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The Stability of Mercaptobenzothiazole Based Soft Scorpionate Complexes

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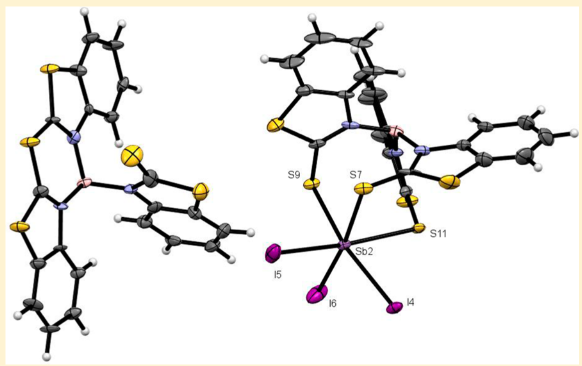
Supporting Information

ABSTRACT: The chemistry of the hydrotris(mercaptobenzothiazolyl)borate anion (Tbz) with metal salts (HgI_2, SbI_3, BiI_3, $CoCl_2$) is reported in an attempt to probe the stability of the of Tbz ligand once coordinated to hard and soft metals. Complexes of Tbz with bismuth, containing the $[Bi(Tbz)I_3]^-$ anion, are stable, but with the other metals this is not the case. Although simple complexes such as [Hg(Tbz)I] and $[E(Tbz)I_3]^-$ (E = Sb, Bi) can be isolated from the reaction mixtures, subsequent reactions lead to ligand modification or decomposition. In the presence of mercury and antimony we observe the formation of a hitherto unseen cationic pentacyclic heterocycle. With cobalt we observe a small quantity of a product which suggests a more complete decomposition. A simple benzothiazole (bz) adduct $[Co(bz)_2Cl_2]$ has been identified, in which the Tbz ligand has disintegrated and the parent heterocycle, mercaptobenzothiazole, has been desulfurized. A rationale for these observations is given.



■ INTRODUCTION

The use of 1-methylimidazole-2-thione as a precursor for the synthesis of scorpionates has stimulated an interest in the use of alternative heterocycles in the synthesis of soft poly(azolyl)-borate anions.[1−13] Not only has there been an increase in the range of heterocycles employed (benzoimidazole-2-thione,[6] 1,3,4-thiadiazole-2-thione,[7,8] benzothiazole-2-thione,[9] thiazolidine-2-thione,[9,10] 1,2,4-triazole-5-thione,[11] pyridine-2-thione,[12] and pyridazine-2-thione[13]), but the range of donor atoms has also expanded, with systems containing nitrogen,[1,2,6] sulfur,[3−13] selenium,[14,15] oxygen,[6] and phosphorus[16] donors (Figure 1) having all been reported. The chemistry being generated using these species is diverse, but within the reports on the complexes of soft scorpionates are results which suggest that in some circumstances these ligands may be prone to decomposition.[4] The hydrotris(mercaptobenzothiazolyl)borate anion (Tbz, Figure 1) was first reported in 2001,[9] yet, apart from the single thallium(I) complex in the original paper, no further metal complexes were reported until 2012.[17] Given the widespread use of these soft scorpionate ligands, this lack of utilization hints at an underlying problem. Indeed a recent study on the alkylation of benzothiazole-2-thione and thiazolidine-2-thione based soft scorpionates demonstrated that the B−N bond is readily severed in response to S-alkylation.[18] The implication is that as electron density is removed from the heterocycle the B−N bond weakens. For the parent methimazole based species the alkylated nitrogen atom within the ring, which bears a negative charge, can compensate for these changes. However, for species which contain an internal sulfur atom, which bears a positive charge, this may not be the case. The inference was that the synthesis of metal complexes derived from the hydrotris(mercaptobenzothiazolyl)borate anion (Tbz, Figure 1) would only be possible with electron-rich, "soft" metals (e.g thallium), but that when challenged with stronger Lewis acids decomposition should occur.[9,18] The recent study by Baba et al.,[17] reporting the synthesis and structure of a cobalt Tbz complex, was thus of

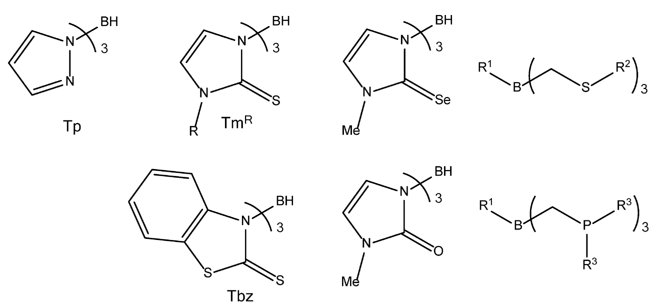


Figure 1. A schematic representation of the developments in scorpionate chemistry. From left to right: hydrotris(pyrazolyl)borate (Tp) (far left) [1, 2]; the soft scorpionates hydrotris(methimazolyl)-borate (Tm^R; R = Me, Ph, ^{t}Bu, etc.)(center left, top) [4, 5] and hydrotris(mercaptobenzothiazolyl)borate (Tbz)(center left, below) [9]; selenium and oxygen donor systems (center right) [6, 14, 15]; and the poly(alkylthioalkyl)borates (right) [3, 16]. The tetrakis-(thioalky)borate anion (top right) was the first alternative soft donor system to be reported [3].

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Table 1. Crystallographic Data

	[Hg(Tbz)I]	$[CPH]_2[Hg_2I_6]\cdot DMF$	$[CPH][Sb(Tbz)I_3]\cdot DMF$	[CPH]I	$Bu_4N[Bi(Tbz)I_3]\cdot DMF$	$[Bi(DMF)_8][Bi_3I_{12}]$
empirical formula	$C_{21}H_{13}B_1Hg_1I_1N_3S_6$	$C_{24}H_{20}B_1Hg_1I_3N_4O_1S_5$	$C_{48}H_{40}B_2I_3N_8O_2S_{11}Sb_1$	$C_{21}H_{13}BIN_3S_5$	$C_{40}H_{56}B_1Bi_1I_3N_5O_1S_6$	$C_{24}H_{56}Bi_4I_{12}N_8O_8$
FW	838.00	1132.33	1563.93	605.35	1415.75	2943.49
crystal system	monoclinic	triclinic	triclinic	trigonal	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$R\bar{3}$	$P\bar{1}$	$P2_1/n$
a/Å	10.0750(6)	9.6385(7)	10.979(5)	31.724(5)	10.0704(4)	15.1874(14)
b/Å	12.7100(8)	12.7847(8)	23.013(5)	31.724(5)	10.7107(6)	30.9071(18)
c/Å	19.6116(10)	16.1011(10)	25.042(5)	12.618(5)	24.3308(10)	15.8134(15)
α/deg	90	98.895(5)	88.715(5)	90	83.541(4)	90
β/deg	90.334(4)	105.408(6)	87.294(5)	90	87.005(3)	117.846(12)
γ/deg	90	105.274(6)	82.975(5)	120	78.366(4)	90
Z	4	2	4	18	2	4
V/Å^3	2511.3(3)	1790.6(2)	6272(3)	10998(5)	2552.9(2)	6563.3
μ_{calc}/mm^{-1}	7.874	7.199	2.325	1.752	5.548	16.375
no. rflns measd	7703	17 446	59361	15 739	20 641	28 093
no. unique reflns (R_{int})	4817(0.0181)	7714(0.0543)	30101(0.0558)	5269(0.0297)	10554(0.1002)	14529(0.0458)
no. observed reflns	4309	5655	20 795	4291	5419	9008
no. parameters	301	354	1359	284	520	521
R ($I > 2\sigma(I)$)	0.0269	0.0643	0.1075	0.0357	0.0653	0.0422
R_w (all reflns)	0.0451	0.1956	0.2728	0.1032	0.1233	0.0818
GOF	1.008	1.042	1.129	1.062	0.879	0.867

some interest and stimulated us to revisit the chemistry of the hydrotris(mercaptobenzothiazolyl)borate anion with salts of mercury, antimony, bismuth, and cobalt.

■ EXPERIMENTAL SECTION

Unless otherwise stated all chemicals were commercially obtained and used without further purification. NaTbz was prepared as previously reported.[18] All NMR spectra were recorded on either a Bruker DPX400 or a Bruker AV500 spectrometer. The spectra were referenced to internal solvent peaks and thus to TMS. Infrared spectra were recorded as KBr discs using a Nicolet Avatar 360 FT-IR spectrometer. Mass spectra were recorded using a Thermo Finnigan LCQDuo by electrospray ion trap and a Thermo scientific LTQ orbitrap for accurate mass. Crystals were coated in mineral oil and mounted on glass fibers. Data were collected at 123 K on an Oxford Instruments CCD diffractometer using graphite monochromated Mo Kα radiation. The heavy atom positions were determined by Patterson methods and the remaining atoms located in the difference electron density maps. Full matrix least-squares refinement was based on F^2 with all non-hydrogen atoms refined anisotropically. While the hydrogen atoms were mostly observed in the difference maps, they were placed in calculated positions riding on the parent atoms. The structure solution and refinement used the programs SHELX-97[19] or SIR 92[20] and the graphical interface WinGX.[21] A summary of the crystallographic parameters is given in Table 1.

Reaction of NaTbz with Mercuric Iodide. Mercuric iodide (0.11 g, 0.25 mmol) and NaTbz (0.13 g, 0.25 mmol) were stirred overnight in $THF/CHCl_3$ (20 mL, 1:1 by volume). A yellow suspension formed which was filtered to give a yellow solid. The solid was extracted with a minimum amount of DMF, filtered, and crystallized by vapor diffusion with diethyl ether (Yield, 0.16 g). An inspection of the sample revealed the presence of two crystal types; both yellow. Although representative examples of each crystal form could be isolated for analysis by X-ray methods, the sample was dominated by $[C_{21}H_{13}B_1N_3S_5]_2[Hg_2I_6]$ (ca. 90%, with the remaining 10% being [Hg(Tbz)I]). ESI-MS $[C_{21}H_{13}N_3S_5B]^+$: 477 (100%), $[Hg(Tbz)]^+$: 712 (16%). FT-IR (KBr, cm^{-1}): 2499 (νB–H). ^{1}H NMR (400 MHz, d_6-DMSO δ): 8.85 (d, 1H), 8.50 (d, 2H), 7.87 (d, 2H), 7.85 (t, 1H), 7.80 (d, 1H), 7.72 (t, 2H), 7.63 (t, 2H), 7.55 (t, 1H). Trace amounts of [Hg(Tbz)I] can be seen in the ^{1}H NMR spectrum at δ = 8.08, 7.55, and 7.31 (*vide infra* and Supporting Information Figure S1).

Reaction of NaTbz with Antimony Triiodide. Antimony triiodide (0.13 g, 0.26 mmol) and NaTbz (0.14 g, 0.27 mmol) were stirred overnight in $THF/CHCl_3$ (1:1 by volume, 10 mL). A blood red colored solution resulted, which deepened in color with time and deposited a red solid (0.15 g). The precipitate was collected, extracted with DMF, filtered, and crystallized by the slow vapor diffusion of the DMF solution with diethyl ether. An inspection of the sample revealed the presence of two crystal types, red and yellow. Although representative examples of each crystal form could be isolated for analysis by X-ray methods, the sample was dominated (ca. 75%) by the yellow material, i.e. $[C_{21}H_{13}N_3S_5B]I$.

ESI-MS $[C_{21}H_{13}N_3S_5B_1]^+$: 478 (100%). FT-IR (KBr, cm^{-1}): 2494 (νB–H). ^{1}H NMR (400 MHz, d_6-DMSO δ): 8.85 (d, 1H), 8.50 (d, 2H), 7.87 (d, 2H), 7.85 (t, 1H), 7.80 (d, 1H), 7.72 (t, 2H), 7.63 (t, 2H), 7.55 (t, 1H). ^{13}C NMR (100 MHz, d_6-DMSO δ): 169.6, 145.6, 143.3, 130.7, 130.1, 129.1, 128.3, 128.2, 125.3, 124.7, 122.5, 116.2, 114.9. Although peak multiplicities are stated, *J*-values are not. The resonances in DMSO are broad and many of the peaks overlap introducing considerable uncertainty to the values extracted.

Reaction of antimony triiodide (0.25 g, 0.50 mmol) and NaTbz (0.29 g, 0.54 mmol) in $THF/CHCl_3$ (1:1 by volume, 20 mL) followed by the same extraction and crystallization procedure yielded only red crystals of $[C_{21}H_{13}B_1N_3S_5]$ $[Sb(Tbz)I_3]$ (Yield, 0.24 g, 59%). Analysis found: C, 33.48; H, 2.02; N, 5.55%. Anal. Calcd for $C_{42}H_{26}B_2I_3N_6S_{11}Sb_1$: C, 33.84; H, 1.76; N, 5.64%.

^{1}H NMR Analysis of the Reaction of Mercuric Iodide with NaTbz. NaTbz (0.015 g, 28 μmol) was dissolved in d_6-DMSO (0.75 mL), and the ^{1}H NMR spectrum was recorded. A solution of HgI_2 (0.014 g, 31 μmol) in d_6-DMSO (0.75 mL) was then introduced into the NMR tube. The sample was thoroughly mixed, and the sample was placed in the magnet. Spectra (16 scans) were recorded at 15 min intervals for 3 h and then daily for a further 5 days. The spectra were calibrated to the residual solvent (resonance position and integral) for display.

^{1}H NMR Analysis of the Reaction of Antimony Iodide with NaTbz. NaTbz (0.011 g, 21 μmol) was dissolved in d_6-DMSO (0.75 mL), and the ^{1}H NMR spectrum was recorded. A solution of SbI_3 (0.011 g, 22 μmol) in d_6-DMSO (0.75 mL) was prepared and introduced into the NMR tube. The sample was thoroughly mixed, and sample was placed in the magnet. Spectra (16 scans) were recorded at 15 min intervals for 3 h and then daily for a further 5 days.

The spectra were calibrated to the residual solvent (resonance position and integral) for display.

Reaction of Bismuth Iodide with NaTbz in Chloroform. A solution of bismuth iodide (0.15 g, 0.25 mmol) in chloroform (10 mL) was stirred with a suspension of NaTbz (0.27 g, 0.51 mmol) in chloroform (10 mL). A dark suspension formed which was filtered to give a purple solution. The solvent was removed to give an orange residue. Vapor diffusion of diethyl ether into a solution of this material dissolved in DMF gave small orange-red colored crystals. ESI-MS $[C_{21}H_{13}N_3S_5B]^+$: 477 (100%), $[C_7H_5NS_2]^-$: 166 (100%). ^1H NMR (400 MHz, d_6-DMSO δ): 7.98 (m, 3H), δ 7.47 (m, 6H), 7.37 (m, 3H). This species does not have an identified cation to balance the $[Bi(Tbz)I_3]$ anion. The ^1H NMR spectrum does not support the presence of an organic cation (e.g., protonated mercaptobenzothiozole), and the inference is that a small highly disordered cation (e.g., H_3O^+or $Na(DMF)_2$) is present in the voids between the anionic layers in the crystal lattice. Analysis found: C, 25.07; H, 1.07; N, 5.57%. Analysis calcd for $C_{21}H_{13}N_3B_1Bi_1I_3S_6{\cdot}2DMF{\cdot}H_3O^+$: C, 25.62; H, 2.39; N, 5.54%. Alternatively Analysis calcd for $C_{21}H_{13}N_3B_1Bi_1I_3S_6{\cdot}[Na(DMF)_2]$: C, 25.54; H, 2.14; N, 5.52%.

NaTbz (0.0552 g, 0.10 mmol) in $CHCl_3$ (5 mL) and tetra-*n*-butylammonium tetrafluoroborate (0.0349 g, 0.11 mmol) in $CHCl_3$ (5 mL) were added to a suspension of BiI_3 (0.0610 g, 0.10 mmol) in $CHCl_3$ (5 mL). The mixture was stirred for 3 h, resulting in a red solution. This was filtered by gravity and taken to dryness. Crystals of $^nBu_4N[Bi(Tbz)I_3]{\cdot}DMF$ were grown by dissolution of the resulting solid in DMF and vapor diffusion with diethyl ether (Yield, 0.09 g, 64%). ^1H NMR (400 MHz, d_6-DMSO δ): 7.98 (m, 3H), δ 7.47 (m, 6H), 7.37 (m, 3H), 3.16 (m, 8H), 1.56 (m, 8H), 1.30 (m, 8H), 0.93 (t, 12H). Analysis found of vacuum-dried crystals: C, 33.53; H, 3.29; N, 4.50%. Analysis Calcd for $C_{37}H_{49}B_1Bi_1I_3N_4S_6{\cdot}0.5$ DMF: C, 33.54; H, 3.84; N, 4.57%.

Reaction of Bismuth Iodide with NaTbz in Acetone, $[Bi(DMF)_8][Bi_3I_{12}]$. A solution of bismuth iodide (0.14 g, 0.24 mmol) in 20 mL of acetone was stirred overnight (16 h) with NaTbz (0.14 g, 0.26 mmol). The deep red suspension was filtered by gravity to give an orange red solution. The solvent was removed to yield a deep purple residue, which was recrystallized by dissolution in DMF and vapor diffusion with diethyl ether. ESI-MS $[C_7H_5NS_2]^-$: 166 (100%). ^1H NMR (500 MHz, Acetone δ): 8.03 (s, 1H), 2.98 (s, 3H), 2.82 (s, 3H). FT-IR (KBr, cm^{-1}): 1624(C═O). Anal. found: C, 8.30; H, 1.26; N, 3.12%. Anal. calcd for $C_{21}H_{56}N_7O_7Bi_4I_{12}$: C, 8.78; H, 1.72; N, 3.42%.

Reaction of Cobalt Bromide with NaTbz. A solution of anhydrous cobalt(II) bromide (0.22 g, 1 mmol) and NaTbz (0.53 g, 1 mmol) were refluxed in acetone (50 mL) for 2 h. The solution was filtered to yield a yellow solid (0.50 g, 92%), and the resulting blue solution was taken to dryness. The resulting solid was recrystallized from acetone/diethyl ether by vapor diffusion to give blue colored crystals suitable for X-ray crystallographic analysis. ESI-MS $[C_7H_5NS_2]^-$: 166 (100%).

■ RESULTS AND DISCUSSION

Sodium hydrotris(mercaptobenzothiazolyl)borate (NaTbz) was prepared in the melt from mercaptobenzothiazole (mp 166 °C) and sodium borohydride in a 3:1 molar ratio as previously described.[18] The subsequent treatment of this species with mercuric iodide followed by recrystallization produced a yellow crystalline mass. Closer inspection of the product revealed the presence of two different crystal types (both pale yellow in color). The minor product formed needle-shaped crystals, while the major product adopted a block-like morphology. Single crystal X-ray diffraction of the minor product revealed it to be the desired complex [Hg(Tbz)I], in which the mercury is bound by a Tbz ligand adopting a κ^3-S,S,S conformation (Figure 2). Consistent with the structure of the mercuric iodide adducts of Tm^{Me} and Tm^{tBut},[22,23] the mercury atom resides in a slightly distorted environment with the iodide lying at a slight angle (∼12°) to the axis nominally defined by the hydride, boron, and mercury atoms.

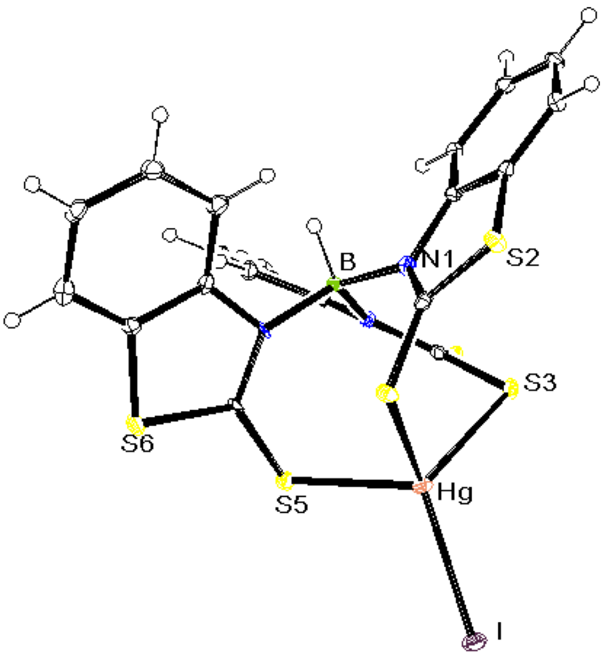

Figure 2. Molecular structure of [Hg(Tbz)I]. Selected bond distances, *d*/Å: Hg−S1, 2.5447(9); Hg−S3, 2.5740(9), Hg−S5, 2.6323(9). Bond angles (deg): S1−Hg−S3, 101.85(3); S1−Hg−S5, 101.13(3); S3−Hg−S5, 102.03(3), S1−Hg−I, 126.90(2); S3−Hg−I, 114.05(2); S5−Hg−I, 107.67(2). The iodine lies at 12° to the axis defined by the hydride, boron, and mercury atoms. Thermal ellipsoids are shown at 30% probability.

Single crystal X-ray diffraction analysis of the major product revealed the $[Hg_2I_6]^{2-}$ salt of a novel **c**ationic **p**entacyclic **h**eterocycle (**CPH**, Figure 3), the latter formed by the coupling of two mercaptobenzothiazole groups with loss of a sulfur

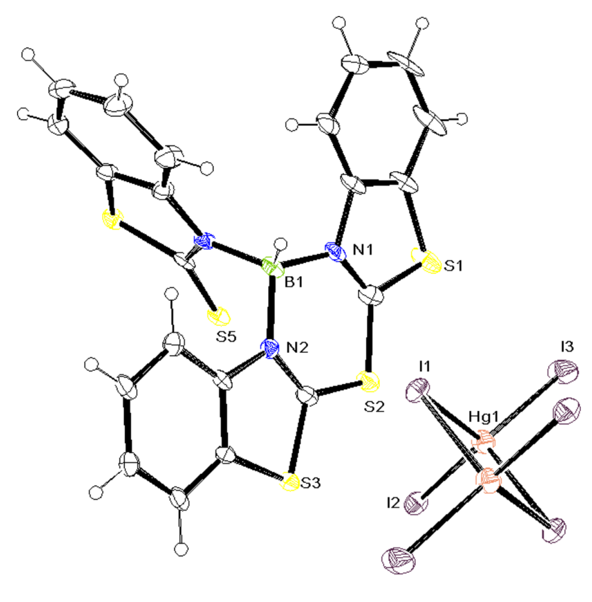

Figure 3. Cationic pentacyclic heterocycle isolated from the reaction of mercuric iodide with NaTbz. There are two CPH cations for every $[Hg_2I_6]^{2-}$ anion. The HgI_3 moiety is located about a crystallographic center of inversion. For clarity the anion is shown in full but only one of the cations is shown.

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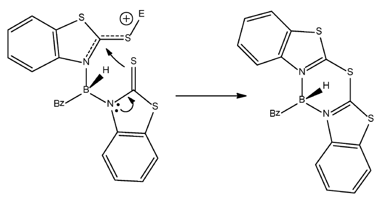
atom. Oxidative ring closure in methimazole based soft scorpionates to form related species has recently been reported.[24] The heterocycle isolated here is in keeping with this study, in that ring closure in the presence of electron withdrawing groups (here HgI) induces desulfurization. Ring closure is possibly assisted by the formation of a transient κ^1-S-TbzHgI complex (Scheme 1) consistent with that observed by Melnick and Parkin in their study of Tm^{tBut}.[23] The central ring of the CPH cation (Figure 3) is almost planar, which suggests that there is substantial delocalization across the rings.

Scheme 1. A Possible Mechanism for Ring Closure (E = HgI_2, SbI_3)



The products of the reaction of NaTbz with antimony iodide depended on the reaction time. If the reaction time was short (3 h) then extraction of the precipitated product into DMF and vapor diffusion with diethyl ether led to a red crystalline material. X-ray crystallography reveals that this contains the $[Sb(Tbz)I_3]^-$ anion, but no identifiable cation as a result of serious crystallographic disorder. Longer reaction times (overnight) followed by a similar extraction and crystallization procedure also resulted in a crystalline mass but now containing two distinct products. In this case they were easily identifiable by eye, since the major product was yellow in color and the minor product red. Structural analysis showed the yellow product to be the iodide salt of the CPH cation (see Supporting Information), while the red material was revealed to be an unusual salt containing a CPH cation and an $[Sb(Tbz)I_3]^-$ anion (Figure 4). If the mixture is stirred for several days the major product is a brown material which was determined to be $CPH[Sb(Tbz)I_3]$. These materials do not undergo further decomposition in the solid state.

The soft scorpionate (Tm^R) complexes of antimony are known to adopt a variety of structures.[25] In contrast to bismuth[25,26] and arsenic[27] complexes, $[E(Tm^{Me})_2]^+$ (which both adopt a regular octahedral geometry), antimony complexes were found to have distorted six- or five-coordinate structures, as a result of a stereochemically active nonbonded electron pair. Thus far, all the species reported were found to be either neutral ($[Sb(\kappa^3\text{-S,S,S-}Tm^{Me})I_2]_2$) or cationic ($[Sb(\kappa^3\text{-S,S,S-}Tm^{Me})(\kappa^2\text{-S,S-}Tm^{Me})]^+$). The species reported here is unusual in that it is not only anionic but it has a more regular geometry at the metalloid suggesting that for this species the nonbonded electron pair is not directional in nature.

The products of the syntheses discussed above show that both complexation and desulphurization/ring closure of the Tbz anion occur. There is no evidence that, under ambient conditions, either decomposition or the observed intramolecular ring closure can occur in NaTbz alone (NMR samples of NaTbz in d_6-dmso or d_6-acetone are unchanged over several weeks),[18] although in the mass spectrum of NaTBz the CPH species is observed. The presence of antimony or mercury ions, perhaps acting as chalcophiles, seems to be essential to the overall process observed here. The fate of the abstracted sulfur atom is not clear, but no formation of H_2S or elemental sulfur is

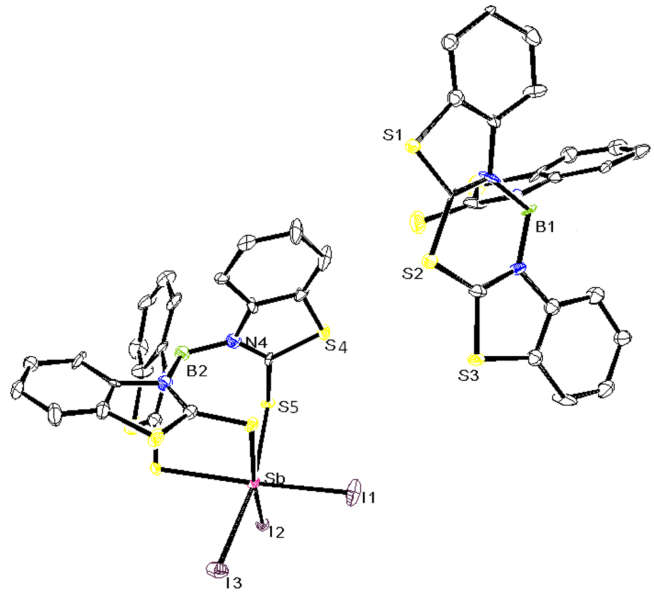


Figure 4. X-ray molecular structure of the hydrotris(benzothiazolyl)-triiodoantimonate salt of CPH. Hydrogen atoms and solvent molecules are omitted for clarity. Thermal ellipsoids are shown at a probability of 50%.

observed and it is possible that metal sulfides are formed. Powder XRD on residues from the antimony reaction show very weak peaks that may be attributable to Sb_2S_3, but we cannot state conclusively that this is the case. While we can propose a reaction sequence which includes the formation of a κ^2 or κ^1 complex which promotes the ring closure and sulfur elimination (Scheme 1), structural analysis alone cannot provide any detail on the events occurring in solution, and consequently we attempted to analyze these reactions using NMR methods. Thus, the ^1H NMR spectra obtained from a solution of SbI_3 and NaTbz in d_6-DMSO were recorded over 2 days at increasing time intervals. The broad resonances from NaTbz prior to addition of the SbI_3 are distinctive of this large anion where the rotation of the mercaptobenzothiazole groups about the B−N bond is slow on the NMR time scale (Figure 5). On the addition of SbI_3 a diminution of these broad resonances is observed. In their place we see the appearance of three resonances (*, Figure 5) which we assigned to the $[Sb(Tbz)I_3]^-$ anion. Not only do the resonances move to lower field in response to the presence of the metalloid and the negative charge, but the spectrum sharpens and resolves into three groups, indicating a lack of exchange on the NMR time scale, which is indicative that the Tbz ligand is coordinated in the κ^3-S,S,S mode.[25] The reaction is not rapid, and detectable amounts of the free Tbz anion are still present in solution at the end of the experiment. The concentration of the antimony complex anion gradually decreases with time. It is notable that the heterocycle is only present in small amounts in solution, and we ascribe this to the relatively low solubility of $CPH[Sb(Tbz)I_3]$. The formation of substantial amounts of mercaptobenzothiazole is also observed in the NMR solution. It is clear that the scorpionate complex of antimony forms readily, but gradually degrades with time. The methods used in the synthesis and isolation of these compounds are not identical to those in the NMR experiment. Thus, while the cationic polycyclic heterocycle, which is obtained as the iodide and the $[Sb(Tbz)I_3]^-$ salts (Figure 4), is observed in both, the synthetic

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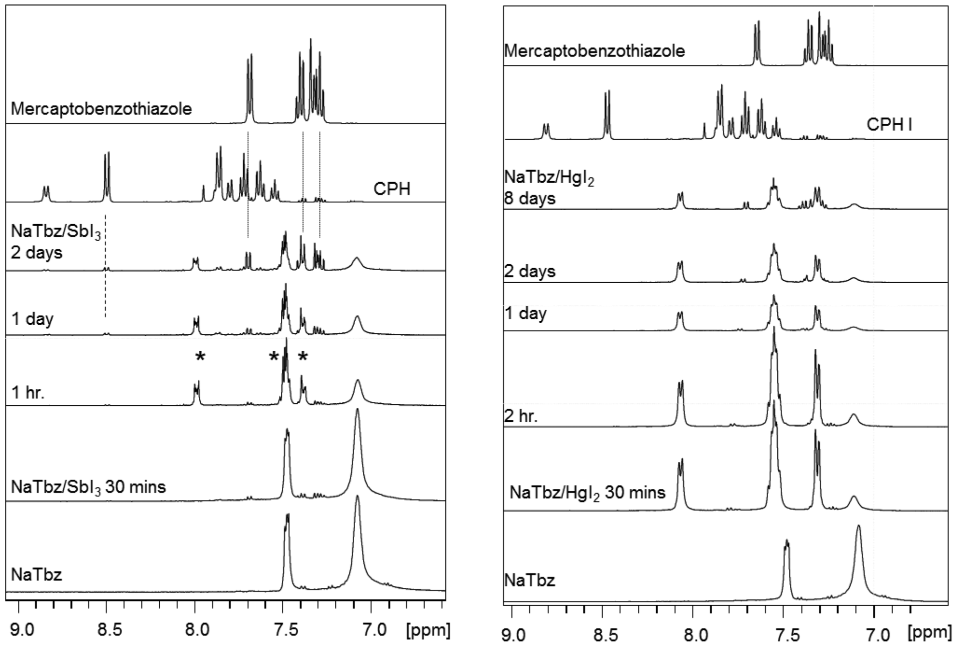

Figure 5. [1]H NMR spectra obtained from the in situ reactions of (left) SbI_3 and (right) HgI_2 with NaTbz in d[6]-DMSO.

procedure fails to isolate the mercaptobenzothiazole, which is formed from the total degradation of coordinated Tbz. Mercaptobenzothiazole is more soluble than the ligand and its complexes and remains in solution either in the initial reaction from which the crude product precipitates or during crystallization.

A similar NMR study was conducted using mercuric iodide (Figure 5). Here the immediate formation of the mercury complex [Hg(Tbz)I] is observed in good yield. In contrast to the reaction with antimony the decomposition products (CPH and mercaptobenzothiazole) are not in great evidence in the solution in the first 24 h. It is notable that as time progresses the complex concentration falls. Concurrent with this observation copious amounts of yellow powder (the iodide salt of the heterocycle) begin to form in the NMR tube. At the conclusion of the experiment, little mercaptobenzothiazole is observed.

Since it was clear that the antimony and mercury complexes were prone to a degree of decomposition, the study was extended to include bismuth in the hope of forming a more stable product with the less Lewis acidic heavier metal. The initial efforts, reacting BiI_3 with NaTbz in both 1:1 and 1:2 ratios resulted in a common product. X-ray analysis of the deep red crystals obtained revealed a $[Bi(Tbz)I_3]^-$ anion. However, despite the acceptable R factor, a cation could not be clearly identified in the heavily disordered residual electron density. Attempts to manipulate the recrystallization were initially unsuccessful. Indeed other solvent systems seemed to promote decomposition. This was the case in acetone solution from which we were able to isolate the novel salt $[Bi(DMF)_8][Bi_3I_{12}]$ (see Supporting Information). However, it was found that addition of $^nBu_4NBF_4$ during the synthesis of this compound resulted in crystals of $^nBu_4N[Bi(Tbz)I_3]\cdot$DMF suitable for X-ray diffraction. The crystal structure analysis confirms an identical, anionic structural motif to that was observed in the antimony complex (Figure 6). The anion has a distorted octahedral geometry, with the intraligand bite angles being a little less than 90° while the angles between the iodine ligands

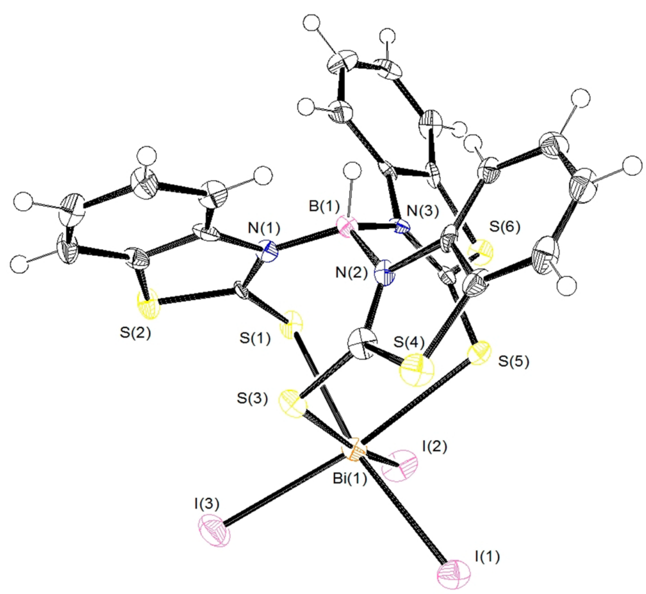

Figure 6. X-ray crystal structure of the $[Bi(Tbz)I_3]^-$ anion in $Bu_4N[Bi(Tbz)I_3]\cdot$DMF. For the sake of clarity the cation and solvent are not shown. Selected bond distances (Å) and angles (deg): Bi(1)−S(1) = 2.841(3), Bi(1)−S(3) = 2.892(3), Bi(1)−S(5) = 2.910(3), Bi(1)−I(1) = 3.0190(9), Bi(1)−I(2) = 2.9930(9), Bi(1)−I(3) = 2.9609(9); S(1)−Bi(1)−S(3) = 88.34(8), S(1)−Bi(1)−S(5) = 85.33(8), S(3)−Bi(1)−S(5) = 85.87(8), I(1)−Bi(1)−I(2) = 94.54(3), I(1)−Bi(1)−I(3) = 98.63(3), I(2)−Bi(1)−I(3) = 99.38(3), I(1)−Bi(1)−S(1) = 169.07(6), I(1)−Bi(1)−S(3) = 95.82(6), I(1)−Bi(1)−S(5) = 84.90(6), I(2)−Bi(1)−S(1) = 80.99(6), I(2)−Bi(1)−S(3) = 169.31(6), I(2)−Bi(1)−S(5) = 92.43(6), I(3)−Bi(1)−S(1) = 91.95(6), I(3)−Bi(1)−S(3) = 81.67(6), I(3)−Bi(1)−S(5) = 167.32(6).

are a little greater than 90°. The Bi−S distances (2.841(3)−2.910(3) Å) are somewhat longer than those in other soft scorpionate complexes of bismuth ($[Bi(Tm)_2I]$, 2.685(4)−2.801(4) Å;[25] $[Bi(Tm_2)]^+$, 2.802(2)−2.806(2) Å[26]), while the Bi−I distances (2.9609(10)−3.0190(10) Å vs 3.153(3) in

$[Bi(Tm)_2I]$[25]) are much shorter. The relatively small deviations from regular octahedral geometry again suggest that the nonbonded electron pair is nondirectional in nature. The anionic nature of the complex possibly accounts for the variations in bond distances. The addition of the anionic ligand to the neutral BiI_3 moiety is presumably not favored, resulting in longer Bi−S contacts. An NMR study, similar to those discussed above for antimony and mercury (see Supporting Information), suggests that the $[Bi(Tbz)I_3]^-$ anion is the only scorpionate product and that it is indefinitely stable in solution, with no decomposition to either the heterocycle or mercaptobenzothiazole being detected. The NMR spectrum of the $[Bi(Tbz)I_3]^-$ anion is essentially identical to that of the species observed in the analogous reaction with antimony, further supporting the identity of the antimony anion, $[Sb(Tbz)I_3]^-$.

The reactions discussed above suggest that the Tbz complexes of the heavier main group elements can be prepared. In line with the predictions made elsewhere,[18] the complexes formed with large, soft metals (bismuth and thallium[9]) are stable. However, as the cations become smaller and more electropositive the complexes are less stable in solution. Consequently the yields are poor and the bulk products are mixtures which are difficult to separate. Our initial study on thallium[9] was in, retrospect, a little fortuitous, as the scorpionate complex isolated was found to be insoluble in the supporting solvent and essentially pure [Tl(Tbz)] precipitated directly from the reaction mixture. Baba et al.[17] used a similar approach in their preparation of $[Co(Tbz)_2]$, which crystallized immediately on formation at the interface of two slowly mixing solutions. Our hypothesis suggests that under normal conditions it would not be possible to isolate the desired scorpionate complex, and it is interesting to note that Baba et al. report that $[Co(Tbz)_2]$ is unstable in DMF solution. To complete this study we decided to revisit the synthesis of $[Co(Tbz)_2]$ and attempt to identify the decomposition products. Consistent with the observations of Baba, on reacting NaTbz with cobalt bromide in acetone we obtained a yellow solid which was analyzed as $[Co(Tbz)_2]$. In addition, a blue solution resulted, from which we obtained modest amounts of dibromobis(benzothiazole) cobalt(II) (Figure 7).

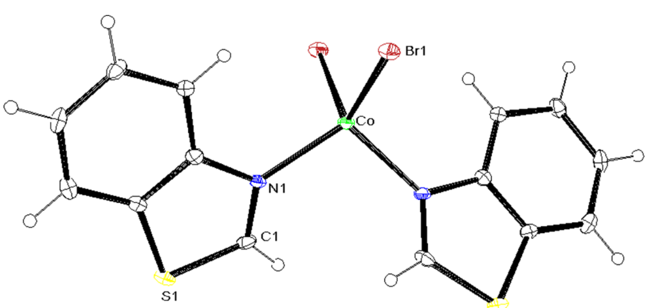

Figure 7. Molecular structure of bis(benzothiazole)dibromocobalt(II). Selected bond lengths (Å) N1−C1, 1.30; C1−S1, 1.70. Thermal ellipsoids are shown at a probability of 30%.

We see again that the poor solubility of the Tbz complex results in the rapid precipitation of the product from solution, thus preserving the bulk of the product. However, there is some evidence of decomposition in the isolation of the benzothiazole complex described above. An analysis of the reaction mixture does not give any evidence for HCP salts, but the release of the desulfurized heterocycle clearly supports a mechanism involving the fission of the B−N bond and the elimination of the thione sulfur. This process is an integral aspect of the mechanism which leads to the formation of HCP. However, in the presence of cobalt this process would seem to potentially be more extensive. The instability of $[Co(Tbz)_2]$ in DMF solution was noted previously, although the decomposition product was not identified.[17]

■ CONCLUSIONS

These studies confirm the inherent instability of certain complexes of the Tbz anion. With large, soft metals complexation is observed, and with bismuth a stable complex anion is the sole product. In the case of antimony and mercury, significant decomposition of the initially formed complexes is apparent over a few hours, resulting in a cationic pentacyclic heterocycle and further degradation to release free benzothiazole-2-thione. With the smaller, and much harder, cobalt(II) ions, the cobalt(II) complex precipitates, but a small amount of a product (a cobalt complex of benzothiazole) indicating a more complete decomposition of the parent Tbz anion is observed. It seems that the inclusion of a sulfur atom in the heterocycle ring results in a less robust scorpionate ligand, as predicted previously,[24] and it is notable that the only other example of such a scorpionate, that utilizing thiazolidine-2-thione, also has no reported metal complexes. It will be interesting to see whether other complexes with these ligands are synthesized in the future.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data in CIF format, additional NMR spectra, and ORTEP diagrams of [CPH]I and $[Bi(DMF)_8][Bi_3I_{12}]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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