The Preparation and Structures of Group 12 (Zn, Cd, Hg) Complexes of the Soft Tripodal Ligand Hydrotris(methimazolyl)borate (Tm)

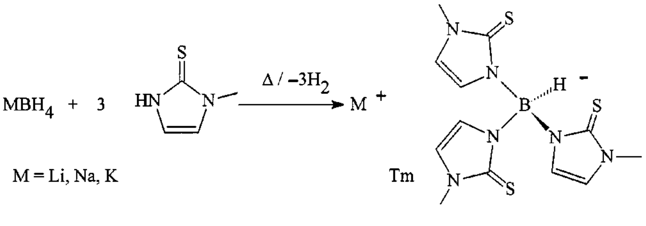
Iain Cassidy,[a] Mark Garner,[a] Alan R. Kennedy,[a] Graeme B. S. Potts,[a] John Reglinski,*[a]
Paul A. Slavin,[a] and Mark D. Spicer*[a]

Keywords: Tripodal ligands / N ligands / S ligands / Group 12 complexes

Complexes of the hydrotris(methimazolyl)borate ligand (Tm) have been prepared with zinc, cadmium and mercury halides. Complexes of type [M(Tm)X] were obtained and characterised by NMR and mass spectrometry. X-ray crystallographic analysis of [Zn(Tm)X] (X = Cl, Br, I) reveals a symmetrical coordination mode of the ligand, but no significant change with different halides, which sit on the approximate C_3 axes of the complexes. The structures of [M(Tm)Br] (M = Cd, Hg) are isomorphous with one another. Again, the ligand is symmetrically coordinated to the metal, but the halide is now significantly displaced from the approximate C_3 axis of the M(Tm) unit, resulting in what approximates to a trigonal pyramidal geometry. Unlike in most distorted mercury structures, little bond length expansion (towards two- or three-coordinate geometries) occurs. This is ascribed to the strong affinity of the thione donors for Hg.
(© Wiley-VCH Verlag GmbH, 69451 Weinheim, Germany, 2002)

Introduction

The tripodal, anionic ligand hydrotris(pyrazolyl)borate (Tp) has been extensively studied since its preparation over 30 years ago.[1,2] Despite the relative ease of preparation of substituted analogues, and thus manipulation of the steric properties of the ligand, it is not possible to substantially alter the donor characteristics. To this end we have recently reported[3,4] the preparation of the novel, soft, anionic tripodal ligand hydrotris(methimazolyl)borate (Tm) (**1**) by adaptation of the method used by Trofimenko to prepare the Tp anion (Scheme 1).



Scheme 1

Tm is broadly analogous to Tp in that it also presents a face-capping donor set, but differs in that: i) the donor set is much softer in character (3 S donor atoms compared to 3 N donor atoms), and ii) the chelate ring size formed on complexation is eight (rather than six in Tp complexes). Tm can be considered to be the softest in a series of 6e$^-$ donor, face-capping anionic ligands *viz* Tp, Cp and Tm.

Our initial studies of the complexation of Tm with late transition metals and with lower main group metals have shown that although the analogy holds with respect to the tripodal bonding mode adopted by the ligand, the chemistry is modulated considerably on going from the hard Tp to the soft Tm ligand. This is manifested particularly in the stability and reactivity of the complexes obtained. For instance, with bismuth(III) we have obtained[5] both the octahedral $[Bi(Tm)_2]^+$ cation and a chloro-bridged dimer $[Bi(Tm)Cl(\mu\text{-}Cl)]_2$, while no examples of Tp complexes of bismuth have been reported. Indeed, in our hands, reaction of NaTp with $BiCl_3$ under identical conditions results in the reduction of the bismuth to its elemental state.[6] Likewise, iodine oxidation of $[Tl^I(Tm)]$ results in the formation of the $[Tl^{III}(Tm)_2]^+$ cation, while [Tl(Tp)] is not oxidised by iodine, but undergoes ligand decomposition.[7] A further difference in reactivity has been noted by Hill,[8] who in an attempt to prepare the Tm analogue of $[Ru(R)(CO)(PPh_3)(Tp)]$ observed intramolecular activation of the bridgehead B−H bond with formation of a metalloboratrane. In the latter example the reactivity apparently arises from the greater flexibility afforded by the eight-membered chelate rings formed by Tm in its metal complexes.

In an effort to further understand the bonding of Tm to metals we decided to investigate the zinc triad of metals. These elements only have a single accessible oxidation state, which should lessen the likelihood of side reactions (which in our experience are mostly redox driven). Furthermore, there has been extensive use of Tp in attempts to model the zinc coordination sphere in metalloenzymes such as carbonic anhydrase and liver alcohol dehydrogenase.[9,10] Recently, to this end, Parkin and Vahrenkamp have prepared

---

[a] Department of Pure and Applied Chemistry, University of Strathclyde,
295 Cathedral Street, Glasgow, G1 1XL, UK

analogues of the Tm ligand either containing an NS_2 donor set[11,12] or with modified steric bulk,[13,14] have reported their zinc complexes and highlighted aspects of their mimicry of the biological system.

We have previously reported in brief the formation and crystal structure of [Zn(Tm)Br],[3] and the preparation of [Zn(Tm)X] (X = Cl, I).[4] The relatively simple tetrahedral structure seems to give an ideal system in which to investigate the effects of metal ion size and counterions on the structures adopted in the absence of problems arising from redox activity. Here we describe the preparation of the full series of group 12 metal halide complexes and analyses of their solid-state structures.

Results and Discussion

The complexes [M(Tm)X] (M = Zn, Cd) are readily prepared by reaction of the metal(II) halide with TlTm in dichloromethane [Equation (1)]; the resulting thallium halide precipitates and reasonably pure materials are obtained after filtration and evaporation of the solvent.

$$MX_2\cdot n\,H_2O \;+\; Tl(Tm) \xrightarrow{CH_2Cl_2} [M(Tm)X] \;+\; TlX\,(+\,nH_2O) \qquad (1)$$

The mercury(II) complexes were less amenable to this method of preparation and so a route using NaTm in acetone was utilised instead. Apparently, the formation of the thallium halide is inhibited in the presence of Hg^{II}. The complexes thus obtained are white to pale yellow powders. The ^1H NMR spectra all show a singlet at about $\delta = 3.5$ (CH_3) and a pair of either singlets or doublets at about $\delta = 6.9$ and $\delta = 7.2$, as would be expected. These resonances are slightly shifted to high field from the free ligand and are generally broadened, suggesting some chemical exchange is taking place. Relatively low solubilities in solvents other than DMSO have ruled out variable temperature NMR studies to investigate this phenomenon. Their formulations are further confirmed by low resolution mass spectrometry. The complexes generally show rather weak parent ion peaks corresponding to [M(Tm)X], indeed in one case the parent is not observed at all. However in all complexes very strong peaks due to $[M(Tm)]^+$ are observed, which suggests relatively facile halide loss but significant stability of the $[M(Tm)]^+$ fragment under these conditions.

The X-ray crystal structures of a series of complexes [M(Tm)X] (where M = Zn and X= Cl, Br, I; M = Cd, Hg and X= Br) have been obtained giving data which allows assessment of the effects of both changing anion and changing metal cation. For the zinc complexes X-ray crystallography reveals the expected pseudo-tetrahedral geometry (Figure 1) with the zinc, halide and B−H all lying on an approximate (or in the case of [Zn(Tm)Br], crystallographic) threefold axis (Figure 2). The S−Zn−S angles are a little less than expected (105−108°) while the S−Zn−X angles are commensurately larger (110−115°). The Zn−S distances are in the narrow range 2.35−2.38 Å, a little longer than the values in Parkin's $[Zn(Tm^{Mes})(HOMe)]$ (2.32−2.34 Å)[13] — possibly reflecting the relative donor abilities of halide and methanol ligands — and show no discernible alteration with changing halide. There are no other structurally characterised monomeric zinc complexes with S_3X (X = halide) donor sets. The only examples of such donor sets are in the zinc thiolate clusters $[Zn_4(\mu\text{-}SPh)_6X_4]$,[15] which have Zn−S distances in the range 2.33−2.38 Å. The Zn−X distances, as expected, closely mirror the change in halide-ion radius. We conclude that there is little influence of the halide on the overall structure. However, changing the metal cation to cadmium or mercury has a profound effect.

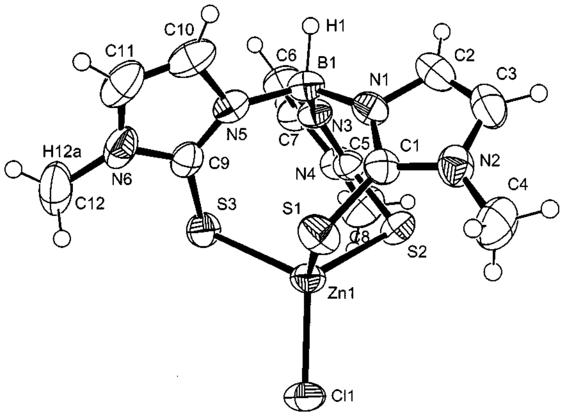


Figure 1. The X-ray Structure of [Zn(Tm)Cl]

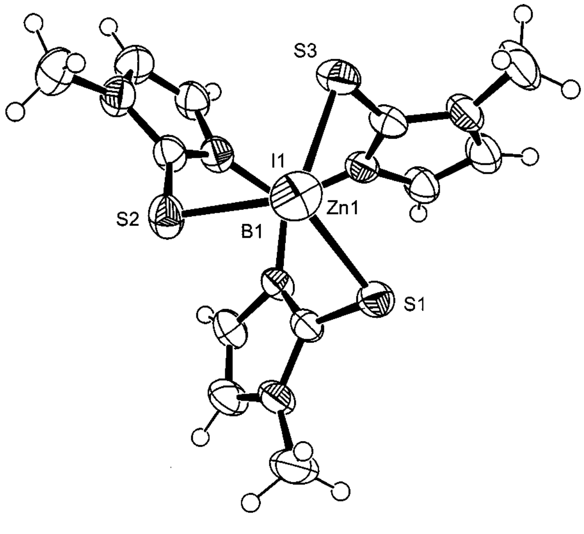


Figure 2. The X-ray Structure of [Zn(Tm)I], viewed down the approximate C_3 axis

The cadmium and mercury structures have remarkably similar structural parameters to one another, indeed it would appear that the compounds are crystallographically isomorphous. While the geometry is best described as highly distorted tetrahedral (Figure 3), the Tm ligand remains symmetrically bound to the metal, with the S−M−S angles lying in the range 100−102°. This is somewhat less than in the corresponding zinc structures (vide supra) suggesting that the metal is displaced further from the ligand pocket. This is borne out by the increased B···M distances. The ligand further accommodates the larger cation by increasing the twist of the methimazole ring from the vertical (C_{3v}) arrangement as measured by the H−B−N−C torsion angles, with values of 36.7, 32.9 and 31.8° for the Zn structures and 40.1 and 40.3° for the Cd and Hg structures, respectively. This is further evidenced by the increase in the mean S···S nonbonded distances resulting from this twist, from 3.74, 3.76 and 3.77 Å in the Zn complexes to 3.97 and 3.98 Å in the Cd and Hg complexes, respectively. The metal and B−H unit are colinear, as in the zinc complexes. However, the halide no longer resides on this axis, but is markedly displaced. This results in a structure that tends towards a trigonal pyramid (Figure 4), with Br, S(1) and S(3) in the basal plane and S(2) in the apical position. The Br−M−S(1) and Br−M−S(3) angles are 120 and 125°, respectively. All the remaining angles are close to 100°.

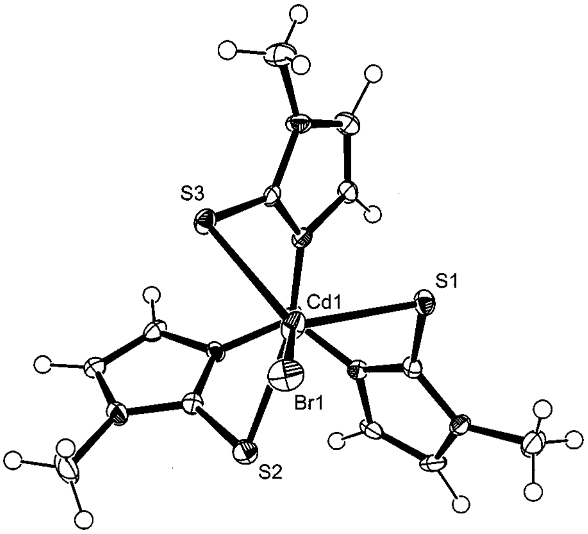


Figure 3. The X-ray Structure of [Cd(Tm)Br], showing the displacement of bromine from the H−B···M axis

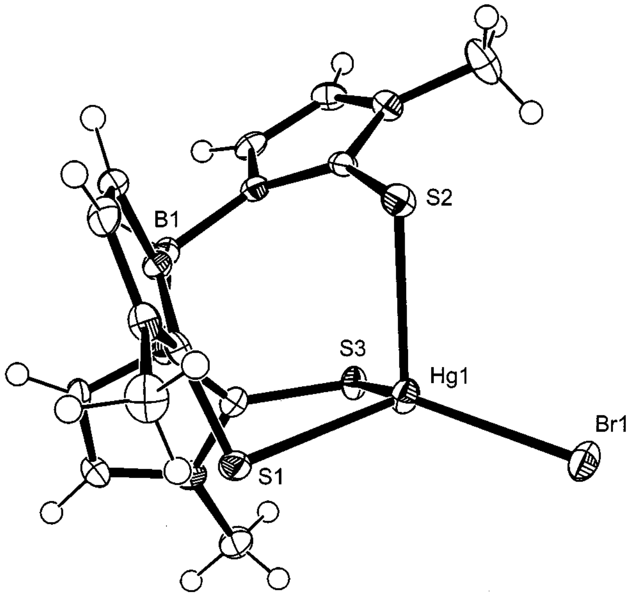


Figure 4. The X-ray Structure of [Hg(Tm)Br], emphasising the flattened trigonal pyramidal coordination geometry

Distorted structures are not uncommon in mercury chemistry, but are observed less frequently in cadmium chemistry. They are usually accompanied by significant lengthening of one or two metal-ligand bonds, tending towards either trigonal planar (e.g. [(Tp^{Me,Me})HgCN][16]) or linear (e.g. [{HOC(py)$_2$(*N*-MeIm)}HgMe][17]) coordination geometries. In this case, however, despite the distorted geometry, the variation of the metal-sulfur bond lengths (2.53−2.63 Å) is somewhat less than in other examples. We suppose that the strong affinity of mercury for sulfur donors (relative to the N-donors cited above) may in part explain this observation, although even in a complex with an S_3X donor set, namely [{C(PSMe$_2$)$_2$(PSPh$_2$)}HgCl], the variation in bond lengths is 2.52−2.72 Å.[18]

Out of curiosity, the reaction of Hg_2Cl_2 with NaTm was also attempted. It was clear that disproportionation of the Hg_2^{2+} core had taken place by the immediate formation of a grey colouration and ultimately by the presence of small drops of metallic mercury. Analysis and NMR spectroscopy suggested that the product was not [Hg(Tm)Cl], and subsequently X-ray crystallography revealed the formation of the previously reported[19] dimer, [Hg(mt)(Hmt)(μ-mt)]$_2$ (Hmt = methimazole). We believe that the destruction of the Tm ligand is driven by the reducing nature of the B−H fragment, and its interaction with the redox active Hg_2^{2+} core.

What is clear from the crystallographic studies is that the Tm ligand binds strongly as a tridentate ligand to the metal centres, even towards metals that commonly exhibit lower coordination numbers. Because of the formation of eight-membered chelates in its metal complexes the ligand is able to show flexibility, adapting to the environment, with S−M−S angles able to vary from less than 90° in octahedral complexes such as [Tl(Tm)$_2$]$^+$ [7] and [Bi(Tm)$_2$]$^+$ [5] through to normal tetrahedral angles in the complexes reported here. While this results in versatility in terms of their ability to coordinate a range of metals, it also renders the ligands susceptible to interaction of the borohydride moiety with the metal and opens a potential route of decomposition, as observed in the reaction with Hg_2Cl_2.

Experimental Section

General: All reagents were obtained commercially and were used as received. NaTm and [Tl(Tm)] were prepared as described previously.[4] NMR spectra were recorded on a Bruker AMX400 spectrometer or a Jeol EX270 spectrometer. Electron Impact Mass Spectra were recorded on a JEOL JMS-AX505HA instrument.

Table 1. Analytical and spectroscopic data

Compound	Microanalysis[a] %C	%H	%N	LRMS[b]	^{1}H NMR	IR ν(B−H)/cm^{-1}
[Zn(Tm)Cl	31.33 (31.88)	3.13 (3.57)	18.49 (18.59)	−,[c] 415	3.54 (s, 3 H) 6.98 (s, 1 H) 7.30 (s, 1 H)	2407
[Zn(Tm)Br]	28.97 (29.03)	3.00 (3.25)	16.40 (16.92)	496, 415	3.55 (s, 3 H) 6.99 (s, 1 H) 7.30 (s, 1 H)	2403
[Zn(Tm)I]·0.5dcm	25.86 (25.69)	2.77 (2.93)	13.70 (14.39)	540, 415	3.55 (s, 3 H) 6.99 (s, 1 H) 7.31 (s, 1 H)	2441
[Cd(Tm)Cl]	30.24 (28.87)	3.85 (3.23)	15.60 (16.84)	500, 464	3.54 (s, 3 H) 6.89 (s, 1 H) 7.23 (s, 1 H)	2453
[Cd(Tm)Br]	26.94 (26.51)	2.48 (2.97)	14.80 (15.46)	543, 463	3.54 (s, 3 H) 6.91 (s, 1 H) 7.25 (s, 1 H)	2403
[Cd(Tm)I]	24.03 (24.40)	2.23 (2.73)	13.25 (14.23)	588,464	3.54 (s, 3 H) 6.96 (s, 1 H) 7.28 (s, 1 H)	−[c]
[Hg(Tm)Cl]·0.25Et$_2$O	26.06 (25.76)	2.81 (3.07)	13.37 (13.87)	−,[c] 552	3.55 (s, 3 H) 7.06 (s, 1 H) 7.32 (s, 1 H)	2394
[Hg(Tm)Br]	22.86 (22.81)	2.03 (2.55)	12.89 (13.30)	631, 551	3.55 (s, 3 H) 7.08 (s, 1 H) 7.32 (s, 1 H)	−[c]
[Hg(Tm)I]	20.77 (21.23)	2.50 (2.38)	12.12 (12.38)	677, 552	3.55 (s, 3 H) 7.09 (s, 1 H) 7.32 (s, 1 H)	−[c]

[a] Found (calcd.). [b] Electron impact MS; M$^+$ (calcd.) [c] Not observed.

[M(Tm)X] (M = Zn, Cd; X = Cl, Br, I). General Method: [Tl(Tm)] (0.200 g, 0.4 mmol) was suspended in acetone (30 mL) and a solution of the metal halide (0.4 mmol) dissolved in the minimum amount of acetone was slowly added. The mixture was stirred overnight at room temperature and the solid formed (TlX) was filtered off. The filtrate was taken to dryness and the resulting solid dried in vacuo. The crude product could be further purified by dissolving in the minimum amount of CH_2Cl_2 and cooling to −18 °C, whereupon colourless crystals were obtained. Crude yields were essentially quantitative, while yields of the recrystallised products were in the range 40−70%.

[Hg(Tm)X] (X = Cl, Br, I). General Method: The mercury(II) halide (2 mmol) and NaTm (2 mmol) were placed in a flask and acetone (25 cm^3) added. The mixture was stirred at room temperature for 20 h. The precipitate formed (NaX) was removed by filtration and the solvent removed in vacuo to yield crude product, which was recrystallised by slow diffusion of n-hexane into a saturated CH_2Cl_2 solution.

Reaction of Hg_2Cl_2 with NaTm: Hg_2Cl_2 (0.314 g, mmol) and NaTm (0.500 g, mmol) were placed in a flask with acetone (50 cm^3). The mixture was refluxed for 4 h and cooled. The solvent was removed on the rotary evaporator and the solid residue extracted with CH_2Cl_2 (3 × 20 cm^3). The solution was concentrated and the product precipitated as a white solid by addition of excess diethyl ether. Yield 0.5 g. Crystals for X-ray diffraction were obtained by slow evaporation of a CH_2Cl_2 solution.

Analytical and spectroscopic data for all the complexes are collected in Table 1.

X-ray Crystallography: Crystals of [Zn(Tm)Cl], [Zn(Tm)Br], [Zn(Tm)I], [Cd(Tm)Br] and [Hg(mt)(Hmt)(μ-mt)]$_2$ were obtained by slow evaporation of CH_2Cl_2 solutions at −18 °C, while crystals of the complex [Hg(Tm)Br] were obtained by diffusion of hexane into a solution of the complex in CH_2Cl_2. X-ray data were collected at 123 K on Rigaku AFC7S ([M(Tm)X], M = Zn; X= Cl, Br, I, M = Cd, X = Br) and Nonius Kappa-CCD ([Hg(Tm)Br]) diffractometers using graphite monochromated Mo-K_α radiation. The structures were solved by Patterson methods (SHELXS-86),[20] expanded by Fourier synthesis and refined by full-matrix least-squares refinement on F^2 with the exception of the Cd complex which was refined on F (SHELXL-97).[21] All calculations used the WinGX graphical interface.[22] Crystallographic data are collected in Table 2, selected bond lengths and angles in Table 3 and the structures shown in Figure 1−4.

Table 2. Crystallographic details

	[Zn(Tm)Cl]	[Zn(Tm)I]	[Cd(Tm)Br]	[Hg(Tm)Br]
Formula	$C_{12}H_{16}BClN_6S_3Zn$	$C_{12}H_{16}BIN_6S_3Zn.CH_2Cl_2$	$C_{12}H_{16}BBrCdN_6S_3$	$C_{12}H_{16}BBrHgN_6S_3$
M$_r$	452.12	628.49	543.60	505.44
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a/Å	12.722(2)	11.166(2)	10.103(2)	10.0799(2)
b/Å	12.626(5)	15.255(4)	10.042(1)	10.0528(2)
c/Å	11.967(2)	13.749(3)	18.957(2)	18.8840(4)
α/°	90	90	90	90
β/°	95.93(11)	99.32(2)	101.39(1)	101.2261(3)
γ/°	90	90	90	90
V/Å^3	1911.9(9)	2311.1(9)	1885.3(5)	1876.70(7)
Z	4	4	4	4
μ (Mo-K_α)/mm^{-1}	1.759	2.912	3.625	8.537
T/K	123	123	123	123
Reflns Measd	5028	6745	4164	15668
Unique Reflns	4613 (R_{int} = 0.016)	5580 (R_{int} = 0.090)	3940 (R_{int} = 0.023)	3825 (R_{int} = 0.061)
Obs Reflns	3375 [I >2σ(I)]	4161 [I > 2σ(I)]	2932 [I > 2σ(I)]	3490 [I > 2σ(I)]
$R1$	0.027	0.058	0.026	0.023
$wR2$	0.071	0.151	-	0.050
GOF	1.011	1.071	1.090	1.109

Table 3. Selected structural parameters [interatomic distances (Å), angles and torsion angles (°)]

	Zn(Tm)Cl	Zn(Tm)Br[a]	Zn(Tm)I	Cd(Tm)Br	Hg(Tm)Br
M−X	2.2409(7)	2.364(2)	2.5797(9)	2.5674(4)	2.5639(4)
M−S(1)	2.3503(8)	2.355(3)	2.3759(16)	2.544(1)	2.5659(9)
M−S(2)	2.3563(9)		2.3476(16)	2.616(1)	2.6377(10)
M−S(3)	2.3644(7)		2.3498(17)	2.5413(9)	2.5344(10)
M···B	3.626	3.674	3.697	3.820	3.820
S(1)−M−S(2)	106.65(3)	105.35(8)	106.10(6)	100.30(3)	100.52(3)
S(1)−M−S(3)	104.77(2)		106.36(6)	102.30(3)	100.11(3)
S(2)−M−S(3)	107.67(2)		104.37(6)	100.78(3)	102.05(3)
X−M−S(1)	113.20(3)	113.33(7)	114.89(4)	121.62(3)	120.49(2)
X−M−S(2)	113.57(3)		109.53(5)	101.94(2)	103.72(2)
X−M−S(3)	110.45(3)		114.75(5)	124.99(3)	125.84(2)
S···S(av)	3.77	3.74	3.76	3.97	3.98
H−B−N−C(av)	36.7	32.9	31.8	40.1	40.3

[a] See ref.[3] The complex lies on a crystallographic C_3 axis.

CCDC-171635 ([Zn(Tm)Cl]), -171636 ([Zn(Tm)I]), -171637 ([Hg(Tm)Br]) and -171638 ([Cd(Tm)Br]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

---

[1] S. Trofimenko, *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London, **1999**.

[2] S. Trofimenko, *Chem. Rev.* **1993**, *93*, 943−980.

[3] M. Garner, J. Reglinski, I. Cassidy, M. D. Spicer, A. R. Kennedy, *Chem. Commun.* **1996**, 1975−1976.

[4] J. Reglinski, M. Garner, I. Cassidy, P. A. Slavin, M. D. Spicer, D. R. Armstrong, *J. Chem. Soc., Dalton Trans.* **1999**, 2119−2126.

[5] J. Reglinski, M. D. Spicer, M. Garner, A. R. Kennedy, *J. Am. Chem. Soc.* **1999**, *121*, 2317−2318.

[6] J. Regliski, M. D. Spicer, Unpublished results.

[7] P. A. Slavin, J. Reglinski, M. D. Spicer, A. R. Kennedy, *J. Chem. Soc., Dalton Trans.* **2000**, 239−240.

[8] A. F. Hill, G. R. Owen, A. J. P. White, D. J. Williams, *Angew. Chem. Int. Ed.* **1999**, *38*, 2759−2761.

[9] G. Parkin, *Chem. Commun.* **2000**, 1971−1985.

[10] H. Vahrenkamp, *Acc. Chem. Res.* **1999**, *32*, 589−596.

[11] C. Kimblin, T. Hascall, G. Parkin, *Inorg. Chem.* **1997**, *36*, 5680−5681.

[12] J. Seebacher, M. Shu, H. Vahrenkamp, *Chem. Commun.* **2001**, 1026−1027.

[13] C. Kimblin, B. M. Bridgewater, D. G. Churchill, G. Parkin, *Chem. Commun.* **1999**, 2301−2302.

[14] M. Tesmer, M. Shu, H. Vahrenkamp, *Inorg. Chem.* **2001**, *40*, 4022−4029.

[15] P. A. W. Dean, N. C. Payne, J. Wranich, J. J. Vittal, *Polyhedron* **1998**, *17*, 2411−2416.

[16] G. G. Lobbia, P. Cecchi, R. Gobetto, G. Digilio, R. Spagna, M. Camalli, *J. Organomet. Chem.* **1997**, *539*, 9−17.

[17] A. J. Canty, N. Chaichit, B. M. Gatehouse, E. E. George, *Inorg. Chem.* **1981**, *20*, 4293−4300.

[18] S. O. Grim, P. H. Smith, S. Nittolo, H. L. Ammon, L. C. Satek, S. A. Sangokoya, R. K. Khanna, I. J. Colquhoun, W. McFarlane, J. R. Holden, *Inorg. Chem.* **1985**, *24*, 2889−2895.

[19] N. A. Bell, W. Clegg, J. R. Creighton, E. S. Raper, *Inorg. Chim. Acta* **2000**, *303*, 12−16.

[20] G. M. Sheldrick, SHELXS-86, *Program for Crystal Structure Solution*, University of Göttingen, **1986**.

[21] G. M. Sheldrick, SHELXL-97, *Program for Crystal Structure Refinement*, University of Göttingen, **1997**.

[22] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837−838.

Received November 27, 2001
[I01477]