text{Sn}$ (Me_8taaH_2 = octamethyldibenzotetraaza[14]annulene) yields the oxo complex, $\{[\eta^4\text{-Me}_8\text{taa}]\text{Sn}(\mu\text{-O})\}_2$; the bridging nature of the oxo ligand provides a marked contrast with the terminal sulfido and selenido counterparts, $[\eta^4\text{-Me}_8\text{taa}]\text{SnE}$ (E = S, Se).

Terminal chalcogenido complexes of the transition[1] and main group[2] elements are presently a major focus of our research. For example, with respect to the main group elements, we have employed (*i*) the sterically demanding tris(3,5-di-*tert*-butyl)pyrazolylhydroborato ligand to enable the isolation of terminal chalcogenido complexes of gallium and indium, *i.e.* $[\mathrm{Tp}^{\mathrm{Bu}^t_2}]$GaE (E = S, Se, Te),[3] and $[\mathrm{Tp}^{\mathrm{Bu}^t_2}]$InSe,[4] and (*ii*) the macrocyclic octamethyldibenzotetraaza[4]annulene ligand to support terminal chalcogenido complexes of germanium and tin, *i.e.* $[\eta^4\text{-Me}_8\text{taa}]$GeE (E = S, Se, Te)[5] and $[\eta^4\text{-Me}_8\text{taa}]$SnE (E = S, Se).[6,7] In this paper, we report the synthesis of the tin oxo counterpart, and describe X-ray diffraction studies which demonstrate that, unlike the [Sn=S] and [Sn=Se] functionalities, the corresponding terminal [Sn=O] moiety is unstable with respect to bridging.

Considering that the terminal sulfido and selenido complexes, $[\eta^4\text{-Me}_8\text{taa}]$SnE (E = S, Se) are readily obtained by reaction of $[\eta^4\text{-Me}_8\text{taa}]$Sn with the elemental chalcogens,[6] it was anticipated that the related oxo species could be generated by the reaction of $[\eta^4\text{-Me}_8\text{taa}]$Sn with an appropriate oxo transfer reagent. Indeed, $[\eta^4\text{-Me}_8\text{taa}]$Sn was found to react cleanly with N_2O to give the orange oxo complex, $\{[\eta^4\text{-Me}_8\text{taa}]\text{Sn}(\mu\text{-O})\}_2$ (Scheme 1).[8] However, in contrast to the monomeric terminal sulfido and selenido complexes, X-ray diffraction studies revealed that the oxo counterpart is dimeric, with bridging oxo ligands (Fig. 1).[9,10] Tin complexes with bridging oxo ligands are common, as illustrated by the cyclic 'stannoxanes', $[\text{R}_2\text{Sn}(\mu\text{-O})]_n$, but are typically obtained by hydrolysis of tetravalent halide precursors, R_2SnX_2,[11] rather than by reactions of divalent precursors with oxo transfer reagents. A notable exception, however, is Lappert's synthesis of $\{[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}(\mu\text{-O})\}_2$ by reaction of $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}$ with Me_3NO.[12,13] In addition to the similar method of synthesis, another feature that is common to both $\{[\eta^4\text{-Me}_8\text{taa}]\text{Sn}(\mu\text{-O})\}_2$ and $\{[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}(\mu\text{-O})\}_2$ is the presence of a four-membered $[\text{Sn}_2\text{O}_2]$ ring. More typically, stannoxanes exist as cyclic trimers with six-membered $[\text{Sn}_3\text{O}_3]$ rings, as exemplified by $[\text{Mes}_2\text{Sn}(\mu\text{-O})]_3$,[14] $[\text{R}_2\text{Sn}(\mu\text{-O})]_3$ (R = Bu^t, Me$_2$EtC),[15] $[(\text{Me}_3\text{Si})_3\text{C}(\text{Me})\text{Sn}(\mu\text{-O})]_3$,[16] $[\{2,4,6\text{-}(\text{CF}_3)_3\text{C}_6\text{H}_2\}_2\text{Sn}(\mu\text{-O})]_3$,[17] and $[(2,6\text{-Et}_2\text{C}_6\text{H}_3)\text{Sn}(\mu\text{-O})]_3$.[18,19]



Scheme 1

The observation that the oxo ligand in the $\{[\eta^4\text{-Me}_8\text{taa}]\text{SnE}\}$ system bridges more readily than does either the sulfido or selenido ligands is particularly interesting, especially in view of the notion embodied by the so-called 'classical double bond rule', one version of which cites: 'elements having a principal quantum number greater than 2 should not be able to form (*p–p*)π bonds to themselves or with other elements.[20] Furthermore, it is noteworthy that all other structurally characterized multiply bonded terminal chalcogenido complexes of tin are restricted to the heavier congeners,[21] with no examples of terminal oxo derivatives; as noted above, however, bridging oxo complexes of tin are well precedented. Regardless of whether or not monomeric $\{[\eta^4\text{-Me}_8\text{taa}]\text{SnO}\}$ is an intermediate in the reaction of $[\eta^4\text{-Me}_8\text{taa}]$Sn with N_2O, the structures of $\{[\eta^4\text{-Me}_8\text{taa}]\text{SnE}\}_n$ suggest that the terminal [Sn=O] moiety is significantly more prone to participate in bridging than is either the [Sn=S] or [Sn=Se] functionalities. Albeit limited, there are other observations which also suggest that the oxo ligand shows a greater propensity to act as a bridging functionality in main group chemistry than do the heavier chalcogenido ligands. For example, the germanium sulfido complex $[\eta^3\text{-}\{(\mu\text{-Bu}^t\text{N})_2(\text{SiMeNBu}^t)_2\}]$GeS exists as a monomer, whereas the oxygen analogue is dinuclear with oxo bridges.[22] Likewise, the sulfido and selenido complexes $\text{Ph}(\eta^2\text{-C}_{10}\text{H}_6\text{NMe}_2)$SiE (E = S, Se) are monomeric, while the oxygen counterpart is trinuclear with a six-membered Si_3O_3 ring.[23] Such behaviour is completely counter to that observed in transition metal systems, where the oxo ligand shows the least tendency to bridge,[24] with terminal oxo complexes being considerably more abundant than terminal sulfido, selenido, and tellurido derivatives.[1] A possible explanation for this difference between oxo complexes of the main group and transition elements is associated with the polarity of

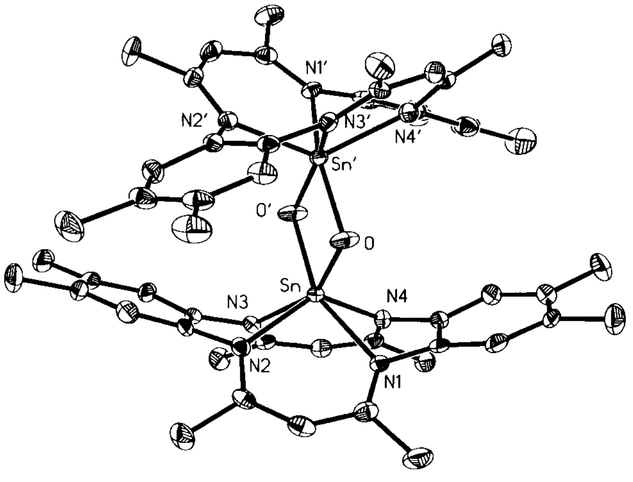


Fig. 1 Molecular structure of $\{[\eta^4\text{-Me}_8\text{taa}]\text{Sn}(\mu\text{-O})\}_2$. Selected bond lengths (Å) and angles (°): Sn–O 2.001(5), Sn–O′ 1.987(5), Sn–N1 2.220(6), Sn–N2 2.142(7), Sn–N3 2.256(7), Sn–N4 2.169(7); O–Sn–O′ 80.1(2), Sn–O–Sn′ 99.8(2).

the M–O bonds. Specifically, oxo ligands bound to electropositive main group elements may be expected to bear a substantial negative charge,[25,26] especially if the metal center has a coordination number greater than three, such that p_π–p_π overlap is unfavourable. For such a situation, the resonance structure $[\overset{+}{M}{-}\overset{-}{O}]$ is an appropriate description of the bonding, and the existence of this dipole would be expected to promote oxo bridging. Transition metal oxo complexes, however, do not normally exhibit such a high degree of polarity due to favourable d_π–p_π overlap (*i.e.* a contribution from the resonance structure $[\overset{-}{M}{\equiv}\overset{+}{O}]$) which serves to reduce the $[\overset{\delta+}{M} \sim \overset{\delta-}{O}]$ polarity of the bond.[27,28] Since the $[\overset{+}{M}{-}\overset{-}{E}]$ resonance structure for main group chalcogenido complexes would be expected to be most significant for oxo derivatives,[29] the propensity for bridging is likewise expected to be greater for oxo complexes than for the heavier chalcogenido counterparts.

Finally, it is noteworthy that the bridging oxo ligand of $\{[\eta^4\text{-Me}_8\text{taa}]\text{Sn}(\mu\text{-O})\}_2$ is readily abstracted by treatment with excess Me_3SiI to give $[\eta^4\text{-Me}_8\text{taa}]\text{SnI}_2$ (Scheme 1), a complex that has previously been synthesized by oxidative addition of I_2 to $[\eta^4\text{-Me}_8\text{taa}]\text{Sn}$.[30]

In summary, oxo transfer from N_2O to divalent $[\eta^4\text{-Me}_8\text{taa}]\text{Sn}$ yields the bridging oxo complex, $\{[\eta^4\text{-Me}_8\text{taa}]\text{Sn}(\mu\text{-O})\}_2$. Since the sulfido and selenido counterparts are mononuclear, it is evident that the oxo ligand in this system shows the greatest propensity to bridge. Such behavior is in marked contrast to that typically observed in transition metal systems.

We thank the National Science Foundation (CHE 96-10497) for support of this research. G. P. is the recipient of a Presidential Faculty Fellowship Award (1992–1997).

Notes and References

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9 $\{[\eta^4\text{-Me}_8\text{taa}]\text{Sn}(\mu\text{-O})\}_2$ monoclinic, space group *C*2/*c* (no. 15), a = 19.199(2), b = 19.12(2), c = 17.263(1) Å, α = 90, β = 110.019(7)°, γ = 90°, U = 5954.7(8) Å^3, Z = 4, R_1 = 0.0505, wR_2 = 0.0983 [$I > 2\sigma(I)$], room temp. CCDC 182/787.

10 The Sn–O bond lengths in $\{[\eta^4\text{-Me}_8\text{taa}]\text{Sn}(\mu\text{-O})\}_2$ [1.987(5) and 2.001(5) Å] compare favorably with the CSD mean (1.98 Å). The search was performed using CSD Version 5.13 for Sn–O interactions with two-coordinate oxygen. 3D Search and Research Using the Cambridge Structural Database, E. H. Allen and O. Kennard, *Chem. Des. Automat. News*, 1993, vol. 8(1), pp. 1 and 31–37.

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19 There are, however, some structurally characterized tin complexes with four-membered rings which incorporate only a single oxygen atom, *e.g.* $[(2,4,6\text{-Pr}^i{}_3\text{C}_6\text{H}_2)_2\text{Sn}(\mu\text{-O})(\mu\text{-S})\text{Sn}(2,4,6\text{-Pr}^i{}_3\text{C}_6\text{H}_2)_2]$[19a] and $[\{(2,6\text{-Et}_2\text{C}_6\text{H}_3)_2\text{Sn}\}_3\text{O}]$.[19b] (*a*) P. Brown, M. F. Mahon and K. C. Molloy, *J. Chem. Soc., Chem. Commun.*, 1989, 1621; (*b*) C. J. Cardin, D. J. Cardin, M. A. Convery and M. M. Devereux, *J. Organomet. Chem.*, 1991, **411**, C3.

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Received in Bloomington, IN, USA, 18th December 1997; 7/09065J