

# Preparation and crystal structure of the [bis{hydrotris(methimazoly)borato}thallium(III)] cation: modulated chemistry resulting from the use of soft and hard tripodal ligands

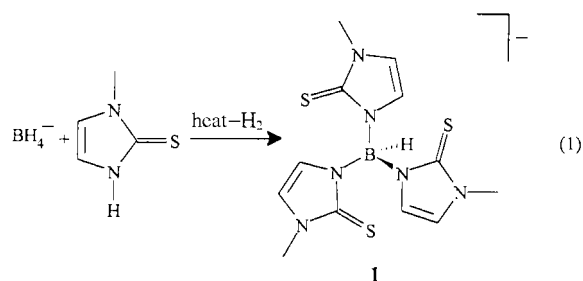
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The synthesis and crystal structure of the [bis{hydrotris(methimazoly)borato}thallium(III)] cation is reported, in which the thallium ion is co-ordinated by six sulfur thione donors in a regular octahedral environment.

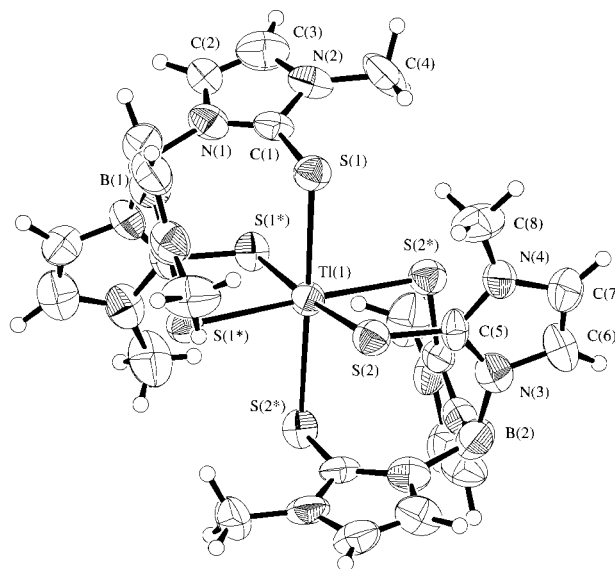
Interest in the preparation and reactivity of soft tripodal ligands has expanded markedly since the report by Riordan and co-workers of the synthesis of their tetrakis{(methylthio)methyl}borate ligands.<sup>1</sup> Whereas other workers have focused on the potential of ligands such as these to act as models of enzymes,<sup>2</sup> our group has chosen to investigate how the chemistry of the metal centre is affected by replacing a hard donor set by a markedly softer motif.<sup>3</sup> Specifically, our studies have centered on the replacement of pyrazole by methimazole<sup>4,5</sup> in the high yield synthesis of Trofimenko (eqn. (1)).<sup>6</sup> Using this simple approach



we have been able to isolate the hydrotris(methimazoly)borate anion, Tm,<sup>†</sup> (1), which we have subsequently shown to function as a soft analogue of the hydrotris(pyrazoly)borate anion, Tp.<sup>5</sup> Furthermore, in a recent report<sup>3</sup> of the reactivity of Tm with bismuth(III) we were able to produce the novel cation [Bi(Tm)<sub>2</sub>]<sup>+</sup> and clearly show that the ligand can be considered as the softest species in the series of 6e<sup>-</sup> donor ligands which includes the cyclopentadienyl anion, Cp, and Tp.

Parkin<sup>7</sup> and Riordan<sup>8</sup> have previously demonstrated that synthetic protocols employing the thallium(I) adducts of their anions provide an effective route by which the tripodal ligand can be transferred to a wide range of other metal cations. Using this approach, we sought to repeat the synthesis of the previously reported<sup>5</sup> complex [Zn(Tm)Br] and to extend the series to the other halide analogues, [Zn(Tm)Cl] and [Zn(Tm)I].<sup>9</sup> However, during the synthesis of [Zn(Tm)I] a small number of orange crystals were also obtained. These were isolated by Pasteur separation and characterized by X-ray crystallography to be the unusual and unexpected species [Tl(Tm)<sub>2</sub>]<sup>+</sup>.<sup>10</sup> Although the thallium(III) complex was only present as a small percentage of the product generated, we were prompted to further investigate the ability of Tm to stabilize thallium(III).

We attempted to generate the [Tl(Tm)<sub>2</sub>]<sup>+</sup> cation directly from the action of NaTm on thallium(III) nitrate but were unable to do so. However, investigation of the starting materials<sup>9</sup> showed a trace amount of the I<sub>3</sub><sup>-</sup> ion to be present in the zinc iodide, which, having an electrode potential similar to iodine afforded



**Fig. 1** The structure of the [Tl(Tm)<sub>2</sub>]<sup>+</sup> cation. Selected bond lengths (Å) and angles (°): Tl(1)–S(1) 2.682(7), Tl(1)–S(2) 2.690(7), B(1)···Tl(1) 4.17(4), B(2)···Tl(1) 4.26(6); S(1)–Tl(1)–S(1') 92.4(2), S(2)–Tl(1)–S(2') 92.2(2), S(1)–Tl(1)–S(2) 84.4(2), S(1)–Tl(1)–S(2') 91.2(2), S(1)–Tl(1)–S(2') 175.3(2).

the oxidative drive for the reaction. This led us to add excess iodine to a solution of [Tl(Tm)] which resulted in the rapid and efficient formation of an orange solid which was readily identifiable by X-ray crystallography,<sup>11</sup> spectroscopy and micro-analysis<sup>12</sup> to be [Tl(Tm)<sub>2</sub>]<sup>+</sup>[TlI<sub>4</sub>]<sup>-</sup>. The success of this synthetic route over the direct action of NaTm on thallium(III) nitrate is believed to result from the pre-complexation of the ligand to the thallium(I) cation. The action of thallium(III) on the free ligand results in decomposition *via* interaction with the reducing borohydride function, while the complexed ligand is apparently resistant to oxidation and furthermore stabilizes the resulting thallium(III) cation. A similar effect is observed with phosphine ligands, which are readily oxidised, yet when complexed to a metal centre can allow the formation of high oxidation state complexes. The nature of the counter ion associated with the [Tl(Tm)<sub>2</sub>]<sup>+</sup> cation obtained from the two synthetic reactions is simply a consequence of the available anions in solution during the reaction. The initial reaction is halide limited whereas the latter is halogen rich and is thus capable of oxidizing all of the thallium in solution generating a complex anion also.

The cations ([Tl(Tm)<sub>2</sub>]<sup>+</sup>) isolated from both reactions are very similar, differing only in the crystallographic symmetry imposed by the space groups in which they crystallised. Only the iodide structure is shown (Fig. 1). The thallium cation is in an approximately octahedral environment. The intra-ligand S–Tl–S angles are slightly greater than 90°, while the inter-ligand S–Tl–S angles are less, resulting in a slight compression

of the octahedron. Clearly the larger cation allows the repulsion between the peripheral methyl groups to be minimised allowing the observed effect. The six Tl–S bonds are all identical within systematic error (2.682(7)–2.690(7) Å). It has previously been shown that the Tm ligand, by forming three eight-membered rings, has little difficulty in accommodating large cations such as bismuth without undue distortion around the boron.<sup>3</sup> A similar situation exists here where the N–B–N angles deviate only slightly (111° and 110° respectively) from a regular tetrahedral geometry.

Surprisingly, structurally characterised thallium(III) complexes in which the coordination sphere is made up exclusively of sulfur donors, would seem to be limited to a few examples of tris(dialkyldithiocarbamate) adducts,<sup>13,14</sup> which are prepared directly from thallic salts. Due to the smaller size of the chelate rings these complexes have a more distorted environment around thallium. However, the six Tl–S bond distances are found to be comparable (at *ca.* 2.66 Å) to those found in the [Tl(Tm)<sub>2</sub>]<sup>+</sup> cations suggesting that there is a structural homology between the tridentate Tm and didentate diethyl-dithiocarbamate species.

The relative stability of the [Tl(Tm)<sub>2</sub>]<sup>+</sup> cation is postulated to arise from the use of soft donors coupled with the provision of a completely enclosed coordination sphere. Reverting to a harder donor *i.e.* NaTp and repeating the synthetic protocol does not generate an analogous ion but leads to the formation of [Tl(Hpz)I]<sub>2</sub>.<sup>15</sup> Curiously, in this instance the thallium(III) centre is not stabilised by the hard ligand and auto-reduces releasing pyrazole, a portion of which is trapped within the coordination sphere of the emerging thallium(I) cation.

The comparison between bismuth and thallium is intriguing insofar as two isostructural cations have now been isolated.<sup>3</sup> Intermediate between these two elements in the periodic table is lead(II) which on reaction with NaTm also produces a 2:1 complex. Although we have as yet been unable to isolate crystals suitable for X-ray diffraction, the analytical and spectroscopic data<sup>16</sup> are consistent with a molecule with a structure similar to the thallium(III) and bismuth(III) complexes.<sup>3</sup> Thus, an interesting feature of the chemistry of Tm reported thus far is its tendency to form mono-ligand complexes (*e.g.* [Zn(Tm)-Br]) with small cations and bis-ligand complexes with larger cations (thallium(III), lead(II) and bismuth(III)) suggesting that further investigation of the heavier Group 12 homologues will identify the transition between these two situations *i.e.* mono and bis species.

In conclusion, the ability of a softer ligand set to stabilize thallium(III) in the manner described above further exemplifies the changes in chemistry which can be achieved simply by altering the donors within an accepted ligand motif (Tp *vs.* Tm).

## Notes and references

† Tm = Hydrotris(methimazolyl)borate = hydrotris(3-methyl-1-imidazolyl-2-thione)borate.

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- 8 P. J. Schebler, C. G. Riordan, I. A. Guzei and A. L. Rheingold, *Inorg. Chem.*, 1998, **37**, 4754.
- 9 Preparation of [Tl(Tm)]. [Tl(Tm)] was prepared by modification of the previously reported method.<sup>4</sup> Na(Tm) (0.5 g, 1.3 mmol) in acetone (75 ml) was added to TlNO<sub>3</sub> in acetone (25 ml). The mixture was refluxed for 4 h and the resultant mixture was filtered. The solid obtained was suspended in water (100 ml) and stirred for a few minutes to remove NaNO<sub>3</sub> and any residual TlNO<sub>3</sub>. The product was filtered, and dried *in vacuo*.
- 10 Preparation of [Zn(Tm)X]. Tl(Tm) was mixed in equimolar quantities with the appropriate zinc(II) halide in acetone (100 ml) on a 0.4 mmol scale. The precipitated thallium halide was separated by filtration and the product, [Zn(Tm)X], crystallised directly from the filtrate on concentration and cooling to –18 °C.
- 11 For [Zn(Tm)Cl]. Found: C, 31.33, H, 3.13; N, 18.49. Expected for C<sub>12</sub>H<sub>16</sub>N<sub>6</sub>S<sub>3</sub>BZnCl: C, 31.88; H, 3.57; N, 18.59%. <sup>1</sup>H NMR (400 MHz, d<sup>6</sup>-dmsO); δ 3.54 (s, 3H, CH<sub>3</sub>), 6.98 (s, 1H, CH), 7.30 (s, 1H, CH). IR ν<sub>B-H</sub> 2407 cm<sup>-1</sup>.
- 12 For [Zn(Tm)I]. Found: C, 25.86; H, 2.77; N, 13.70. Expected for C<sub>12</sub>H<sub>16</sub>N<sub>6</sub>S<sub>3</sub>BZnI·0.5CH<sub>2</sub>Cl<sub>2</sub>: C, 25.69; H, 2.93; N, 14.39%. <sup>1</sup>H NMR (400 MHz, d<sup>6</sup>-dmsO); δ 3.55 (s, 3H, CH<sub>3</sub>), 5.73 (s, CH<sub>2</sub>Cl<sub>2</sub>), 6.99 (s, 1H, CH), 7.31 (s, 1H, CH). IR ν<sub>B-H</sub> 2441 cm<sup>-1</sup>.
- 13 Crystal data for [Tl(Tm)<sub>2</sub>]I·2H<sub>2</sub>O·3CH<sub>2</sub>Cl<sub>2</sub>: C<sub>27</sub>H<sub>42</sub>B<sub>2</sub>Cl<sub>6</sub>I<sub>12</sub>O<sub>2</sub>S<sub>6</sub>Tl, *M* = 1328.71, cubic, *a* = 17.272(3) Å, *U* = 5152(1) Å<sup>3</sup>, *T* = 295 K, space group *P*2<sub>1</sub>3 (no. 198), *Z* = 4, μ(Mo-Kα) = 4.29 mm<sup>-1</sup>, 5032 reflections measured, 1684 unique (*R*<sub>int</sub> = 0.078) of which 1373 with *F* > 2σ(*F*) were used in all calculations. *R* = 0.071, *R*<sub>w</sub> = 0.075.
- 14 The structure of the cation in [Tl(Tm)<sub>2</sub>][TlI<sub>4</sub>] is essentially the same as in [Tl(Tm)<sub>2</sub>]I. Crystal data for [Tl(Tm)<sub>2</sub>][TlI<sub>4</sub>]: C<sub>24</sub>H<sub>32</sub>B<sub>2</sub>I<sub>4</sub>N<sub>12</sub>S<sub>6</sub>Tl<sub>2</sub>, *M* = 1618.94, triclinic, *a* = 10.468(2), *b* = 10.543(2), *c* = 10.620(2) Å, *a* = 87.41(2), *β* = 88.53(1), *γ* = 86.64(1)°, *U* = 1168.6(4) Å<sup>3</sup>, *T* = 295 K, space group = *P*1̄ (no. 2), *Z* = 1, μ(Mo-Kα) = 9.819 mm<sup>-1</sup>, 5392 reflections measured, 5107 unique (*R*<sub>int</sub> = 0.019). Refinement on *F*<sup>2</sup> used all reflections. *R* = 0.054, *wR* = 0.133. CCDC reference number 186/1792. See <http://www.rsc.org/suppdata/dt/a9/a908236k> for crystallographic files in .cif format.
- 15 The micro-analysis and spectroscopic characterisation obtained for [Tl(Tm)<sub>2</sub>][TlI<sub>4</sub>] are consistent with expected values. Found: C, 18.08; H, 1.87; N, 10.20 and S, 12.10%. Expected for C<sub>24</sub>H<sub>32</sub>N<sub>12</sub>S<sub>6</sub>B<sub>2</sub>Tl<sub>2</sub>I<sub>4</sub>: C, 17.81; H, 1.99; N, 10.38 and S, 11.88%. <sup>1</sup>H NMR (400 MHz, d<sup>6</sup>-dmsO); δ 3.57 (s, 3H, CH<sub>3</sub>), 6.97 (d, 1H, CH), 7.00 (d, 1H, CH) (*J* = 3.0 Hz). IR ν<sub>B-H</sub> = 2368 cm<sup>-1</sup>.
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- 17 D. L. Kepert, C. L. Raston, N. K. Roberts and A. H. White, *Aust. J. Chem.*, 1978, **31**, 1927.
- 18 Found: C, 9.32; H, 1.28; N, 6.68. Expected for C<sub>6</sub>H<sub>8</sub>N<sub>4</sub>Tl<sub>2</sub>I<sub>2</sub>: C, 9.02; H, 1.01; N, 7.02%. <sup>1</sup>H NMR (400 MHz, d<sup>6</sup>-dmsO); δ 6.34 (s, 1H, CH), 7.72 (s, 2H, CH).
- 19 Found: C, 30.90; H, 3.55; N, 16.75; S, 20.20; Cl, 4.01. Expected for C<sub>24</sub>H<sub>32</sub>B<sub>2</sub>N<sub>12</sub>S<sub>6</sub>Pb·0.5CH<sub>2</sub>Cl<sub>2</sub>: C, 30.90; H, 3.49; N, 17.65; S, 20.20; Cl, 3.72%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>); δ 3.69 (br s, 3H, CH<sub>3</sub>), 6.69 (br, m, 2H, CH), 5.32 (s, 1H, 0.5CH<sub>2</sub>Cl<sub>2</sub>).

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