# A 'metallic tape' stabilized by an unprecedented ($\mu_5$-$\kappa^2$,$\kappa^2$,$\kappa^2$,$\kappa^1$,$\kappa^1$-) scorpionate binding mode†

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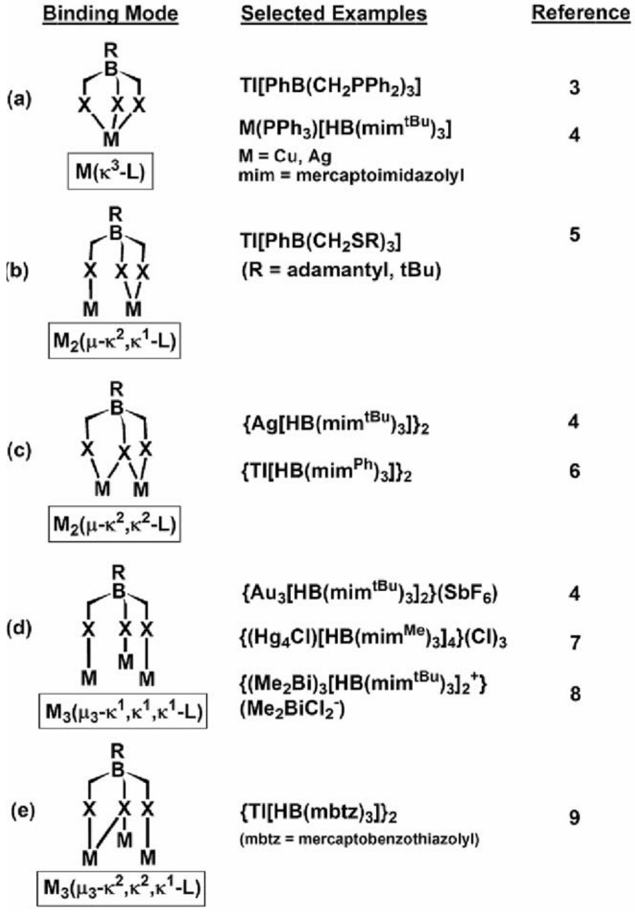
**The Janus scorpionate ligand, tris(mercaptothiadiazolyl)borate, exhibits extraordinary coordination capacity and versatility, binding from two up to five metal cations as demonstrated by its thallium(I) salt, a compound that serves as a model for metal–surface binding.**

Poly(pyrazolyl)borates have been ubiquitous in coordination chemistry since their inception in the mid 1960's.[1] These and other related facially-coordinating tridentate ligands have been given the moniker of 'scorpionates' owing to the similarity between their binding mode and the manner in which a scorpion grabs its prey.[2] Traditionally, scorpionates are spectator ligands that use hard nitrogen ligands to bind a single metal. More recently, however, there has been interest in the chemistry of scorpionates that incorporate softer Lewis donors such as phosphorus[3] or sulfur,[4–9] especially since the greater pi-acidic character of these donors might be exploited for the binding of unusual low-valent, electron-rich, transition metal centers (or heavier main group metals). One consequence of such studies has been the discovery that 'soft scorpionates' can exhibit numerous binding modes and are capable of binding from one up to three metals, as summarized in Fig. 1.

We recently reported on alkali metal complexes of tris(mercaptothiadiazolyl)borate, $[HB(mtda)_3]^-$, the so-called Janus scorpionate (Fig. 2), that can bind metals on either face or both faces of the same anionic ligand framework.[10] The Janus scorpionate can be considered a hybrid of Trofimenko's tris(pyrazolyl)borates[1,2] and of Reglinski's tris(mercaptoimidazolyl)borates,[11] and is a close relative of Bailey's and Marchiò's thioxotriazolylborates.[12] Importantly, we have demonstrated that the different donor sets on either face of the Janus scorpionate (N,N,N- or S,S,S-) allow for controlled organization of metallochains according to Pearson's Hard–Soft Acid–Base concept.[13] It was hoped that we could further take advantage of the ligand's ambidentate nature, the important electrochemical activity[14] (exploited in battery applications) and desirable surface adsorption properties[15] displayed by its constituent heterocycles to allow for layer-by-layer self-assembly of future conducting materials. During the course of our comprehensive study of the Janus scorpionate's coordination chemistry, we discovered that this ligand displays a remarkable capacity for binding metals in terms of both the variety of



| Binding Mode | Selected Examples | Reference |
|---|---|---|
| (a) $M(\kappa^3\text{-}L)$ | $Tl[PhB(CH_2PPh_2)_3]$<br>$M(PPh_3)[HB(mim^{tBu})_3]$<br>M = Cu, Ag<br>mim = mercaptoimidazolyl | 3<br>4 |
| (b) $M_2(\mu\text{-}\kappa^2,\kappa^1\text{-}L)$ | $Tl[PhB(CH_2SR)_3]$<br>(R = adamantyl, tBu) | 5 |
| (c) $M_2(\mu\text{-}\kappa^2,\kappa^2\text{-}L)$ | $\{Ag[HB(mim^{tBu})_3]\}_2$<br>$\{Tl[HB(mim^{Ph})_3]\}_2$ | 4<br>6 |
| (d) $M_3(\mu_3\text{-}\kappa^1,\kappa^1,\kappa^1\text{-}L)$ | $\{Au_3[HB(mim^{tBu})_3]_2\}(SbF_6)$<br>$\{(Hg_4Cl)[HB(mim^{Me})_3]_4\}(Cl)_3$<br>$\{(Me_2Bi)_3[HB(mim^{tBu})_3]_2{}^+\}(Me_2BiCl_2{}^-)$ | 4<br>7<br>8 |
| (e) $M_3(\mu_3\text{-}\kappa^2,\kappa^2,\kappa^1\text{-}L)$ | $\{Tl[HB(mbtz)_3]\}_2$<br>(mbtz = mercaptobenzothiazolyl) | 9 |

**Fig. 1** Known binding modes for tri-substituted 'soft' scorpionates.

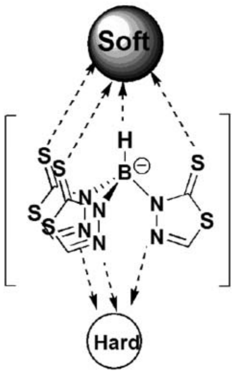


**Fig. 2** Illustration of the Janus scorpionate ligand and its binding behavior towards alkali metal cations.

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coordination modes and the number of metals it can bind simultaneously, as exemplified in its thallium salt.

The thallium compound Tl[HB(mtda)$_3$] is best prepared by metathesis between TlPF$_6$ and (NBu$_4$)[HB(mtda)$_3$] in THF where both starting materials and (NBu$_4$)(PF$_6$) are soluble but the desired product is not. The use of alkali metals salts, M[HB(mtda)$_3$] (M = Na, K), as reagents is viable but less advantageous due to the sparing solubility of these latter compounds in THF, acetone or acetonitrile, making the final separation (from insoluble Tl[HB(mtda)$_3$]) tedious. The low solubility of Tl[HB(mtda)$_3$] (insoluble in hydrocarbons, ethereal, halogenated solvents, sparingly soluble in acetone, CH$_3$CN, or MeOH, but soluble in DMF and DMSO) was fairly surprising as thallium scorpionates tend to be quite soluble; this unusual property is suggestive of an aggregated/oligomeric structure.

Crystals of a DMF solvate of Tl[HB(mtda)$_3$] suitable for X-ray diffraction were obtained by vapor diffusion of Et$_2$O into DMF solutions of the compound and the results of the diffraction study verified the polymeric structure of the thallium scorpionate.‡ There are two types of ligands in the structure, those coordinated on the top surface (Fig. 3, blue) and those coordinated on the side (Fig. 3, black) of a thallium cation tape. The former ligand is incredibly bound to five thallium atoms through the sulfur donors (which are directed along the B → H vector). In this case, as can be seen in the top left of Fig. 3, two sulfurs fit into the two tetrahedral 'pockets' formed by five 'close-packed' neighboring Tl$^+$ cations while the remaining sulfur is sandwiched between two thallium atoms at the edge of the tape, representing a $\mu_5$-($\kappa^2$,$\kappa^2$,$\kappa^2$,$\kappa^1$,$\kappa^1$)-binding mode. As is illustrated on the bottom left of Fig. 3, the second type of scorpionate binds in a more usual $\mu$-($\kappa^2$,$\kappa^2$)-binding mode. These latter ligands bind two Tl$^+$ cations *via* sulfur donors where two of the ligand's three 'arms' span the metals while the remaining 'arm' is sandwiched between the two metal centers. The polymeric chain of metal cations in Tl[HB(mtda)$_3$] resembles that in Tl[HB(mbtz)$_3$][9] but there are important differences. In the latter compound the chain is supported by cation–pi interactions involving benzo-rings; this is not possible in the current case. As can be seen in Fig. 4, the polymeric structure of Tl[HB(mtda)$_3$] is assembled solely by metal–sulfur bonds. The local coordination geometry around thallium can best be described as distorted octahedral with TlS$_6$ units where the Tl$^+$–S distances range from 3.146 Å to 3.391 Å and average 3.264 Å; these distances fall within the normal limits for such bonding interactions (Supporting Information). The TlS$_6$ octahedra are assembled in a manner reminiscent of a fragment of the CdI$_2$ structure-type. There are two connected rows of TlS$_6$ octahedra that propagate along the *a*-direction. Each row is comprised of *trans*-edge-shared TlS$_6$ octahedra forming chains. The two chains are then connected *via cis*-edge-sharing, such that each TlS$_6$ octahedron is edge-shared with four nearest neighbors, forming an S–Tl–S layer. It should be noted that high sulfur coordination numbers, with sulfur bound to three or even four thallium centers, have previously been observed with low-dimensional thallium–sulfido coordination polymers supported by more traditional thiolate ligands.[16,17]

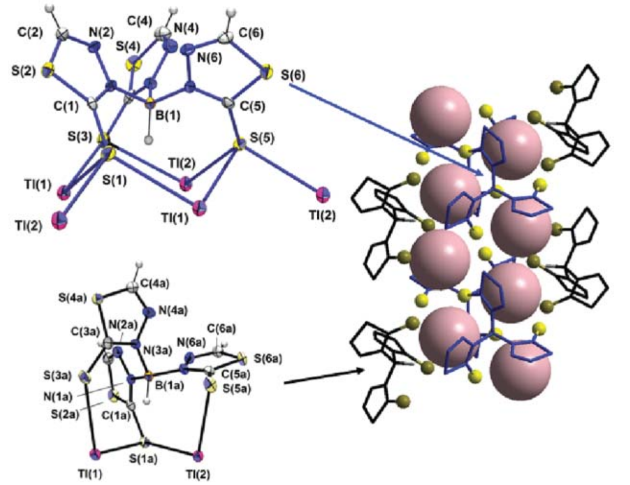

**Fig. 3** A portion of the crystal structure of Tl[HB(mtda)$_3$]·DMF solvate containing two independent scorpionate units (highlighted in blue or black) bound to thallium (pink) with solvent molecules removed for clarity (50% probability ellipsoids shown). Top left: Labelling of a scorpionate that binds five Tl$^+$ cations in a $\mu_5$-$\kappa^2$,$\kappa^2$,$\kappa^2$,$\kappa^1$,$\kappa^1$-manner. Bottom left: Labelling of a scorpionate that binds two Tl$^+$ cations in a $\mu$-$\kappa^2$,$\kappa^2$-fashion. Right: A view of the extended structure of the resulting thallium (pink)–sulfido (yellow spheres) coordination polymer with the backbones of the $\mu_5$- and $\mu$-scorpionates highlighted in blue and black, respectively.

As a consequence of different ligand binding modes, there are two types of borohydride environments in the *crystalline solvate*. The boron-hydride from the side-binding ligand resides on average 2.99 Å from two thallium centers while the boron-hydride from the top-binding ligand resides 3.32 Å on average from three metal centers; both distances are far less than 3.55 Å, the sum of the van der Waals radii of the elements.[18] Coincidentally, there are two bands for B–H stretches in the solid-state IR spectrum of the solid solvate at 2475 cm$^{-1}$ and 2422 cm$^{-1}$ (KBr pellets), presumably from the two types of ligands. These stretches are lower in energy than the sodium (2491, 2506 cm$^{-1}$), potassium (2501 cm$^{-1}$), or the (NBu$_4$)$^+$ (2517 cm$^{-1}$) counterparts, suggesting stronger B–H···M agostic interactions[19] likely due to both the greater number of metal cations involved in the interactions and the larger van der Waals radii of thallium compared to the alkali metals.[18] Importantly, the as-formed amorphous powder of Tl[HB(mtda)$_3$] only shows one B–H stretch at 2503 cm$^{-1}$, which also from solubility considerations likely indicates a different polymeric structure type for the powder.

The negligible difference in the solution properties (NMR, IR, voltammetry, and ESI(+) MS data) of Tl[HB(mtda)$_3$] compared to the tetrabutylammonium and alkali metal Janus scorpionate derivatives[10] indicates that the thallium compound is extensively dissociated in solution. Thus, in DMSO-d$_6$, the thallium salt has a chemical shift of $\delta_H$ 8.59 *versus* 8.56 for the (NBu$_4$)$^+$ salt. The IR spectra of CH$_3$CN solutions showed a stretch at 2504 cm$^{-1}$ like all

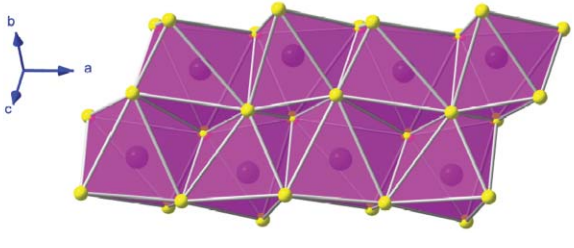

**Fig. 4** Coordination environment around thallium cations in Tl[HB(mtda)$_3$]·DMF solvate.

other derivatives of this ligand. Moreover, the ESI(+) mass spectrum for the thallium salt in $CH_3CN$ (with 0.1% v/v formic acid added) contained peaks for solvated thallium cations like $[Tl(CH_3CN)_n]^+$ ($n$ = 0, 1, 2) in addition to the $[HTl(L)]^+$ and $[Tl_2L]^+$ fragments, similar to that observed for the alkali metal salts which were also dissociated in solution.

In summary, the Janus scorpionate $[HB(mtda)_3]^-$ exhibits remarkable diversity in its binding behavior toward main group metals. With alkali metals the ligand binds in a bridging μ-($\kappa^3$-S,S′,S″-$\kappa^3$-N,N′,N″-) mode whereas with the relatively larger monovalent thallium cation, the ligand utilizes only its sulfur donors but two different binding modes are found. One type binds two metals in a μ-($\kappa^2$,$\kappa^2$) fashion whereas the other type remarkably binds five thalliums in a $\mu_5$-($\kappa^2$,$\kappa^2$,$\kappa^2$,$\kappa^1$,$\kappa^1$-L) binding mode. The observation of a triply-bridging S–($M_3$) interaction in $Tl[HB(mtda)_3]$ and in $Tl[HB(mbtz)_3]$[9] suggests that it may be possible for one soft scorpionate ligand to use its sulfurs to bind six metals in a $\mu_6$-($\kappa^2$,$\kappa^2$,$\kappa^2$,$\kappa^1$,$\kappa^1$,$\kappa^1$-L) mode, a mode that might be anticipated for the binding of a metal or metal–cation surface. To this extent, one focus of our continued studies using this and other soft scorpionates is on the stabilization of photoconductive $Tl_2S$ nanoparticles[20] that have an inverse $CdI_2$ structure type with alternating Tl–S–Tl layers and, hence, surface-exposed, coordinatively-unsaturated $Tl^+$ cations.

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## Notes and references

‡ Crystal data for $Tl[HB(mtda)_3]\cdot DMF$: $C_9H_{11}BN_7OS_6Tl$ (640.79), monoclinic, space group $P2_1/n$, $a$ = 9.1394(2), $b$ = 18.5785(5), $c$ = 22.8438(7) Å, $\beta$ = 91.218(2)°, $V$ = 3877.92(18) $Å^3$, $Z$ = 8, $\rho$(calc) = 2.199 g $cm^{-3}$, $\mu$(CuKα) = 22.2 $mm^{-1}$, $T$ =100(2) K, 5552 independent reflections ($R_{int}$ = 0.031), final $R$ indices (488 parameters) for 5120 independent reflections [$I > 2\sigma(I)$] are $R1$ =0.0265, $wR2$ = 0.0545, GOF = 1.148. CCDC 631340. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b618519c

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17 As one reviewer noted, it is possible that the capability for this ligand to adopt partial thiolate character (in one resonance form) may help to direct the formation of the thallium–sulfido coordination polymer. Greater thiolate character of the C=S bond should manifest itself in C–S bond lengthening due to the expected increased polarization induced by coordinating greater numbers of metal cations. For mercaptothiadiazolyl heterocycles considered in this work and in reference 10, there is a small increase in the average C=S bond length with increasing metal coordination. Thus, the average C=S distances increase from 1.669 Å (in $[NBu_4][HB(mtda)_3]$) with unbound C=S fragments, to 1.675 Å for C=S–M fragments (M = Na, K, Tl), to 1.692 Å for C=S–$Tl_2$ and to 1.694 Å for C=S–$Tl_3$. This potentially interesting bonding behavior will be addressed in greater detail in future publications by this group as more data for this system are obtained and if the bond-lengthening is found to be statistically significant.

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