Multiple Bonding Between Germanium and the Chalcogens: The Syntheses and Structures of the Terminal Chalogenido Complexes (η^4-Me_8taa)GeE (E = S, Se, Te)

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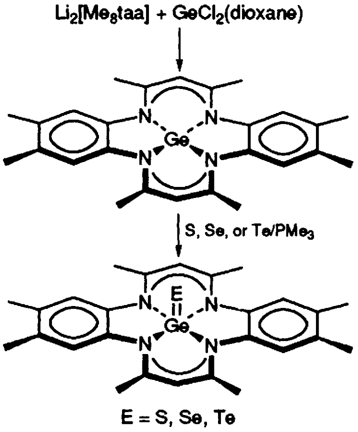
A series of terminal chalcogenido complexes of germanium supported by ligation of the macrocyclic octamethyldibenzotetraaza[14]annulene dianion (η^4-Me_8taa)GeE (E = S, Se, Te) has been prepared by addition of the chalcogen to (η^4-Me_8taa)Ge; structural studies on these complexes indicate that the bonding of the Ge≈E moiety is best described as intermediate between the $\overset{+}{\text{Ge}}-\overset{-}{\text{E}}$ and Ge=E resonance structures.

Multiple bonding plays a prominent role in the chemistry of the first-row elements, carbon, nitrogen and oxygen. In contrast, complexes that exhibit multiple bonding to the heavier congeners of these elements are much less common.[1] For example, even though much effort has been directed towards the study of multiple bonding to germanium, neutral complexes that exhibit [Ge=O] and [Ge=S] multiple bonds are almost completely limited to those of reactive intermediates.[1,2] Notable exceptions, however, are the [Ge=S] derivatives [η^3-{(μ-Bu^{t}N)$_2$(SiMeNBu^t)$_2$}]GeS[3a,b] and [2,4,6-{($Me_3Si)_2CH\}_3C_6H_2$][2,4,6-($Pr_2^iCH)_3C_6H_2$]GeS.[3c] In this paper, we address the nature of multiple bonding between germanium and the heavier chalcogens (S, Se, and Te), and report the syntheses and structures of germanium complexes that possess terminal selenido and tellurido ligands.

The macrocyclic tetramethyldibenzotetraaza[14]annulene dianion (Me_4taa)$^{2-}$ has been previously used to stabilize terminal oxo and sulfido derivatives of titanium, namely (η^4-Me_4taa)TiO and (η^4-Me_4taa)TiS.[4,5] In view of a crude structural analogy that may be anticipated between the Groups 4 and 14 elements, we speculated that a series of terminal chalcogenido derivatives of germanium could also be stabilized by ligation of similar macrocyclic ligands, and particularly the octamethyldibenzotetraaza[14]annulene ligand [Me_8taa]$^{2-}$.[6]

The four-coordinate germanium complex (η^4-Me_8taa)Ge is readily prepared by the metathesis of $GeCl_2$(1,4-dioxane)[7] with Li_2[Me_8taa] in THF (Scheme 1), a synthesis analogous to that for the less substituted derivative (η^4-Me_4taa)Ge.[8] Significantly, the vacant axial coordination site in (η^4-Me_8taa)Ge permits this divalent complex to be an excellent precursor for the series of tetravalent terminal chalcogenido complexes (η^4-Me_8taa)GeE (E = S, Se, Te). Thus, the orange sulfido and selenido derivatives are readily obtained by the direct addition of the elemental chalcogen to a solution of (η^4-Me_8taa)Ge in benzene, whereas the synthesis of the red tellurido analogue requires the presence of PMe_3 (Scheme 1).† To our knowledge, (η^4-Me_8taa)GeSe and (η^4-Me_8taa)GeTe are the first terminal mono-selenido and -tellurido complexes of germanium. Indeed, terminal tellurido derivatives are extremely rare for all elements. For example, the first terminal tellurido complex of a transition metal, namely W(PMe_3)$_4$(Te)$_2$, has only recently been reported.[9,10]



Scheme 1

The molecular structures of the terminal chalcogenido complexes (η^4-Me_8taa)GeE (E = S, Se, Te) have been determined by X-ray diffraction, and ORTEP drawings for the selenido and tellurido derivatives are shown in Figs. 1 and 2.‡ Of central importance to the present study is the nature of the germanium–chalcogenido interaction, which may be represented by three resonance structures: $\overset{+}{\text{Ge}}-\overset{-}{\text{E}} \longleftrightarrow \text{Ge}=\text{E} \longleftrightarrow \overset{-}{\text{Ge}}\equiv\overset{+}{\text{E}}$. Such a bonding scheme is similar to that described for tertiary phosphine oxides R_3PO,[11] with the exception that the double bond representation P=O is not appropriate for R_3PO, because the π interactions (e symmetry) must occur in a pairwise manner in complexes with C_{3v} symmetry.[11] In order to address which of the above resonance structures best describes the Ge≈E interaction in (η^4-Me_8taa)GeE, consideration must be given to the Ge≈E bond lengths (Table 1).

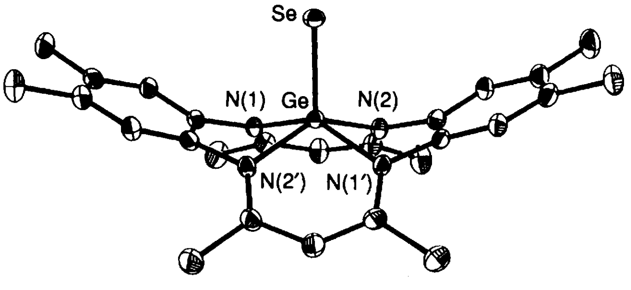


Fig. 1 Molecular structure of (η^4-Me_8taa)GeSe (the sulfido analogue is isostructural)

Table 1 Selected structural data for (η^4-Me_8taa)GeE (E = S, Se, Te)

E	d(Ge≈E)/Å	$d(\text{Ge–E})_{\text{calc}}$/Å[a]	$d(\text{Ge=E})_{\text{calc}}$/Å[b]	$d(\text{Ge–N}_{\text{av}})$/Å	$d(\text{Ge}\cdots\text{N}_4)$/Å[c]
S	2.110(2)	2.26	2.06	1.98(1)	0.63
Se	2.247(1)	2.39	2.19	1.99(1)	0.63
Te	2.466(1)	2.59	2.39	1.96(1)	0.68

[a] $d(\text{Ge–E})_{\text{calc.}}$ is the sum of the single-bond covalent radii of Ge and E (see ref. 12). For comparison, the mean Ge–E bond lengths for compounds listed in the Cambridge Crystallographic Database are $d(\text{Ge–S})_{\text{av.}}$ = 2.26 Å, $d(\text{Ge–Se})_{\text{av.}}$ = 2.37 Å, and $d(\text{Ge–Te})_{\text{av}}$ = 2.59 Å. [b] $d(\text{Ge=E})_{\text{calc.}}$ is the sum of the double-bond covalent radii of Ge and E (see ref. 12). For comparison, the following terminal Ge≈E bond lengths are known: $(GeS_4)^{4-}$ (2.21 Å), $(Ge_4S_{10})^{4-}$ (2.12 Å), $(GeSe_4)^{4-}$ (2.35 Å) and $(Ge_4Se_{10})^{4-}$ (2.26 Å) (see B. Krebs, *Angew. Chem., Int. Ed. Engl.* 1983, **22**, 113). [c] $d(\text{Ge}\cdots\text{N}_4)$ is the displacement of Ge from the macrocyclic N_4 plane.

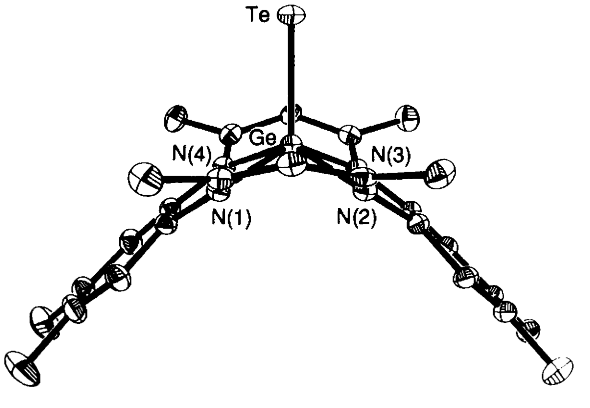


Fig. 2. Molecular structure of (η^4-Me_8taa)GeTe

Comparison of the Ge$\approx$E bond lengths in (η^4-Me_8taa)GeE with those calculated on the basis of the sum of the relevant single and double bond covalent radii for Ge and E,[12] suggests that the bonding is appropriately described as intermediate between the $\overset{+}{Ge}$–$\overset{-}{E}$ and Ge=E resonance structures. In accord with this suggestion, the Ge$\approx$E bond lengths in (η^4-Me_8taa)-GeE are shorter than respective Ge–E bond lengths in other complexes,§ with the exception of the aforementioned terminal sulfido complexes [η^3-{(μ-NBu^t)$_2$($SiMeNBu^t$)$_2$}]GeS [d(Ge–S) = 2.063(3) Å] and [2,4,6-{$(Me_3Si)_2CH$}$_3C_6H_2$]-[2,4,6-(Pr_2^iCH)$_3C_6H_2$]GeS [2.049(3) Å].[3]

Although other metrical details of the structures of (η^4-Me_8taa)GeE are similar, as illustrated by (*i*) the average Ge–N bond lengths [1.96(1) Å–1.98(1) Å], and (*ii*) the displacements of Ge from the macrocyclic N_4 plane (0.63–0.68 Å), an interesting difference is associated with the configuration of the (η^4-Me_8taa) ligand. Thus, whereas the sulfido and selenido complexes are isostructural in the solid state and adopt an identical configuration of the saddle-shaped ligand, the structure of the tellurido complex is unique in that the (η^4-Me_8taa) ligand exhibits the inverted configuration. The configuration of the (η^4-Me_8taa) ligand that is adopted by the sulfido and selenido complexes is such that the benzo groups are directed from the macrocyclic N_4 plane *towards* the [GeE] moiety (Fig. 1), whereas for the tellurido analogue, the benzo groups are directed *away* from the [GeTe] moiety (Fig. 2).

In summary, the series of terminal chalcogenido complexes of germanium (η^4-Me_8taa)GeE (E = S, Se, Te) have been prepared. Structural studies on these complexes indicate that the bonding of the Ge$\approx$E moiety is best described as a composite of the $\overset{+}{Ge}$–$\overset{-}{E}$ and Ge=E resonance structures.

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Footnotes

† PMe_3 has been demonstrated to act as a catalyst for related transformations involving elemental tellurium. See ref. 9.

‡ *Crystal data*: $C_{26}H_{30}GeN_4S\cdot 4CHCl_3$ monoclinic, $C2/c$ (no. 15), a = 21.820(5), b = 9.628(2), c = 21.727(4) Å, β = 109.55(1)°, V = 4301(2) Å^3, Z = 4, R = 0.0591, R_w = 0.0747. $C_{26}H_{30}GeN_4Se\cdot 4CHCl_3$; monoclinic, $C2/c$ (no. 15), a = 21.921(5), b = 9.719(2), c = 21.820(4) Å, β = 109.80(1)°, V = 4359(2) Å^3, Z = 4, R = 0.0588, R_w = 0.0734. $C_{26}H_{30}GeN_4Te\cdot 2CHCl_3$; monoclinic, $P2_1/c$ (no. 14), a = 12.256(4), b = 14.822(4), c = 19.396(4) Å, β = 94.52(2)°, V = 3513(2) Å^3, Z = 4, R = 0.0513, R_w = 0.0695. Both (η^4-Me_8taa)GeS and (η^4-Me_8taa)GeSe reside on crystallographic two fold axes.

§ A search of the Cambridge Crystallographic Database indicates the following metrical data for Ge–E single bond interactions (given in the order mean, range, and number of observations in the distribution): d(Ge–S) = 2.26, 2.06–2.84 Å, 145; d(Ge–Se) = 2.37, 2.31–2.77 Å, 38; d(Ge–Te) = 2.59, 2.59–2.60 Å, 8.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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