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Terminal Sulfido and Selenido Complexes of Tin: Syntheses and Structures of [η^4-Me_8taa]SnE (E = S, Se)

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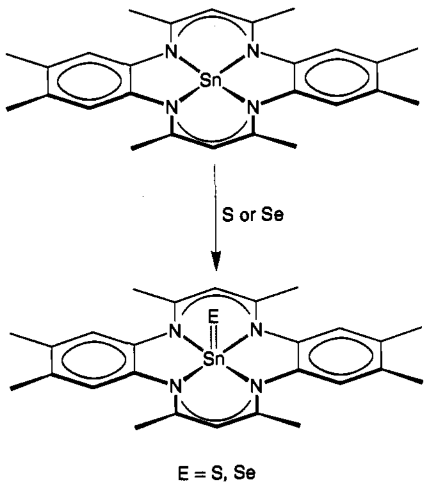
It is commonly recognized that the heavier congeners of the main group elements exhibit a reduced tendency to engage in multiple bonding.[1,2] Such a trend is aptly illustrated with respect to the group 14 elements.[1,2] For example, in contrast to the ubiquitous C═C double bond, complexes with Si═Si double bonds are rare,[3] with the first stable disilene $Mes_2Si{=}SiMes_2$ being discovered only in 1981.[4] Complexes with multiple bonds to the heavier congeners of the group 14 elements continue to attract interest, and much effort has been directed toward the study of heteronuclear multiple bonding. In particular, multiple bonding to the chalcogens has received considerable attention,[5-7] and some recent significant advances for germanium have been made with the syntheses and structural characterization of the terminal sulfido complexes $\{\eta^3\text{-}[(\mu\text{-}Bu^tN)_2(SiMeNBu^t)_2]\}GeS$[8] and (Tb)(Tip)GeS.[9,10] In this paper, we (i) describe the syntheses and structures of terminal sulfido and selenido complexes of tin and (ii) compare the abilities of germanium and tin to support such functionalities.

We have recently reported the use of the macrocyclic octamethyldibenzotetraaza[14]annulene dianion, $[Me_8taa]^{2-}$,[11] to stabilize a series of terminal sulfido, selenido, and tellurido complexes of germanium, [η^4-Me_8taa]GeE (E = S, Se, Te).[12] Adopting a similar approach, we have now isolated the orange terminal sulfido and selenido complexes of tin by addition of the elemental chalcogen to the axial coordination site in divalent [η^4-Me_8taa]Sn (Scheme 1).[13-15] The molecular structures of [η^4-Me_8taa]SnE (E = S, Se) have been determined by X-ray diffraction (Figure 1),[16] thereby confirming the presence of the terminal chalcogenido ligand in these complexes. The sulfido and selenido complexes are also characterized by ^{119}Sn NMR resonances at -301 and –444 ppm [$^1J(^{119}Sn-^{77}Se) = 3450$ Hz], respectively (relative to Me_4Sn).

Scheme 1



Compounds that are related to [η^4-Me_8taa]SnE (E = S, Se) include the porphyrin complexes (POR)SnE (E = S, Se) synthesized by Guilard and Kadish[17] and the aryl derivatives [(Tb)(Tip)SnE] (E = S, Se) reported by Okazaki.[18,19] However, the terminal chalcogenido moieties in these complexes have not been structurally characterized by X-ray diffraction. Indeed, the monomeric species [(Tb)(Tip)SnE] (E = S, Se) have only been generated in solution and actually exist as chalcogenido-bridged dimers $[(Tb)(Tip)Sn(\mu\text{-}E)]_2$ in the solid state,[18,19] even though the germanium complex (Tb)(Tip)GeS is monomeric.[9]

The molecular structure of divalent four-coordinate [η^4-Me_8taa]Sn has also been determined by X-ray diffraction,[16] and the principal structural change that is observed upon coordination of the chalcogen involves a decrease (by 0.25–0.29 Å) in the displacement of the Sn atom from the N_4 plane (Table 1). The Sn≈E bond lengths in [η^4-Me_8taa]SnE are much closer to the sum of the double bond covalent radii of Sn and E than the sum

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(14) All new compounds have been characterized analytically and spectroscopically (see supplementary material).

(15) The less substituted derivatives [η^4-Me_4taa]Sn,[15a] *trans*-[η^4-Me_4taa]$SnCl_2$,[15b] and *trans*-[η^4-Me_4taa]Sn(η^1-NO_3)$_2$[15b] have been recently reported. (a) Atwood, D. A.; Atwood, V. O.; Cowley, A. H.; Atwood, J. L.; Román, E. *Inorg. Chem.* **1992**, *31*, 3871–3872. (b) Belcher, W. J.; Brothers, P. J.; Land, M. V.; Rickard, C. E. F.; Ware, D. C. *J. Chem. Soc., Dalton Trans.* **1993**, 2101–2105.

(16) [η^4-Me_8taa]SnS·4$CHCl_3$ is monoclinic, $P2_1/c$ (No. 14), $a = 9.766(2)$ Å, $b = 25.377(8)$ Å, $c = 18.238(4)$ Å, $\beta = 104.34(2)°$, $V = 4379(2)$ Å^3, $Z = 4$, $R = 0.0538$, $R_w = 0.0671$. [η^4-Me_8taa]SnSe·2$CHCl_3$ is monoclinic, $P2_1/n$ (No. 14), $a = 11.588(2)$ Å, $b = 18.106(5)$ Å, $c = 16.132(3)$ Å, $\beta = 92.77(2)°$, $V = 3371(2)$ Å^3, $Z = 4$, $R = 0.0426$, $R_w = 0.0553$. [η^4-Me_8taa]Sn is monoclinic, $P2_1/n$ (No. 14), $a = 8.028(1)$ Å, $b = 21.810(4)$ Å, $c = 13.664(2)$ Å, $\beta = 103.75(1)°$, $V = 2324(1)$ Å^3, $Z = 4$, $R = 0.0356$, $R_w = 0.0490$.

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Table 1. Selected Structural Data for [η^4-Me_8taa]Sn and [η^4-Me_8taa]SnE (E = S, Se)

	$d(Sn{\approx}E)$/Å	$d(Sn{-}E)_{calc}$/Å[a]	$d(Sn{=}E)_{calc}$/Å[b]	$d(Sn{-}N_{av})$/Å	$d(Sn{\cdots}N_4)$/Å[c]
[Sn]S[d]	2.274(3)	2.44	2.24	2.14[2]	0.83
[Sn]Se	2.394(1)	2.57	2.37	2.15[1]	0.87
[Sn]				2.26[2]	1.12

[a] $d(Sn{-}E)_{calc}$ is the sum of the single bond covalent radii of Sn (1.40 Å) and E (S, 1.04 Å; Se, 1.17 Å).[20] For comparison, the mean Sn–E bond lengths for $(R_3Sn)_2E$ compounds listed in the Cambridge Crystallographic Database are $d(Sn{-}S)_{av}$ = 2.45 Å and $d(Sn{-}Se)_{av}$ = 2.53 Å. [b] $d(Sn{=}E)_{calc}$ is the sum of the double bond covalent radii of Sn (1.30 Å) and E (S, 0.94 Å; Se, 1.07 Å).[20] [c] $d(Sn{\cdots}N_4)$ is the displacement of Sn from the macrocyclic N_4 plane. [d] [Sn] ≡ [η^4-Me_8taa]Sn.

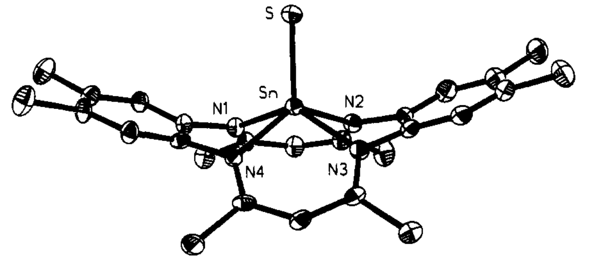

Figure 1. Molecular structure of [η^4-Me_8taa]SnS (the structure of the selenido analogue is similar).

of their single bond covalent radii[20] and are therefore indicative of considerable multiple bond character derived from the combination of the resonance structures shown below:

$$\overset{+}{Sn}{-}\overset{-}{E} \longleftrightarrow Sn{=}E \longleftrightarrow \overset{-}{Sn}{\equiv}\overset{+}{E}$$

Moreover, the Sn≈E bond lengths in [η^4-Me_8taa]SnE are also shorter than the respective average values for the formal single bonds in the anions $[SnS_4]^{4-}$ (2.39 Å)[21] and $[SnSe_4]^{4-}$ (2.52 Å).[22-24]

Despite the successful syntheses of the terminal sulfido and selenido complexes of tin, [η^4-Me_8taa]SnE (E = S, Se), we have at present been unable to isolate the corresponding tellurido derivative [η^4-Me_8taa]SnTe by the synthetic method that was described for the germanium analogue [η^4-Me_8taa]GeTe.[12,25] Assuming that tellurium transfer to [η^4-Me_8taa]Sn is not kinetically inhibited, this observation implies that the Sn≈Te interaction in [η^4-Me_8taa]SnTe is weaker than the corresponding Ge≈Te interaction in [η^4-Me_8taa]GeTe.[26]

The lower bond energy for the Sn≈Te *versus* Ge≈Te interaction is in accord with the aforementioned observation that the ability of the main group elements to partake in multiple bonding is reduced for the heavier congener. Indeed, the π-bond energy associated with the Sn=S bond has been calculated to be considerably lower than the corresponding values for C=S, Si=S, and Ge=S.[27]

Further evidence to support the notion that Sn≈E bond energies are lower than the corresponding Ge≈E bond energies is provided by the observation that both [η^4-Me_8taa]SnS and [η^4-Me_8taa]SnSe transfer the chalcogenido ligand to the germanium derivative [η^4-Me_8taa]Ge (eq 1).[13,28] Similarly, Woo has also demonstrated

$$[\eta^4\text{-}Me_8taa]SnE + [\eta^4\text{-}Me_8taa]Ge \rightarrow [\eta^4\text{-}Me_8taa]Sn + [\eta^4\text{-}Me_8taa]GeE \quad (1)$$

reversible sulfur and selenium transfer between the tin centers of the porphyrin derivatives (TPP)SnE and (TTP)Sn.[29]

In summary, the terminal sulfido and selenido complexes of tin [η^4-Me_8taa]SnE (E = S, Se) have been prepared by addition of the chalcogen to [η^4-Me_8taa]Sn. The Sn≈E interactions in these complexes are weaker than those in the corresponding germanium derivatives, as supported by the observation that the chalcogen in [η^4-Me_8taa]SnE may be transferred to germanium in [η^4-Me_8taa]Ge.

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Supplementary Material Available: Tables of analytical, spectroscopic, and crystallographic data, and preparative details for [η^4-Me_8taa]Sn and [η^4-Me_8taa]SnE (E = S, Se) (30 pages); listing of observed and calculated structure factors (34 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(24) Moreover, the terminal Sn–Se bond length in [η^4-Me_8taa]SnSe is also shorter than the formal single bonds in anionic oligomers. See, for example, $[Cs]_4[Sn_2Se_6]$ [2.447(1) and 2.452(2) Å],[24a] $[Tl]_4[Sn_2Se_6]$ [2.503(2)–2.582(2) Å],[24b] $[Na]_4[Sn_2Se_6]$ [2.456(1)–2.482(1) Å],[24c] $[K]_4[Sn_3Se_8]$ [2.473(1) Å],[24d] and $[Rb]_4[Sn_2Se_6]$ [2.464(3) and 2.459(3) Å].[24e] (a) Sheldrick, W. S.; Braunbeck, H. G. *Z. Naturforsch.* **1989**, *44b*, 851–852. (b) Jaulmes, S.; Houenou, P. *Mater. Res. Bull.* **1980**, *15*, 911–915. (c) Krebs, B.; Uhlen, H. *Z. Anorg. Allg. Chem.* **1987**, *549*, 35–45. (d) Sheldrick, W. S. *Z. Naturforsch.* **1988**, *43b*, 249–252. (e) Sheldrick, W. S.; Schaaf, B. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1041–1045.

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(26) A crude estimate of *ca.* 51 kcal mol^{-1} may be obtained as the upper limit for the Sn≈Te interaction in [η^4-Me_8taa]SnTe. Thus, considering Sn≈Te dissociation to give [η^4-Me_8taa]Sn and elemental Te and assuming that S°([η^4-Me_8taa]Sn) ≈ S°([η^4-Me_8taa]SnTe), ΔG° for the reaction is given by $D(Sn{\approx}Te) - \Delta H_{subl}(Te) - TS^\circ(Te)$. At 298 K, $\Delta G^\circ < 0$, and given the values $\Delta H_{subl}(Te)$ = 47.0 kcal mol^{-1} and $S^\circ(Te_{cryst})$ = 11.9 cal mol^{-1}K^{-1}, (taken from *CRC Handbook*), an upper limit of 50.5 kcal mol^{-1} may be estimated for the Sn≈Te interaction. Conversely, since the germanium analogue [η^4-Me_8taa]GeTe is stable with respect to dissociation into [η^4-Me_8taa]Ge and elemental Te at room temperature, it is evident that the value of *ca.* 51 kcal mol^{-1} also represents a lower limit for the Ge≈Te interaction in this complex. *CRC Handbook of Chemistry and Physics*, 69th ed. Weast, R. C. Ed.; CRC Press Inc.: Boca Raton, FL, 1989; p D-88.

(27) C=S (56.1 kcal mol^{-1}), Si=S (46.2 kcal mol^{-1}), Ge=S (40.0 kcal mol^{-1}), Sn=S (31.8 kcal mol^{-1}). Cited in ref 19.

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(29) $(TPP)H_2$ = *meso*-tetraphenylporphyrin; $(TTP)H_2$ = *meso*-tetra-*p*-tolylporphyrin. Woo, L. K., personal communication.