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Hydridotris(thioxotriazolyl)borate (Tt), an Ambidentate (N_3/S_3) Tripodal Ligand. X-ray Crystal Structures of Sodium, Bismuth(III), Tin(IV), and Manganese(I) Complexes

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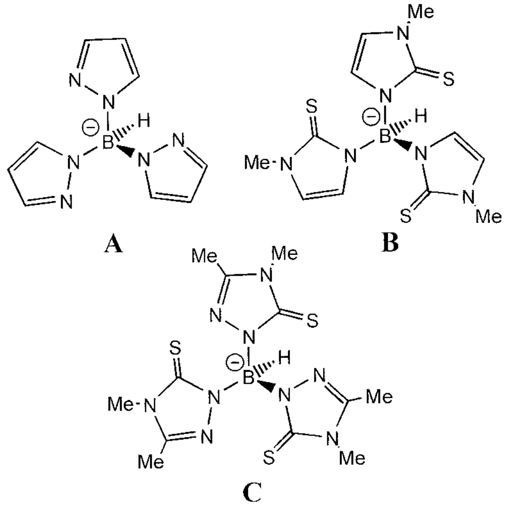
Treatment of the heterocycle 5-thioxo-4,5-dihydro-3,4-dimethyl-1,2,4-triazole (thioxotriazole) with sodium tetrahydroborate at 210 °C provides the new [N_3/S_3] ambidentate tripod ligand hydridotris(thioxotriazolyl)borate (Tt) as its sodium complex salt. Complexes of this ligand with sodium, bismuth(III), tin(IV), and manganese(I) have been synthesized and characterized by X-ray crystallography. The structures of these complexes illustrate the ambidentate character of the ligand with the softer metals bismuth and tin exhibiting sulfur coordination, while sodium and manganese(I) bond via the ligand nitrogen donors. In the [S_3] coordination mode the ligand creates eight-membered chelate rings with the metal with the consequence that the metal ligand unit adopts a propeller-type conformation with C_3-symmetry. However, in the [N_3] mode six-membered chelate rings are formed analogous to the familiar hydrotris(pyrazolyl)borate (Tp) ligand.

Tripodal ligands belonging to the hydridotris(pyrazolyl)borate (Tp) family (**A**, Chart 1) have been used extensively in the coordination chemistry of transition and main group metals.[1,2] They can be regarded as relatively *hard* donor ligands having three pyrazole nitrogen atoms that can be involved in metal coordination. The analogous hydridotris(methimazolyl)borate anion (Tm) (**B**, Chart 1) has recently been prepared by Reglinski and Spicer in order to explore the properties of a softer coordination environment in an anionic, tripodal ligand, provided in this case by the three thione sulfur atoms of the methimazole rings.[3] The two ligand systems also differ fundamentally in the number of atoms linking the central boron atom to the donor atoms; the Tp ligand has a single nitrogen atom linking the two, while in the Tm ligand the link is provided by a diatomic N−C unit. The two ligand systems may thus be categorized as $E(LD)_3$ and $E(L_2D)_3$ tripods respectively (E = tripod central atom, L = linking atom, D = donor atom). The structural consequences of this difference are displayed in the dimensions of the chelate rings formed upon metal complex formation and the molecular symmetry generated as a consequence of the conformations adopted by these rings. Thus, complexes of the Tp family of ligands contain three six-membered chelate rings and the resulting complexes exhibit a local coordination environment of C_{3v} symmetry, while Tm ligand complexes contain three eight-membered chelate rings, thus generating a more flexible twisted or propeller-like ligand conformation and local C_3 symmetry.[4] The Tm ligand is in fact the first to display this type of chirality conferred by the conformation of the bicyclic system formed on coordination of such an $E(L_2D)_3$ ligand, an arrangement previously thought to be thermodynamically unstable.[5] More recently, hybrid tripodal ligands have been synthesized with a mixed [S_2N] donor set by incorporating distinct methimazole and pyrazole moieties within the same hydridoborate-centered ligand.[6]

Chart 1



A **B**

C

We report here the synthesis and initial coordination studies of hydridotris(thioxotriazolyl)borate (Tt),[7] a new [S_3/N_3] tripodal ligand of this type, containing three 5-thioxo-4,5-dihydro-3,4-

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(4) "Local symmetry" refers to the arrangement of a single ligand around a metal. The two possible local symmetries that arise for a symmetrically coordinating tripod ligand are then C_{3v} and C_3.

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dimethyl-1,2,4-triazolyl (thioxotriazolyl) groups around a hydridoborate center (**C**, Chart 1). The use of this heterocycle effectively provides a highly flexible ligand offering a combination of the properties of the Tp and Tm ligands within the same species. Thus, the possible coordination modes which arise are $[N_3]/E(LD)_3$, $[N_2S]/E(LD)_2(L_2D)$, $[S_2N]E(LD)(L_2D)_2$, and $[S_3]/E(L_2D)_3$, all of which may, in principle, be adopted according to the steric and electronic requirements of the metal. Since the donor set is represented by three equivalent thioxotriazole rings, in the absence of other factors, C_{3v} and C_3 local symmetries should result when the ligand is coordinated in $[N_3]$ and $[S_3]$ modes, respectively.

Experimental Section

General Procedures. All solvents and reagents are commercially available and were used as received, except acetonitrile and dichloromethane, which were distilled from 4A (1−2 mm) molecular sieves and CaH_2, respectively. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 250 spectrometer operating at room temperature. Chemical shifts are reported in parts per million referenced to residual solvent protons. Mass spectra were run on a Thermoquest Finnigan LCQ mass spectrometer in the negative ion mode using a nitrobenzyl alcohol matrix. Infrared spectra were recorded as KBr pellets from 4000 to 400 cm^{-1} on a Perkin-Elmer FT-IR Paragon 1000 spectrometer.

Preparation of 5-Thioxo-4,5-dihydro-3,4-dimethyl-1,2,4-triazole. In a 100 cm^3 round-bottom flask, 4-methyl-3-thiosemicarbazide (10 g, 95 mmol) was heated to reflux for 3 days in glacial acetic acid (45 cm^3). The solution was then concentrated to half of the original volume by vacuum distillation. Upon cooling, a white solid precipitated, which was filtered and washed with cold water (20 cm^3). The colorless product was then dissolved in hot water (ca. 100 cm^3) and extracted into dichloromethane (3 × 50 cm^3) in a separating funnel. The CH_2Cl_2 solution was concentrated under reduced pressure, and a colorless product was collected (7.9 g, 61 mmol 64%). Mp: 195−197 °C. IR (KBr disks, cm^{-1}): 3149s, 3088m, 2973s, 1596s, 1514s, 1343s, 1099s, 783m, 676m. ^1H NMR (D_2O): δ 2.27s, 3.38s. Mass spectrum (*m*/*z*, *I* (%)): 129, 100 (M), 130, 66 (M + 1). Anal. Calcd for $C_4H_7N_3S$: C, 37.19; H, 5.46; N, 32.53. Found: C, 37.52; H, 5.23; N, 32.39.

Preparation of Hexaaquasodium [Bis(hydridotris(thioxotriazolyl)borato)] Sodiate, $[Na(H_2O)_6][Na(Tt)_2]$ (1). 5-Thioxo-4,5-dihydro-3,4-dimethyl-1,2,4-triazole (2.56 g, 20 mmol) and sodium tetrahydroborate (0.215 g, 5.6 mmol) were mixed together in a 100 mL round-bottom flask fitted to a volumetric device for measuring hydrogen evolution. Upon stirring, the temperature was raised gently to 180 °C, whereupon evolution of hydrogen gas began. The mixture melted at approximately 210 °C, and the mixture was maintained at this temperature until 3 molar equiv of hydrogen gas had evolved (ca. 400 cm^3). The reaction mixture was allowed to cool to room temperature. The resulting yellow glassy solid was washed with chloroform (3 × 20 cm^3) and acetone (3 × 20 cm^3). The resulting white powder was filtered off and recrystallized from water, yielding colorless crystals of $[Na(H_2O)_6][Na(Tt)_2]$ (2.52 g, 2.66 mmol, 40%). Some problems were encountered as the thioxotriazole sublimes at ca. 200 °C escaping from the reaction environment and thus limiting the reaction yield. IR (KBr disk, cm^{-1}): 3454s, 2958w, 2541m, 1641m, 1575s, 1477m, 1430s, 1330s, 1084s, 1070s, 994s, 819s, 687m, 636m. ^1H NMR (d_6-dmso): δ 2.13 (s, 3H, CH_3), 3.32 (s, 3H, CH_3). ^{13}C NMR (d_6-dmso): δ_C 10.3 (CH_3), 29.2 (CH_3), 145.9 (C_{quat}), 168.1 (C_{quat}). Mass spectrum (*m*/*z*, *I* (%)): 128.2, 100 (base peak), 396.1, 15 (M^-). Anal. Calcd for $C_{24}H_{50}B_2N_{18}Na_2O_6S_6$: C, 30.45; H, 5.32; N, 26.63. Found: C, 30.75; H, 4.93; N, 26.51.

Recrystallization of **1** from slow diffusion of Et_2O into a DMF solution of the complex gave colorless prismatic crystals corresponding to the compound $[Na(Tt)(DMF)_3]\cdot Et_2O$ (**2**). IR (KBr disks, cm^{-1}): 2956w, 2664w, 1653m, 1576s, 1473m, 1419s, 1334s, 1089s, 987s, 822s, 686m, 638m. ^1H NMR (d_6-dmso): δ 2.16 (s, 3H, CH_3), 3.34 (s, 3H, CH_3). ^{13}C NMR (d_6-dmso): δ 11.3 (CH_3), 30.0 (CH_3), 146.2 (C_{quat}), 168.5 (C_{quat}).

Preparation of [Bis(hydridotris(triazolyl)borato)]bismuth(III) Chloride Monohydrate, $[Bi(Tt)_2]Cl\cdot H_2O$ (3). $BiCl_3$ (0.056 g, 0.178 mmol) was dissolved in methanol (10 cm^3) and was added to a methanolic (25 cm^3) suspension of **1** (0.34 g, 0.359 mmol). The reddish precipitate that formed was dissolved in hot water (15 cm^3) and, after cooling, extracted in chloroform (6 × 5 cm^3). The solvent was removed from the resulting purple solution, and $[Bi(Tt)_2]Cl\cdot H_2O$ was collected (0.228 g, 0.121 mmol, 68%). IR (KBr disk, cm^{-1}): 3413s, 2958w, 2502w, 1635m, 1576s, 1476m, 1425s, 1345s, 1083s, 994m, 829m. ^1H NMR (d_4-CD_3OD): δ 2.44 (s, 3H, CH_3), 3.59 (s, 3H, CH_3). Anal. Calcd for $C_{24}H_{38}B_2BiClN_{18}S_6$ H_2O: C, 27.32; H, 3.79; N, 23.89. Found: C, 27.64; H, 3.90; N, 23.22. Recrystallization of the reddish powder from an acetonitrile/water solution gave red crystals structurally characterized by X-ray crystallography as $[Bi(Tt)_2]Cl\cdot 6H_2O\cdot CH_3CN$ (**3a**).

Preparation of Trichloro[hydridotris(triazolyl)borato]tin(IV), $[Sn(Tt)Cl_3]$ (4). Under a nitrogen atmosphere, a solution of tin tetrachloride (0.045 g, 0.172 mmol) in dichloromethane (10 cm^3) was added to a stirred suspension of **1** (0.605 g, 0.640 mmol) in the same solvent (40 cm^3). After 2 h the solution was filtered and the yellow precipitate collected. The yellow powder was then suspended in acetonitrile (100 cm^3) and filtered. The clear, yellow solution was dried under vacuum, and the yellow solid was collected (0.04 g 0.065 mmol, 38%). Suitable crystals of compound **4** were obtained from a DMF solution. IR (KBr disk, cm^{-1}): 2922w, 2486m, 1567s, 1472m, 1427s, 1330m, 1248s, 1076s, 826m, 671m. ^1H NMR (d_6-dmso): δ 2.50 (s, 3H, CH_3), 3.63 (s, 3H, CH_3). ^{13}C NMR (d_6-dmso): δ 11.3 (CH_3), 30.0 (CH_3), 153.7 (C_{quat}), 157.8 (C_{quat}). Anal. Calcd for $C_{12}H_{19}BCl_3N_9S_3Sn$: C, 23.19; H, 3.07; N, 20.29. Found: C, 23.58; H, 2.66; N, 19.89.

Preparation of Tricarbonyl[hydridotris(triazolyl)borato]manganese(I), $[Mn(Tt)(CO)_3]$ (5). Under a nitrogen atmosphere, a mixture of $Mn(CO)_5Br$ (0.350 g, 1.274 mmol) and **1** (0.598 g, 0.684 mmol) was heated to reflux in acetonitrile (35 cm^3) for 1 h. The resulting orange suspension was then filtered and the orange precipitate collected, dissolved in water (ca. 100 cm^3), and extracted in dichloromethane (3 × 50 cm^3). The yellow clear solution was dried under vacuum and 0.357 g of yellow product collected (56%). Crystals of compound **5** suitable for X-ray crystallography were obtained from an acetonitrile solution. IR (KBr disk, cm^{-1}): 2963w 2922w, 2591m, 2039vs, 1958vs, 1928vs, 1569m, 1490s, 1432s, 1335s, 1260m, 1104s, 1069m, 823s, 689m. ^1H NMR (d_3-acetonitrile): δ 2.66 (s, 3H, CH_3), 3.52 (s, 3H, CH_3). Anal. Calcd for $C_{15}H_{19}BMnN_9O_3S_3$: C, 33.65; H, 3.58; N, 23.55. Found: C, 33.15; H, 3.39; N, 23.89.

X-ray Crystallography. Crystals were mounted on glass fibers on a Bruker AXS Smart Apex area detector diffractometer. Graphite-monochromatized Mo Kα ($\lambda = 0.71073$ Å) radiation was used. Relevant crystallographic information is summarized in Table 1, and selected bond lengths and angles are listed in Table 2. Cell constants were obtained from a least-squares refinement of 4999 ($5° < 2\theta < 53°$) (**1**), 6026 ($5° < 2\theta < 53°$) (**2**), 5875 ($5° < 2\theta < 53°$) (**3a**), 10193 ($4° < 2\theta < 53°$) (**4**), and 2089 ($4° < 2\theta < 48°$) (**5**) reflections, respectively. The intensity data were collected using the $\omega-2\theta$ scan technique to the maximum 2θ value given in Table 1. No crystal decay was observed for any of the compounds; an absorption correction was applied using the program SADABS[8] which resulted in transmission factors in the ranges 0.89−0.96 (**1**), 0.68−1.00 (**2**), 0.15−0.80 (**3a**), 0.72−0.86 (**4**) and 0.78−1.00 (**5**), respectively. The structures were solved by direct methods (SIR97)[9] and refined with full-matrix least squares (SHELXL-97),[10] using the Wingx software package.[11] Non-hydrogen atoms were refined anisotropically, and the H atoms were placed at their calculated positions except for B−*H* and *H*₂O in $[Na(H_2O)_6][Na(Tt)_2]$ (**1**) and B−*H*

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(7) Tt = Hydrotris(thioxotriazolyl)borate where thioxotriazolyl = 5-thioxo-4,5-dihydro-3,4-dimethyl-1,2,4-triazolyl.

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Table 1. Summary of X-ray Crystallographic Data for **1**, **2**, **3a**, **4**, and **5**

	$[Na(Tt)_2]Na(H_2O)_6$ (**1**)	$[Na(Tt)(DMF)_3]\cdot Et_2O$ (**2**)	$[Bi(Tt)_2]Cl\cdot 6H_2O\cdot CH_3CN$ (**3a**)	$[Sn(Tt)Cl_3]$ (**4**)	$[Mn(Tt)(CO)_3]$ (**5**)
empirical formula	$C_{24}H_{50}B_2N_{18}Na_2O_6S_6$	$C_{25}H_{50}BN_{12}NaO_4S_3$	$C_{26}H_{53}B_2BiClN_{19}O_6S_6$	$C_{12}H_{19}BCl_3N_9S_3Sn$	$C_{15}H_{19}BMnN_9O_3S_3$
fw	946.78	712.75	1186.28	621.39	535.32
color, habit	colorless, bolck	colorless, block	red, block	yellow, block	yellow, block
cryst size, mm	0.20 × 0.18 × 0.16	0.25 × 0.25 × 0.22	0.38 × 0.30 × 0.16	0.22 × 0.17 × 0.15	0.1 × 0.08 × 0.08
cryst syst	trigonal	trigonal	trigonal	monoclinic	monoclinic
space group	$R3$	$P3$	$R3$	$P2_1/c$	$C2/c$
a, Å	14.6195(15)	13.272(3)	13.941(5)	16.397(2)	21.560(8)
b, Å	14.6195(15)	13.272(3)	13.941(5)	11.1712(19)	14.499(5)
c, Å	17.5023(17)	11.728(3)	22.285(9)	12.9856(15)	15.183(6)
β, deg.				105.936(2)	105.730(8)
V, Å^3	3239.6(6)	1789.2(8)	3751(3)	2287.3(6)	4568(3)
Z	3	2	3	4	8
T, K	150(2)	293(2)	293(2)	293(2)	293(2)
λ, Å (Mo Kα)	0.71073	0.71073	0.71073	0.71073	0.71073
ρ(calcd), Mg/m^3	1.456	1.323	1.576	1.805	1.557
μ, mm^{-1}	0.397	0.269	3.886	1.762	0.890
θ range, deg	1.99−26.34	1.74−26.31	1.92−26.37	1.29−26.37	1.71−23.99
no. of reflns/obsd $F > 2\sigma(F)$	6086/1465	10273/2440	6978/1702	12650/4648	10833/1450
R1[a]	0.0284	0.0313	0.0377	0.0197	0.0560
wR2[b]	0.0819	0.0804	0.0831	0.0547	0.1094

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$.

in $[Na(Tt)(DMF)_3]\cdot Et_2O$ (**2**), $[Sn(Tt)Cl_3]$ (**4**), and $[Mn(Tt)(CO)_3]$ (**5**), which were found and refined. The B−*H* hydrogen atoms of $[Bi(Tt)_2]Cl\cdot 6H_2O\cdot CH_3CN$ (**3a**) were found but not refined. The chloride ion of **3a** was found to be disordered and distributed in three positions along the C_3 crystallographic axes with occupancy factors of 0.22, 0.20, and 0.08, respectively. Diethyl ether solvent molecules in **2** and acetonitrile and water solvent molecules in **3a** were severely disordered and were treated using the PLATON SQUEEZE program.[12] The programs Parst[13] and ORTEP[14] were also used. Full listings of bond lengths and angles, atomic positional parameters, and anisotropic displacement parameters in CIF format are provided as Supporting Information.

Results and Discussion

Reaction of sodium borohydride in the melt with 5-thioxo-1*H*-4,5-dihydro-3,4-dimethyl-1,2,4-triazole (thioxotriazole)[15] at 210 °C following Trifimenko's synthetic method provides sodium hydridotris(thioxotriazolyl)borate (Tt) in 40% yield as a white solid with liberation of 3 mol of H_2. X-ray crystallography shows that this salt is formulated as $[Na(H_2O)_6][Na(Tt)_2]$ (**1**) (Figure 1). Reglinski has previously synthesized the $[Tm_2Bi][Tp_2Na]$ salt, in which, as expected, the soft (Tm) ligand is coordinated to Bi(III) while the hard (Tp) ligand prefers the sodium cation.[16] In this salt each metal is in an octahedral environment; the $[Tm_2Bi]^+$ cation displays a C_3 local symmetry while the (Tp) ligands adopt the trigonal (C_{3v}) η^3-coordination around the sodium. In **1**, however, the hydrogen bonding of the *exo*-thione sulfur atoms above and below the $[Na(Tt)_2]^-$ complex to the hydrogen atoms of three *fac* water ligands in the $[Na(H_2O)_6]^+$ complex induces a twist about the 3-fold axis of the anion reducing the local symmetry to C_3 and results in the formation of hydrogen-bonded polymeric chains in the crystal. The Tt ligands therefore adopt a propeller-like structure with angles between triazoline planes of 104° and angles between triazoline planes and the B−H vector of 24° (cf. 120° and 0°, respectively, for C_{3v} local symmetry). The sodium ion is in a heavily distorted octahedral environment with intraligand N−Na−N angles of 77.87(4)° and corresponding interligand angles of 102.13(4)°. The Na−N bond lengths are 2.469(1) Å. In the $[Na(H_2O)_6]^+$ cation the Na atom is also in a distorted octahedral environment induced by the hydrogen bonding described above. The O−Na−O angles are 83.83(4)° and 96.17(4)°, and the Na−O bond lengths are 2.434(1) Å (Table 2).

Recrystallization of **1** from DMF/Et_2O results in formation of the mono-Tt complex $[Na(Tt)(DMF)_3]$ (**2**), which by X-ray crystallography is shown to crystallize as its mono ether solvate. In the molecule, of which there are two in the cell but related by symmetry, the atoms Na, B, and H attached to B lie on crystallographic 3-fold axes. The Na atom is coordinated by one Tt ligand in an $[N_3]$ mode and by the oxygen atoms of three DMF molecules (Figure 2). The metal is in a distorted octahedral geometry with Tt intraligand angles (N2−Na−N22) of 74.12(4)°, considerably smaller than the O−Na−O2, O−Na−N2, and O2−Na−N2 angles, which are all greater than 90° (Table 2). The Na−N2 and Na−O bond lengths are 2.505(1) and 2.294(1) Å, respectively. A considerable distortion of the Tt ligand is observed upon coordination to the metal. The ligand adopts a propeller-like structure with angles between triazoline planes and the B−H vector of 18° (cf. 0° for C_{3v} local symmetry), and with dihedral angles between triazoline planes of 110° (cf. 120° for C_{3v} local symmetry).

Treatment of bismuth trichloride with 2 molar equiv of **1** in methanol suspension provided a reddish precipitate, which was dissolved in water and extracted into chloroform. Removal of the chloroform gave a red powder in 68% yield, which analyzed as $[Bi(Tt)_2]Cl\cdot H_2O$ (**3**).[17] However, recrystallization from an acetonitrile/water solution provided red crystals, which X-ray crystallography showed to be $[Bi(Tt)_2]Cl\cdot 6H_2O\cdot CH_3CN$ (**3a**)

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(17) The minimum molecular formula found by X-ray diffraction is $[Bi(Tt)_2]Cl\cdot 6H_2O\cdot CH_3CN$, while the elemental analysis data support the formula $[Bi(Tt)_2]Cl\cdot H_2O$. The elemental analysis was performed on a sample of the compound as a powder obtained before crystallization from acetonitrile/water solution.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**, **2**, **3a**, **4**, and **5**

$[Na(H_2O)_6][Na(Tt)_2]$ (**1**)			
Na(1)−N(2)	2.469(1)	O(1w)−Na(2)−O(2w)	96.17(4)
B−N(1)	1.552(1)	B−H	1.06(3)
Na(2)−O(1W)	2.434(1)	S−C(1)	1.692(1)
N(2)−Na(1)−N(2a)	77.87(4)	N(1)−B−H	110.89(9)
N(2)−Na(1)−N(2e)	102.13(4)	N(1)−B−N(1a)	108.0(1)
O(1w)−Na(2)−O(3w)	83.83(4)		
$[Na(Tt)(DMF)_3]\cdot Et_2O$ (**2**)			
Na−O	2.294(1)	B−H(1)	1.07(2)
Na−N(2)	2.505(1)	S−C(1)	1.686(1)
B−N(1)	1.559(1)	N(2)−Na−N(22)	74.12(4)
O−Na−O2	96.76(5)	N(1)−B−N(12)	108.0(1)
O2−Na−N(2)	94.34(4)	N(1)−B−H(1)	110.95(9)
O−Na−N(2)	92.81(4)		
$[Bi(Tt)_2]Cl\cdot 6H_2O\cdot CH_3CN$ (**3a**)			
Bi−S	2.801(1)	B−H	1.10
B−N(1)	1.549(5)	S−C(1)	1.719(5)
S−Bi−S(a)	91.01(4)	N(1)−B−N(1a)	110.0(4)
S−Bi−S(d)	88.99(4)	N(1)−B−H	109.0
$[Sn(Tt)Cl_3]$ (**4**)			
Sn−Cl(1)	2.4195(5)	S(2)−C(12)	1.723(2)
Sn−Cl(2)	2.4032(6)	S(3)−C(13)	1.729(2)
Sn−Cl(3)	2.4079(6)	B−N(13)	1.552(3)
Sn−S(1)	2.5585(5)	B−N(1)	1.553(3)
Sn−S(3)	2.5745(6)	B−N(12)	1.554(3)
Sn−S(2)	2.6154(6)	B−H	1.04(2)
S(1)−C(1)	1.720(2)	Cl(1)−Sn−S(3)	84.01(2)
Cl(2)−Sn−Cl(1)	95.27(2)	Cl(3)−Sn−S(2)	82.62(2)
Cl(3)−Sn−Cl(1)	93.14(2)	Cl(1)−Sn−S(2)	87.86(2)
Cl(2)−Sn−Cl(3)	95.26(2)	S(1)−Sn−S(3)	92.39(2)
Cl(2)−Sn−S(1)	84.21(2)	S(1)−Sn−S(2)	92.79(2)
Cl(3)−Sn−S(1)	90.50(2)	S(3)−Sn−S(2)	90.83(2)
Cl(2)−Sn−S(3)	91.42(2)	N(13)−B−H	106(1)
N(13)−B−N(1)	109.7(2)	N(1)−B−H	110(1)
N(13)−B−N(12)	109.6(2)	N(12)−B−H	112(1)
N(1)−B−N(12)	109.5(2)		
$[Mn(Tt)(CO)_3]$ (**5**)			
Mn−C(1)	1.805(9)	S(1)−C(11)	1.648(6)
Mn−C(2)	1.796(9)	S(2)−C(12)	1.640(7)
Mn−C(3)	1.820(8)	S(3)−C(13)	1.657(6)
Mn−N(21)	2.079(5)	B−N(11)	1.549(8)
Mn−N(22)	2.094(5)	B−N(12)	1.546(7)
Mn−N(23)	2.101(5)	B−N(13)	1.522(8)
C(1)−Mn−C(2)	89.2(4)	B−H	1.12(4)
C(2)−Mn−C(3)	91.3(4)	N(21)−Mn−N(22)	85.6(2)
C(1)−Mn−C(3)	89.8(3)	N(21)−Mn−N(23)	86.8(2)
C(2)−Mn−N(21)	90.1(3)	N(22)−Mn−N(23)	85.1(2)
C(3)−Mn−N(21)	91.1(3)	N(11)−B−N(12)	107.4(5)
C(1)−Mn−N(22)	95.0(3)	N(11)−B−N(13)	107.4(5)
C(3)−Mn−N(22)	91.8(3)	N(12)−B−N(13)	106.8(5)
C(1)−Mn−N(23)	92.3(3)	N(11)−B−H	112(2)
C(2)−Mn−N(23)	91.6(3)	N(12)−B−H	110(2)
		N(13)−B−H	113(2)

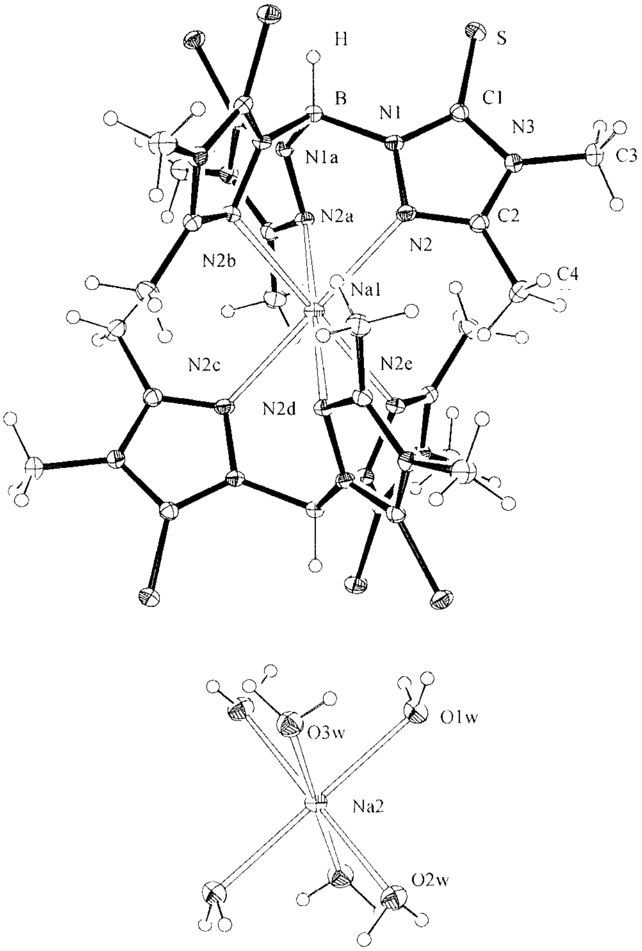

Figure 1. ORTEP drawing of $[Na(H_2O)_6][Na(Tt)_2]$ (**1**) with 30% thermal ellipsoids.

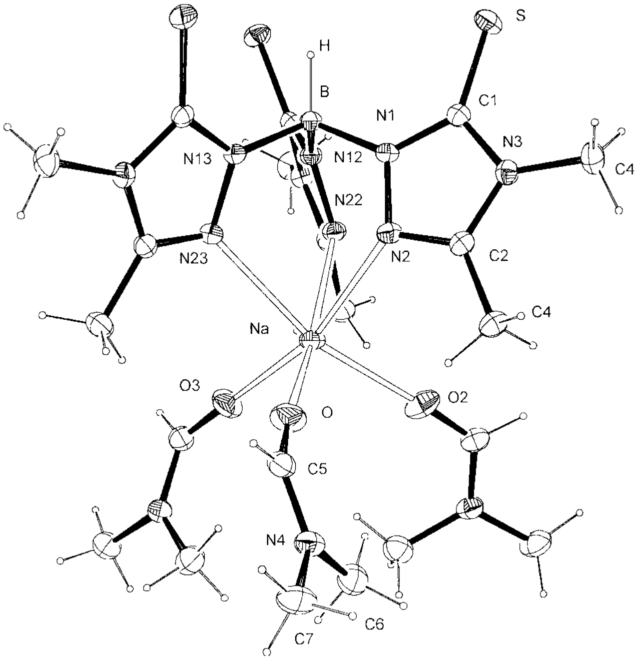

Figure 2. ORTEP drawing of $[Na(Tt)(DMF)_3]$ (**2**) with 30% thermal ellipsoids.

(Figure 3). The bismuth atom is octahedral, bound by the six thione groups of the thioxotriazolyl rings, lies on a crystallographic C_3 axis, and is also located on an inversion center. The Bi−S bond lengths are 2.801(1) Å, and the ligand bite angles and interligand angles are close to 90°, indicating the high coordination symmetry around the metal. The angles between the Bi−B vector and the triazole planes are 36°, indicating a considerable twist of the ligand upon coordination to the Bi(III) ion. The ligands thus adopt a propeller-like conformation as observed for complexes of the Tm ligand.[3,18] The C−S bond lengths of 1.719(5) Å are longer than those in the sodium complexes **1** [1.692(1) Å] and **2** [1.686(1) Å], and also longer than those in the Mn(I) complex **5** to be discussed below [1.648(6)$_{av}$ Å], in which the thione groups are uncoordinated. The chloride anion is disordered in three positions along

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[18] (a) Gardner, M.; Reglinski, J.; Cassidy, I. D.; Spicer, M. D.; Kennedy, A. R. *Chem. Commun.* **1996**, 1975; (b) Slavin, P. A.; Reglinski, J.; Spicer, M. D.; Kennedy, A. R. *J. Chem. Soc., Dalton Trans.* **2000**, 239.

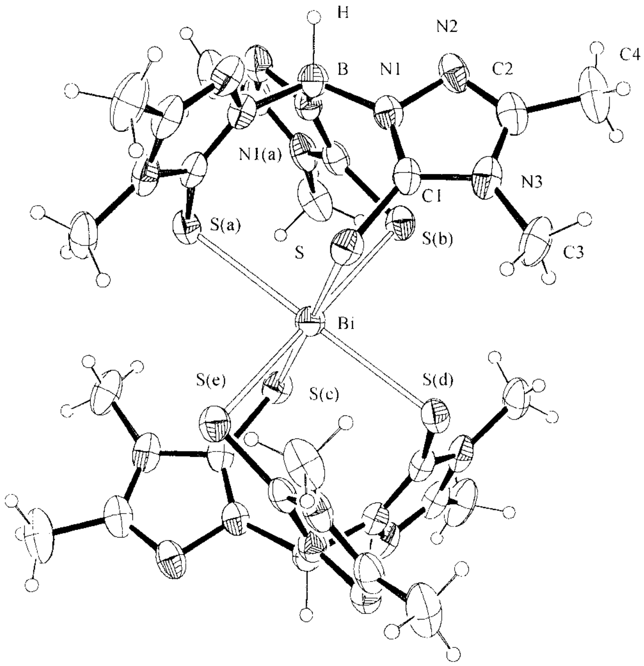

Figure 3. ORTEP drawing of the $[Bi(Tt)_2]^+$ cation in **3a** with 30% thermal ellipsoids.

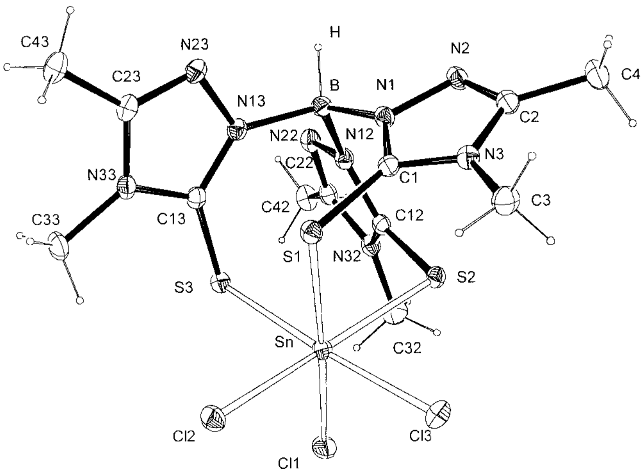

Figure 4. ORTEP drawing of $[Sn(Tt)Cl_3]$ with 30% thermal ellipsoids.

the ternary axes, and the acetonitrile and water solvent molecules are severely disordered in the structural voids.

The treatment of **1** with $SnCl_4$ in dichloromethane provides yellow $[Sn(Tt)Cl_3]$ (**4**) in 38% yield. X-ray crystallography shows the unit cell to contain four discrete molecules, and even though the complex exhibits pseudo-C_3 symmetry, it crystallizes in a monoclinic space group, $P2_1/c$. The Sn(IV) ion is in a moderately distorted octahedral geometry bound by three thione groups of the Tt ligand and by three *fac*-chloro ligands (Figure 4). The Sn−S and Sn−Cl bond lengths range from 2.5585(5) to 2.6154(6) Å and 2.4032(6) to 2.4195(5) Å, respectively. The ligand angles, S−Sn−S, and the Cl−Sn−Cl angles are greater than 90° while the Cl−Sn−S angles range from 82.62(2)° to 91.42(2)°, indicating the distortion of the octahedral environment around the metal. The B atom is in a slightly distorted tetrahedral geometry with N1−B−N1 angles not significantly different, whereas N1−B−H angles range from 106(1)° to 112(1)°. The angles between the triazoline planes are close to 90°, and the angles between the Sn−B vector and the triazoline planes vary from 32° to 39°, indicating a slight distortion of the ligand upon coordination to the metal despite retaining pseudo-C_3 symmetry.

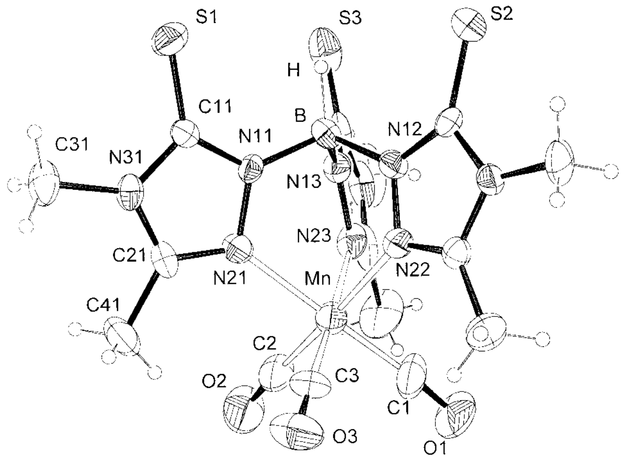

Figure 5. ORTEP drawing of $[Mn(Tt)(CO)_3]$ with 30% thermal ellipsoids.

The only structurally characterized examples of trichlorotin(IV) complexes with boron-centered tripodal ligands are the ones with the hydridotris(pyrazolyl)borate (Tp) ligand and its derivatives. Nevertheless, some structural comparisons can be made, taking due note of the differences between the Tt and Tp ligands. In the structurally characterized complexes $[Sn(Tp)Cl_3]$,[19] $[Sn(Tp^{4Me})Cl_3]$,[20] $[Sn(Tp^*)Cl_3]$,[21] and $[Sn(Tp^{*4Cl})Cl_3]$,[22] the Sn−Cl bond lengths range from 2.332(7) to 2.3912(9) Å and are shorter than those found in **4**, which range from 2.4093(5) to 2.4032(6) Å in accord with the greater trans influence of the thione groups of the $[S_3]$-coordinated Tt ligand in comparison with the pyrazolyl nitrogen donors in the Tp complexes. The angles between the triazoline planes in $[Sn(Tt)Cl_3]$ are close to 90°, as already observed for the $[Bi(Tt)_2]^+$ cation, while in the Tp complexes little deviation from the ideal value of 120° required for C_{3v} local symmetry is observed.

The treatment of $[BrMn(CO)_5]$ with **1** in acetonitrile under reflux provides the complex $[Mn(Tt)(CO)_3]$ (**5**). X-ray crystallography shows the complex to exhibit noncrystallographic C_3 symmetry, and the complex crystallizes in the monoclinic space group $C2/c$. The ligand is $[N_3]$ coordinated despite the presence of the three thione groups available for coordination. It can thus be argued that the greater stability of the six-membered chelate rings of the $[N_3]$-coordinated ligand compared to the eight-membered ones of the $[S_3]$ coordination mode overcomes the anticipated preference of the manganese(I) tricarbonyl moiety for sulfur donor ligands. Three *fac*-carbonyl groups complete the slightly distorted octahedral geometry of the metal (Figure 5). Mn−N and Mn−C bond lengths range from 2.079(5) to 2.101(5) Å and 1.796(9) to 1.820(8) Å, respectively. The ligand bite angles N−Mn−N vary from 85.1(2)° to 86.8(2)° and the C−Mn−C angles are close to 90° while the C−Mn−N angles are greater than 90° (Table 2). The B atom is in a tetrahedral geometry with N1−B−N1 and N1−B−H angles not significantly different (Table 2). A comparison of the $[Mn(Tt)(CO)_3]$ structure with its hydridotris(pyrazolyl)borate (Tp) analogues $[HB\{3,5\text{-}(CF_3)_2Pz\}_3Mn(CO)_3]$,[23] $[HB\{3\text{-}(CF_3)Pz\}_3Mn(CO)_3]$,[23]

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(19) Calogero, S.; Stivano, L.; Lobbia, G. G.; Cingolati, A.; Cecchi, P.; Valle, G. *Polyhedron* **1995**, *14*, 1731.

(20) Lobbia, G. G.; Valle, G.; Calogero, S.; Cecchi, P.; Santini, C.; Marchetti, F. *J. Chem. Soc., Dalton Trans.* **1996**, 2475.

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(22) Lobbia, G. G.; Cecchi, P.; Calogero, S.; Valle, G.; Chiarini, M.; Stieviano, L. *J. Organomet. Chem.* **1995**, *503*, 297.

$[HB(Pz)_3Mn(CO)_3]$,[24] and $[HB\{3,5\text{-}(CH_3)_2Pz\}_3Mn(CO)_3]$[24] indicates significant similarities between the $[N_3]$-coordinated Tt ligand and the Tp ligands since the Mn−C and Mn−N bond lengths in $[Mn(Tt)(CO)_3]$ (Table 2) are closely comparable with those in these complexes.[23,24] Moreover, a better understanding of the complex symmetry and the donor properties of the Tt ligand can be derived from an analysis of the infrared stretching frequencies of the carbonyl groups. For a metal in an octahedral geometry bound by three *fac*-carbonyl groups and by a symmetric tripodal ligand, two CO stretching frequencies would be expected for a C_{3v}-symmetric complex (A and E), whereas for C_3 symmetry the degeneracy of the E modes is lifted and three CO stretching frequencies are predicted (A and 2 × E). In the $[Mn(Tt)(CO)_3]$ complex three bands are present in the carbonyl region (2039, 1958, and 1928 cm^{-1}). This is a somewhat surprising observation, which initially led us to the expectation that the ligand was $[S_3]$ coordinated, as the deviation from C_{3v} symmetry, as shown by the X-ray crystal structure, is small and represents a presumably low energy, conformational distortion from the more symmetrical structure. However, it is clear that, on the time scale of the infrared experiment, the complex exhibits C_3 symmetry. The possibility that the complex exists as a mixture of $[N_3]$ and $[S_3]$ linkage isomers in solution was considered, but the ^1H NMR spectrum clearly indicates the presence of only one species. The CO stretching frequencies for $[Mn(Tt)(CO)_3]$ fall between the values found in the complexes $[HB\{3,5\text{-}R_2Pz\}_3Mn(CO)_3]$ (R = CF_3, CH_3), and consequently the thioxotriazolyl nitrogen donors of the Tt ligand display a donor character intermediate between $(3,5\text{-}CH_3)_2Pz$ and $(3,5\text{-}CF_3)_2Pz$.

Conclusions

The Tt complexes reported here illustrate the ambidentate flexibility of this new ligand, employing the harder nitrogen donors in the formation of the sodium and manganese complexes **1**, **2**, and **5** and the softer sulfur donors for complexation of bismuth and tin in **3** and **4**. The coordination of the Tt ligand to the relatively soft manganese(I) tricarbonyl moiety via its nitrogen donors provides some indication of the position of the crossover point between nitrogen and sulfur coordination, which is anticipated to be somewhat shifted from the position predicted from a simple consideration of nitrogen versus sulfur donor properties by the differences in thermodynamic stability of six- and eight-membered chelate rings. The question of whether mixed $[N_2S]$ and $[NS_2]$ coordination modes are accessible remains a moot point. The Tm ligand has been shown to exhibit considerable flexibility in the dimensions of its coordination site, and a similar flexibility would be anticipated for the $[S_3]$-coordinated Tt ligand. Increases in the size of the coordinated metal result in adjustments of the torsion angles within the Tm ligand to allow the metal to move further out of the ligand coordination pocket while maintaining optimal sulfur−metal bond distances and geometry, thus illustrating a mode of flexibility unavailable to tripod ligands of the $E(LD)_3$ (Tp) type. For the Tt ligand, therefore, the possibility that, for metals of a given electronic requirement, a change in coordination mode may be induced by an increase in metal size also exists, and we are consequently synthesising pairs of appropriate complexes to illustrate this feature. The intriguing possibility of coupling this size effect with the hard/soft selectivity of the ligand coordination modes and a redox process [e.g., Fe(II)/(III)] also presents itself.

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Supporting Information Available: Listings of atomic coordinates of the non-hydrogen and hydrogen atoms, anisotropic displacement parameters, and bond lengths and angles for **1**−**5** in the form of CIF files and plots of the structures of **1** and **3a** viewed down the B−H vectors. This material is available free of charge via the Internet at http://pubs.acs.org.

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