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Methyl, hydrochalcogenido, and phenylchalcogenolate complexes of zinc in a sulfur rich coordination environment: syntheses and structural characterization of the tris(2-mercapto-1-*tert*-butylimidazolyl)hydroboratozinc complexes $[\mathrm{Tm}^{\mathrm{Bu}^t}]\mathrm{ZnMe}$, $[\mathrm{Tm}^{\mathrm{Bu}^t}]\mathrm{ZnEH}$ (E = S, Se) and $[\mathrm{Tm}^{\mathrm{Bu}^t}]\mathrm{ZnEPh}$ (E = O, S, Se, Te)†

Jonathan G. Melnick, Arefa Docrat and Gerard Parkin*
Department of Chemistry, Columbia University, New York, New York 10027, USA.
E-mail: parkin@chem.columbia.edu

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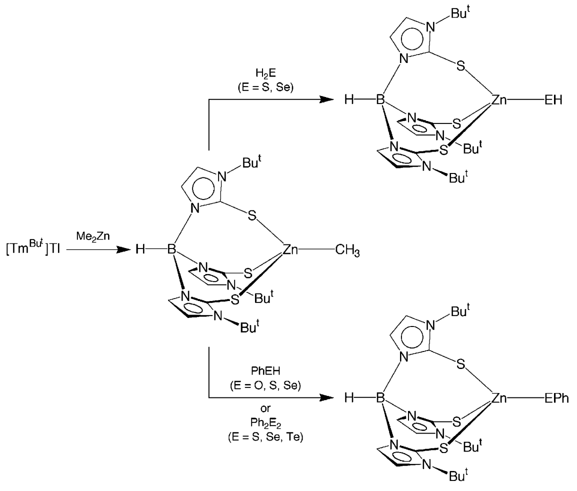
A series of hydrochalcogenido and phenylchalcogenolate complexes of zinc supported by tris(2-mercapto-1-*tert*-butylimidazolyl)hydroborato ligation, $[\mathrm{Tm}^{\mathrm{Bu}^t}]\mathrm{ZnEH}$ (E = S, Se) and $[\mathrm{Tm}^{\mathrm{Bu}^t}]\mathrm{ZnEPh}$ (E = O, S, Se, Te) have been synthesized from $[\mathrm{Tm}^{\mathrm{Bu}^t}]\mathrm{ZnMe}$; structural characterization by X–ray diffraction indicates that the variation in Zn–E bonding as a function of the chalcogen is significantly different from that in other series of metal–chalcogenolate compounds.

Metal complexes that feature chalcogenido ligands (E = O, S, Se, Te) have been shown to exhibit diverse structures and reactivity.[1] Hydrochalcogenido (EH)[2] and chalcogenolate (ER)[3] counterparts are likewise of interest and have relevance to diverse areas such as (i) metalloenzymes,[4] (ii) hydrodesulfurization, and (iii) II–VI semiconductors.[5] Despite this widespread interest, however, the vast majority of studies has focused on derivatives of the lightest congener, oxygen, *i.e.* hydroxide and alkoxide/aryloxide derivatives. As a simple illustration, while several examples of terminal zinc hydroxide compounds have been structurally characterized by X–ray diffraction,[4a] there are no structurally characterized examples of complexes with terminal hydroselenido or hydrotellurido ligands. In this paper, we report the first synthesis and structural determination of a terminal hydroselenido complex of zinc, together with the synthesis and structural characterization of a complete series of Zn–EPh (E = O, S, Se, Te) chalcogenolate complexes.

A variety of tris(2-mercapto-1-R-imidazolyl)hydroborato ligands, $[\mathrm{Tm}^{\mathrm{R}}]$ has recently been employed to study the chemistry of zinc in a sulfur rich environment, with particular emphasis having been given to aspects pertaining to bioinorganic chemistry.[6] Notably absent from these studies, however, are simple zinc alkyl derivatives of the type $[\mathrm{Tm}^{\mathrm{R}}]\mathrm{ZnR}$. It has previously been demonstrated that tris(pyrazolyl)hydroborato zinc hydride and alkyl compounds, $[\mathrm{Tp}^{\mathrm{R,R^*}}]\mathrm{ZnH}$ and $[\mathrm{Tp}^{\mathrm{R,R^*}}]\mathrm{ZnR'}$, are useful precursors for a variety of other $[\mathrm{Tp}^{\mathrm{R,R^*}}]\mathrm{ZnX}$ derivatives,[7] and we therefore sought to synthesize analogous $[\mathrm{Tm}^{\mathrm{R}}]\mathrm{ZnR'}$ complexes as precursors for hydrochalcogenido and chalcogenolate derivatives.

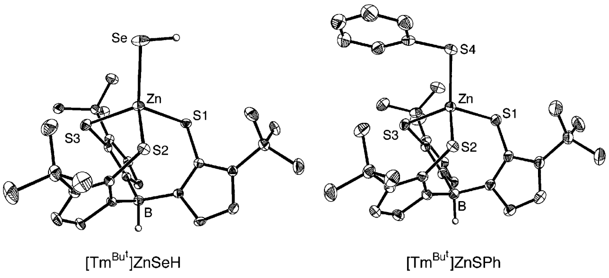
Significantly, the zinc methyl compound $[\mathrm{Tm}^{\mathrm{Bu}^t}]\mathrm{ZnMe}$ can be readily obtained *via* the reaction of $[\mathrm{Tm}^{\mathrm{Bu}^t}]\mathrm{Tl}$[8] with $\mathrm{Me_2Zn}$ (Scheme 1). Decisive evidence for the presence of a zinc–methyl ligand in $[\mathrm{Tm}^{\mathrm{Bu}^t}]\mathrm{ZnMe}$ is provided by the observation of a singlet at δ 0.28 in the ^{1}H NMR spectrum and a quartet at δ −8.5 ($^1J_{\mathrm{C-H}}$ = 119 Hz) in the ^{13}C NMR spectrum. Furthermore, the molecular structure of $[\mathrm{Tm}^{\mathrm{Bu}^t}]\mathrm{ZnMe}$ has been determined by X–ray diffraction, making it the first structurally characterized monomeric zinc methyl compound with a $[\mathrm{S_3ZnC}]$ coordination environment;[9] the Zn–C bond length [1.973(3) Å] is, nevertheless, very similar to that of the $[\mathrm{Tp}^{\mathrm{Bu}^t}]\mathrm{ZnMe}$ counterpart [1.971(4) Å] which features a $[\mathrm{N_3ZnC}]$ coordination motif.



Scheme 1

As anticipated, cleavage of the Zn–C bond of $[\mathrm{Tm}^{\mathrm{Bu}^t}]\mathrm{ZnMe}$ provides facile access to the desired hydrochalcogenido and chalcogenolate complexes. Thus, the hydrosulfido and hydroselenido compounds, $[\mathrm{Tm}^{\mathrm{Bu}^t}]\mathrm{ZnSH}$ and $[\mathrm{Tm}^{\mathrm{Bu}^t}]\mathrm{ZnSeH}$, are obtained *via* the reaction of $[\mathrm{Tm}^{\mathrm{Bu}^t}]\mathrm{ZnMe}$ with $\mathrm{H_2S}$ and $\mathrm{H_2Se}$, respectively.[10]† The SH and SeH functional groups are characterized by signals at δ −0.84 and −3.20, respectively, in the ^{1}H NMR spectrum and the molecular structures as determined by X-ray diffraction‡ confirm that the hydrochalcogenido ligands are bonded in a terminal fashion. In this regard, although related $[\mathrm{Tp}^{\mathrm{RR'}}]\mathrm{ZnSH}$ complexes have been synthesized[7b,c,11] and structurally characterized,[11a] $[\mathrm{Tm}^{\mathrm{Bu}^t}]\mathrm{ZnSeH}$ is the first structurally characterized zinc–hydroselenido compound (Fig. 1).

The corresponding phenylchalcogenolate compounds $[\mathrm{Tm}^{\mathrm{Bu}^t}]$-ZnEPh may likewise be obtained *via* reaction of $[\mathrm{Tm}^{\mathrm{Bu}^t}]\mathrm{ZnMe}$ with either PhEH (E = O, S, Se) or $\mathrm{Ph_2E_2}$ (E = S, Se, Te),[12]† thereby affording a complete series of isostructural phenylchalcogenolate



$[\mathrm{Tm}^{\mathrm{Bu}^t}]\mathrm{ZnSeH}$ $[\mathrm{Tm}^{\mathrm{Bu}^t}]\mathrm{ZnSPh}$

Fig. 1 Molecular structures of $[\mathrm{Tm}^{\mathrm{Bu}^t}]\mathrm{ZnSeH}$ and $[\mathrm{Tm}^{\mathrm{Bu}^t}]\mathrm{ZnSPh}$.

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† Electronic supplementary information (ESI) available: Experimental details and crystallographic data for $[\mathrm{Tm}^{\mathrm{Bu}^t}]\mathrm{ZnMe}$, $[\mathrm{Tm}^{\mathrm{Bu}^t}]\mathrm{ZnEH}$ (E = S, Se), $[\mathrm{Tm}^{\mathrm{Bu}^t}]\mathrm{ZnEPh}$ (E = O, S, Se, Te) and $[\mathrm{Tm}^{\mathrm{Bu}^t}]\mathrm{ZnI}$. See http://www.rsc.org/suppdata/cc/b4/b412218f/

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Table 1 Zn–E bond lengths in [Tm$^{\mathrm{Bu^t}}$]ZnEH and [Tm$^{\mathrm{Bu^t}}$]ZnEPh derivatives

	d(Zn–EH)/Å	d(Zn–EPh)/Å	$\Sigma r_{\mathrm{cov}}{}^{a}$/Å
O	1.896(4)^{b}	1.925(4)	1.98
S	2.265(1)	2.272(1)	2.28
Se	2.374(1)	2.394(1)	2.44
Te	—	2.568(1)	2.65

^{a} Sum of covalent radii. ^{b} Value for [Tm$^{\mathrm{Ph}}$]ZnOH taken from ref. 6*e*.

compounds for E = O, S, Se and Te, as illustrated for [Tm$^{\mathrm{Bu^t}}$]ZnSPh in Fig. 1. Complete series of isostructural chalcogenolate complexes that allow for systematic structural comparisons are very rare, and the only series of which we are aware are Cp*$_2$Zr(EPh)$_2$[13] and [Tp$^{\mathrm{Me_2}}$]$_2$SmEAr.[14]

The most interesting structural comparisons of [Tm$^{\mathrm{Bu^t}}$]ZnEH and [Tm$^{\mathrm{Bu^t}}$]ZnEPh pertain to the Zn–E bond lengths, as summarized in Table 1. Firstly, it is evident that the Zn–EH bond length is similar to that of the respective Zn–EPh bond, thereby indicating that the nature of the substituent on the chalcogen appears to exert little effect on the Zn–E bond length. Secondly, the change in Zn–E bond length as a function of the chalcogen corresponds closely to the variation in covalent radius of E (Table 1).[15] This observation is most significant in view of the fact that this trend is *not* observed for Cp*$_2$Zr(EPh)$_2$[13] and [Tp$^{\mathrm{Me_2}}$]$_2$SmEAr,[14] for which the M–O bond lengths are anomalously short. Thus, whereas the difference in Zn–O and Zn–S bond lengths for [Tm$^{\mathrm{Bu^t}}$]ZnEPh (0.35 Å) is similar to the difference in covalent radius of O and S (0.30 Å), the differences in M–O and M–S bond lengths for Cp*$_2$Zr(EPh)$_2$ (0.53 Å) and [Tp$^{\mathrm{Me_2}}$]$_2$SmEAr (0.70 Å) are considerably greater than the difference in covalent radii. The anomalously short M–O bond lengths for Cp*$_2$Zr(EPh)$_2$[13] and [Tp$^{\mathrm{Me_2}}$]$_2$SmEAr,[14] have been rationalized in terms of a significant ionic component to the M–O interaction; the ionic component also provides an explanation for large M–O–R bond angles as a result of electrostatic repulsion between M$^{\delta+}$ and R$^{\delta+}$, which is an alternative explanation to that involving lone pair donation.[13,16] The good correlation between Zn–E bond length and covalent radius for the zinc complexes [Tm$^{\mathrm{Bu^t}}$]ZnEX (X = H, Ph) provides evidence that, relative to zirconium and samarium, the bonding for the zinc system is more covalent in nature. In this regard, the difference in M–O and M–S bond lengths also correlates well with the Pauling electronegativities of the different metals: Zn (1.6), Zr (1.4), and Sm (1.1–1.2).[17]

In addition to the Zn–O bond length, another noteworthy aspect of the structure of [Tm$^{\mathrm{Bu^t}}$]ZnOPh is that an additional molecule of phenol hydrogen bonds to the phenoxy oxygen with an O···O separation of 2.65 Å. Such an interaction is interesting because it is not observed in a variety of [Tp$^{\mathrm{Bu^t,Me}}$]ZnOAr derivatives,[7e] although it is known for hydroxide derivatives.[18,19]

Finally, it is of note that several of the hydrochalcogenido and chalcogenolate compounds may be interconverted. For example, [Tm$^{\mathrm{Bu^t}}$]ZnSH reacts with PhSH at room temperature to yield [Tm$^{\mathrm{Bu^t}}$]ZnSPh, while [Tm$^{\mathrm{Bu^t}}$]ZnSPh reacts with PhSeH to yield [Tm$^{\mathrm{Bu^t}}$]ZnSePh. Alkylation of zinc thiolate ligands is of relevance to a variety of biological transformations[4] and, in this regard, the SH and SPh ligands of [Tm$^{\mathrm{Bu^t}}$]ZnSH and [Tm$^{\mathrm{Bu^t}}$]ZnSPh are rapidly alkylated by MeI to give [Tm$^{\mathrm{Bu^t}}$]ZnI and MeSX (X = H, Ph).[20]

In summary, the zinc methyl compound [Tm$^{\mathrm{Bu^t}}$]ZnMe provides access to a series of terminal hydrochalcogenido and phenylchalcogenolate derivatives of zinc, [Tm$^{\mathrm{Bu^t}}$]ZnEH (E = S, Se) and [Tm$^{\mathrm{Bu^t}}$]ZnEPh (E = O, S, Se, Te). The variation in Zn–E bond length as a function of the chalcogen indicates that the metal–chalcogen interactions are more covalent than in previously studied series of metal chalcogenolate complexes.

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