

Metal polypyrazolylborates. X. Thienylmercury(II) derivatives: the X-ray crystal structure of [(5-Me)Thien-2-yl]Hg-(μ -Pz)₂B(Pz)₂

Giancarlo Gioia Lobbia^{a,*}, Patrizio Cecchi^b, Federico Giordano^c, Carlo Santini^a

^a Dipartimento di Scienze Chimiche, Università di Camerino, via S. Agostino 1, I-62032 Camerino, Italy

^b Dipartimento di Agrobiologia ed Agrochimica, Università della Tuscia, Via S. C. De Lellis, I-01100 Viterbo, Italy

^c Dipartimento di Chimica, Università di Napoli "Federico II", via Mezzocannone 4, 80134 Napoli, Italy

Received 23 October 1995

Abstract

Thienylmercury(II) polypyrazolylborates (Tp* = hydridotris-(3,5-dimethylpyrazol-1-yl)borato, Tp^{Me} = hydridotris(3-methylpyrazol-1-yl)borato, pzTp = tetrakis(pyrazol-1-yl)borato) have been synthesised and characterised through elemental analysis, electrical conductivity, molecular weights, and spectral measurements (IR in the solid state and ¹H, ¹³C, ¹⁹⁹Hg NMR in solution). The structure of [(5-Me)Thien-2-yl]Hg-(μ -Pz)₂B(Pz)₂ has been determined (*Pbcn*; *a* = 22.530(6), *b* = 9.366(4), *c* = 19.310(5) Å; *Z* = 8; *R* = 0.054). The mercury(II) atom is tricoordinated in an approximately planar 'T-shaped' configuration.

Keywords: X-ray structure; Hg; ¹⁹⁹Hg-NMR; Polypyrazolylborates; Organomercury(II) compounds; Thienylmercury(II) derivatives

1. Introduction

Since Trofimenko's discovery of poly(pyrazolyl)borato ligands [1], much work has been carried out on their (organo)metal derivatives [2–4]. Since we are interested in d¹⁰ metal polypyrazolylborates, e.g. tin(IV) and organotin(IV) [5], mercury (II) and organomercury (II) derivatives [6], we decided to extend our study to organomercurials from thiophene.

In a previous paper dealing with organomercury compounds it was concluded [6b] that they are fluxional and contain substantially two-coordinated mercury (because of the absence of coupling constants with the pyrazole rings and the almost identical values of the coupling constants to H or C in Pz-rings to those found in their corresponding precursors). This can be compared with the four-coordination (distorted tetrahedral) and the non-fluxionality found in the case of inorganic mercury complexes [6a].

Thiophenes can be easily mono- (and in some cases) poly-mercurated [7]. The ligands Tp* and Tp^{Me} (Tp* = hydridotris-(3,5-dimethylpyrazol-1-yl)borato, Tp^{Me} = hydridotris(3-methylpyrazol-1-yl)borato) are considered

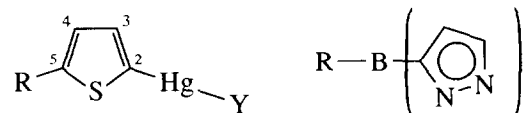
to be sterically demanding [8–10] with respect to Tp or pzTp (pzTp = tetrakis(pyrazol-1-yl)borato).

Another point of interest is linked to the reduction of the Hg ions observed (in solution) with the ligand Tp, but not with Tp* within a time span enough to allow isolation and recording of NMR spectra. In particular, it was found that Hg²⁺, Hg₂²⁺ [6a], R(Ar)–Hg⁺ [6b], or R(Ar)–S–Hg⁺ [6c] ions underwent reduction to metallic mercury at the expense of the ligand's hydridic B–H, though R(Ar)–Hg⁺ ions did so less readily [6b].

Coordination numbers, fluxionality, or ease of reductive decomposition might be affected by a possible interaction of the thiophene ring with mercury ion in the present compounds.

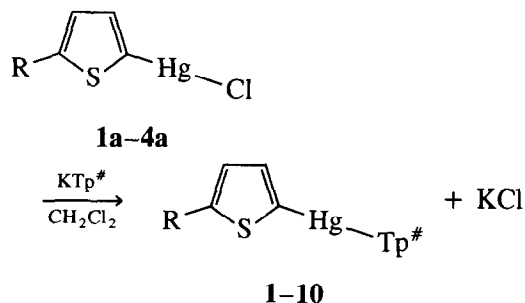
2. Results and discussion

The following numbering scheme has been chosen throughout, which assigns the 2-position to the carbon bonded to mercury.



* Corresponding author.

Interaction of potassium salts of each ligand KTp^* , KTp^{Me} , or KpzTp with several organo-mercurials from either thiophene or substituted thiophenes smoothly proceeds in dichloromethane solution/suspension and afford the compounds **1–10** according to the following reaction scheme:



$\text{R} = \text{H}, \text{Me}, \text{Et}, 5\text{-Cl-Hg-Thien-2-yl}$; $\text{Tp}^\# = \text{Tp}, \text{Tp}^{\text{Me}}, \text{Tp}^*, \text{pzTp}$

The precursors were prepared following established mercuration procedures [7] and include monomercurated thiophenes **1a–3a**, and the dimercurated **4a** (2,2'-bis(chloromercury)-5,5'-dithienyl).

No corresponding compounds could be isolated in

these conditions when KTp was employed, as found when in the presence of other organic groups linked to mercury [6b]. Indeed, the deposition of metallic mercury is fast enough to prevent isolation of the above complexes. In the case of $\text{R} = \text{CN}$, the isolation of the corresponding compound with Tp has been possible thanks to the water solubility of the precursor and insolubility of the product.

The products obtained from Tp^* , Tp^{Me} or pzTp were identified by the analytical data which are shown in Table 1 together with the yields, specific conductivities, and some molecular weight determinations by osmometry; melting points are given for compounds containing the ligands Tp^{Me} or pzTp which, at variance with those of Tp^* , do not decompose on heating.

Conductivity data show that they are not electrolytes in acetone solution, and most of them are monomeric in dichloromethane.

2.1. Infrared spectra and NMR data

The infrared spectra show several bands expected for the ligand moieties; The 'ring breathing' bands appear

Table 1
Yields, analyses, and physical properties of compounds

No.	Compound ^a	Yield	m.p. (°C)	Elemental analysis Found(Calcd.) (%)			Mw ^b	Specific conductivity ^d $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$
				C	H	N		
1		82	— ^c	39.13 (39.29)	4.52 (4.34)	14.21 (14.47)	607 (581)	(1.0) 13.6
2		80	— ^c	40.94 (41.13)	4.58 (4.66)	14.42 (14.39)	613 (595)	(1.0) 8.6
3		74	— ^c	41.11 (41.42)	4.71 (4.80)	13.48 (13.80)	633 (608)	(1.0) 9.9
4		76	241–3	35.76 (45.67)	3.44 (3.55)	15.36 (15.60)		(1.0) 10.4
5		74	226–8	36.58 (36.93)	3.80 (3.83)	14.94 (15.20)	560 (553)	(0.95) 12.3
6		71	222–4	37.82 (38.14)	4.05 (4.09)	14.64 (14.82)		(1.0) 4.5
7		80	192–4	33.94 (34.15)	2.72 (2.69)	19.64 (19.91)		(1.0) 11.2
8		83	184–6	35.02 (35.40)	2.83 (2.97)	19.20 (19.43)	566 (577)	(1.0) 10.4
9		78	150–2	36.17 (36.59)	3.11 (3.24)	18.71 (18.96)		(1.0) 9.6
10		44	— ^c	39.34 (39.11)	4.72 (4.56)	14.89 (15.20)		(1.0) 150

^a Tp^* is hydrotris(3,5-dimethylpyrazol-1-yl)borato, $\text{C}_{15}\text{H}_{22}\text{N}_6\text{B}$; $\text{Tp}^{3\text{Me}}$ is hydrotris(3-methylpyrazol-1-yl)borato, $\text{C}_{12}\text{H}_{16}\text{N}_6\text{B}$; pzTp is tetrakis(pyrazol-1-yl)borato, $\text{C}_{12}\text{H}_{12}\text{N}_8\text{B}$.

^b Molecular weight by osmometry in dichloromethane, Found (Calcd.).

^c Decomposes gradually when heated.

^d Acetone solution at room temperature; molar concentration $\times 10^{-3}$ indicated in parentheses.

Table 2
¹H NMR data

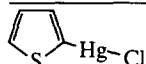
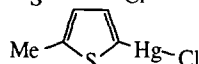
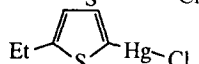
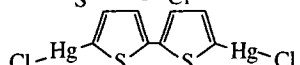
No.	Compound ^{a,b}	Thiophene			Pyrazole		
		5-H ^c	4- or 3-H	Me or Et	5- or 3-H	4-H	5- or 3- Me(s)
1a		7.78 d	7.30 t	7.14 d	—	—	—
2a		—	6.90 d	6.95 d	2.47	—	—
3a		—	7.06 s	7.06 s ^d	1.28; 2.87	—	—
4a		—	7.40 d	7.08 d	—	—	—
1		7.75 d	7.44 t	7.27 d	—	—	5.85 s
2		—	7.07 d	7.00 d	2.58	—	5.84 s
3		—	7.10 d	7.03 d	1.38; 2.98	—	5.80 s
4		7.75 d	7.46 t	7.08 d	—	7.59 d	6.00 d
5		—	7.08 d	7.00 d	2.60	7.58 d	6.00 d
6		—	7.10 d	7.02 d	1.38; 2.98	7.60 d	6.00 d
7		7.12 d	7.00 t	6.84 d	—	7.72 d	7.38 d
8		—	7.00 d	6.82 d	2.56	7.73 d	7.40 d
9		—	7.10 d	6.88 d	1.36; 2.96	7.74 d	7.40 d
10		—	7.50 d	7.14 d	—	—	5.80 s

^a Tp* is HB(3,5-Me₂Pz)₃; Tp^{3Me} is HB(3-MePz)₃; pzTp is B(Pz)₄.^b CDCl₃ solutions except 1a, 2a in DMSO, and 3a in acetone.^c ppm from Me₄Si, calibration from internal deuterium solvent lock.^d 3-H and 4-H are here incidentally isochronous.Table 3
¹³C NMR data

Compound no.	Solvent	Thiophene					Pyrazole		
		C-2	C-3	C-4	C-5	Others	C-3 or C-5	C-4	Others
1a	DMSO	146.5	129.1	134.1	126.6				
2a	DMSO	144.4	125.3	134.4	142.5	Me: 2.47			
3a	(CD ₃) ₂ CO	155.9	124.4	135.4	151.8	Et: 16.4, 23.8			
4a	DMSO	147.5	123.6	135.8	140.7				
1	CD ₂ Cl ₂	125.2	127.3	129.1	134.9		148.9	145.6	105.2
2	CD ₂ Cl ₂	— ^a	126.1	135.2	143.3	Me: 15.3	148.9	145.6	105.1
3	CDCl ₃	— ^a	123.8	134.5	— ^a	Et: 16.0, 23.4	148.3	144.8	104.9
4	CDCl ₃	125.8	127.1	128.9	134.8		149.5	136.3	104.2
5	CDCl ₃	— ^a	125.8	134.8	138.8	Me: 15.2	149.5	136.3	104.2
6	CDCl ₃	— ^a	123.8	134.6	138.9	Et: 16.1, 23.5	149.6	136.3	104.2
7	CDCl ₃	127.1	125.8	129.7	134.9		142.1	136.1	105.9
8	CDCl ₃	— ^a	125.8	134.9	— ^a	Me: 15.3	142.2	136.1	105.9
9	CDCl ₃	— ^a	123.9	134.8	152.2	Et: 16.0, 23.4	142.1	135.1	105.9
10	CDCl ₃	— ^a	123.8	135.5	— ^a		148.7	144.9	104.9

^a Not observed.

Table 4
¹⁹⁹Hg NMR data ^a

RHg-Cl (-δ)	RHg-Tp* (-δ)	RHg-Tp ^{Me} (-δ)	R-Hg-pzTp (-δ)
	970	779	801
	976	784	806
	977	788	808
	993	786	—

^a CDCl₃ solution except RHgCl in DMSO.

at *ca.* 1540 cm⁻¹ and 1505–1510 cm⁻¹ for Tp* and Tp^{Me} respectively; an analogous displacement in frequency for the medium intensity signal corresponding to the B–H stretching is observed for the compounds containing either of the two ligands, namely falling at 2510–2520 for Tp* and 2465–2470 for Tp^{Me}. The C–H stretching vibrations due to the pyrazole ring are quite visible above 3120 cm⁻¹.

The NMR data collected are reported in Tables 2 (¹H), 3 (¹³C), and 4 (¹⁹⁹Hg) for compounds 1–10 together with their starting precursors for comparison.

The proton spectra are in agreement with the proposed formulae; the 3- and 4-protons in the thiophene ring(s) present in our compounds (Table 2) show absorptions at different frequencies ranging from 7.75 to 7.00 ppm, although in 5-ethylthienyl-2-mercury chloride (3a) the 3-H and 4-H are superimposed. The broad signal due to B–H absorption is almost detected through integration.

In ¹³C NMR spectra (Table 3) the chemical shifts for the pyrazole groups always show slightly higher values than those for the starting KTp*, KTp^{Me}, or KpzTp compounds.

From ¹H- and ¹³C NMR spectra, coupling constants could be detected between protons or carbons on thiophene moiety and mercury respectively. In particular, they include ³J[H(3)–Hg] (117–130), ⁴J[H(4)–Hg] (34–37), ⁴J[H(5)–Hg] (75–76), ²J[C(3)–Hg] (219–

Table 5
Coupling constants

	³ J(H3)	⁴ J(H4)	⁴ J(H5)	² J(C3)	³ J(C4)	³ J(C5)
1a	126	37	75	245	140	158
2a	127	36	—	223	146	—
3a	123	36	—	225	150	—
1	117	35	76	240	149	152
2	— ^a	— ^a	—	225	135	—
3	121	34	—	220	125	—
8	123	36	—	— ^a	— ^a	—
9	130	36	—	219	131	— ^a

^a Not observed.

245), ³J[C(4)–Hg] (125–150), ³J[C(5)–Hg] (152–158), measured in Hz (Table 5). The corresponding values for the (substituted)thienylmercury chlorides are very close to those of the complexes. Furthermore, satellite peaks due to coupling of mercury with hydrogens or carbons in the pyrazole ring could not be detected. So, according to previous data [6b], the mercury in the present compounds should be substantially dicoordinate and fluxional in solution. The weaker interaction found in the solid state in MeHg · pzTp [11], also confirmed in the crystal structure of 8, should help in establishing a fluxional behaviour involving the exchange of all four pyrazole rings as donors to the metallic centre.

The ¹⁹⁹Hg spectra (Table 4) always show singlets whose chemical shifts range from –779 to –992. In each case the mercury chemical shifts for the Tp* or Tp^{Me} complexes are higher than those observed for the corresponding thiophene-derived organomercury chlorides, while the reverse is true for those of pzTp. Furthermore, a plot of δ for the 5-substituted complexes against the 5-unsubstituted ones is very regular within this type of complex, and the pzTp causes a greater displacement than Tp^{Me} or Tp*, as shown in Fig. 1. This suggests that there are no sudden changes in

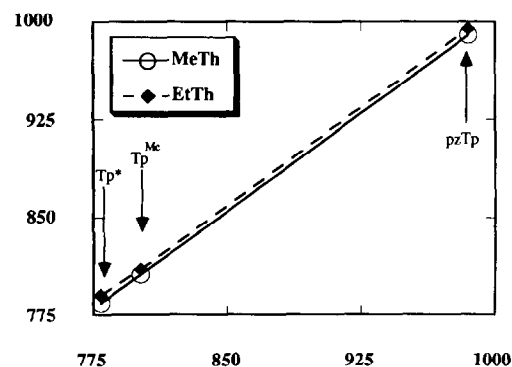


Fig. 1. Plot of $\delta(^{199}\text{Hg})$ values for 5-Me- and 5-Et-thienyl complexes vs. the thienyl ones. The relevant equations of the fitted lines are: $-\delta(5\text{-Me}) = 05.00 + 1.00[-\delta(5\text{-H})]$; $R = 0.99999$; $-\delta(5\text{-Et}) = 12.70 + 0.99[-\delta(5\text{-H})]$; $R = 0.99997$.

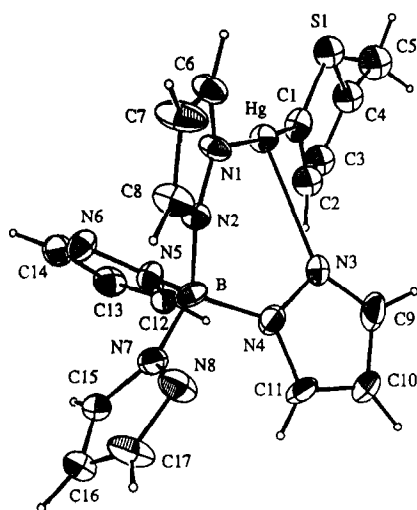


Fig. 2. ORTEP view of [(5-Me)Thien-2-yl]Hg-(μ -Pz)₂B(Pz)₂ with the atom-labelling scheme. Only one conformation of the disordered 5-methyl-thienyl group is shown.

structure among the compounds, even with the pzTp ligand which is a weaker donor [12] than the other two.

2.2. X-ray crystal structure of [(5-Me)Thien-2-yl]Hg-(μ -Pz)₂B(Pz)₂

A perspective view of the molecule is presented in Fig. 2, where only one conformation, out of the two found for the disordered 5-methyl-thienyl group, is shown. The mercury(II) atom is tricoordinated in a 'T-shaped' arrangement. The pzTp ligand acts as a bidentate donor forming a strong Hg–N(1) bond (2.09(1) Å) and a weak Hg–N(3) bond (2.62(1) Å). The first one is nearly collinear with the other strong bond made by Hg with the second unidentate ligand (Hg–C(1), 1.98(2) Å). The mercury atom and the coordinated atoms lie approximately in a plane (the maximum deviation from the best plane through them is 0.024 Å for Hg).

The geometrical features of coordination are pre-

sented in Table 6 and compared with those found in the other complexes of Hg(II) and pzTp so far studied by X-ray analysis [11,13].

In all examined cases, the six-membered ring HgN₄B displays a boat conformation having the Hg and B atoms out of the best plane through the four N atoms. Although the nature of the co-ligand X, intermolecular associations [13], and packing forces can induce significant changes, the comparison of the structural data [11,13] shows that the T-shaped coordination of these (pzTp)-Hg-X complexes is substantially saved. In particular the structural data of Table 6 indicates that, whereas the 5-methyl-thienyl and the methyl complexes of Hg(II) are very close, notable differences can be detected in the Me–S complex, where an association between two molecules occurs through a Hg···S bonding interaction. Such an association is not present in our molecule because the sulphur atom is engaged in granting the aromaticity of the ring and therefore little electron density remains on it to be further donated to other acceptors. In the Me–S complex it is worth noting that the marked departure of the X–Hg–N(1) angle from the ideal value of 180° is to be correlated with the lengthening of the stronger Hg–N(1) bond and with the shortening of the weaker Hg–N(3) bond compared with the two other complexes in Table 6.

The geometry of the pzTp ligand is quite regular. The four pyrazolyl rings, tetrahedrally bonded to B, are planar within the experimental error (maximum displacement out of the mean plane is 0.02(1) Å for N(1)) and their bond lengths and angles fall in the expected ranges.

The coordination geometry is similar to that in the complex methylmercury(II)[tetrakis(pyrazol-1-yl)borato] [11] and [bis(pyrazol-1-yl)methane]methylmercury(II) nitrate [14] and [bis(2-pyridyl)methane]methylmercury(II)nitrate [15]. As for MeHg(pzTp) [11], the title complex forms discrete molecules in the solid state without particular intermolecular interactions.

Table 6

Comparison of geometrical data for 'T-shaped' complexes of Hg(II) with tetrakis(pyrazol-1-yl)borato ligand and a variable X ligand coordinated at the Y atom; distances in Å, angles in degrees

	This work	Ref. [11]	Ref. [13]
X	5-Me-Thien-2-yl	Methyl	Me–S
Y	C	C	S
Hg–Y	1.98(2)	2.05(4)	2.330(2)
Hg–N(1)	2.09(1)	2.07(4)	2.141(7)
Hg–N(3)	2.62(1)	2.65(4)	2.434(8)
X–Hg–N(1)	174.8(5)	169(2)	161.7(2)
X–Hg–N(3)	103.3(5)	112(1)	111.7(2)
N(1)–Hg–N(3)	81.5(4)	78(1)	84.3(2)
Displacements of Hg and B respectively, from the best plane through N(1)–N(2)–N(3)–N(4)	0.87, 0.67	0.70, 0.41	0.87, 0.72

3. Experimental

3.1. General remarks

Concentrations were always carried out under reduced pressure (water aspirator). The samples were dried in vacuo until constant weight (20°C, ca. 0.1 Torr). Carbon, hydrogen, and nitrogen analyses were carried out in our department; molecular weight determinations were performed at Pascher's Mikroanalytisches Laboratorium, Remagen, Germany. Infrared spectra were recorded from 4000 to 600 cm⁻¹ on a 1600 Series FTIR instrument. NMR spectra were recorded on a Varian VX-300 spectrometer operating at room temperature (300 MHz for ¹H, 75 MHz for ¹³C, 53.65 MHz for ¹⁹⁹Hg). The electrical resistances of solutions were measured with a Crison CDTM 522 conductimeter at room temperature. Melting points were taken on an IA 8100 Electrothermal Instrument.

Starting thienylmercury chlorides were prepared according to the literature [7].

3.2.1. [Hydridotris(3,5-dimethyl-1H-pyrazol-1-yl)borate](2-thienyl)mercury(II)] 1

A dichloromethane solution (25 ml) of 2-thienylmercurychloride C₄H₃SHgCl [7] (319 mg, 1 mmol) kept at 10°C was added to a stirred suspension of potassium hydridotris(3,5-dimethyl-1H-pyrazol-1-yl)borate, KTp* (337 mg; 1 mmol), in dichloromethane (30 ml) (10°C). As KTp* slowly dissolved, separation of KCl was observed (ca. 1.5 h). The solution was kept under stirring for another 0.5 h and then filtered; the filtrate was evaporated to dryness under reduced pres-

Table 7
Summary of crystallographic data

Crystal size (mm ³)	0.06 × 0.06 × 0.15
Formula	HgSBN ₈ C ₁₇ H ₁₇
Fw	576.8
Crystal system	orthorhombic
Space group	<i>Pbcn</i>
<i>a</i> (Å)	22.530(6)
<i>b</i> (Å)	9.366(4)
<i>c</i> (Å)	19.310(5)
<i>V</i> (Å ³)	4075(4)
<i>Z</i>	8
<i>F</i> (000)	2208
<i>D_c</i> (g cm ⁻³)	1.88
<i>λ</i> (Cu Kα) (Å)	1.54056
<i>θ</i> _{max} (deg)	75
<i>μ</i> (cm ⁻¹)	156.6
No. of indep. refl.	4126
No. of refl. above 3σ(<i>I</i>)	2314
No. of refined parameters	205
Goodness of fit	1.089
<i>R</i>	0.054
<i>R_w</i>	0.061

Table 8

Final fractional atomic coordinates and displacement parameters (Å² × 10³) of the non-hydrogen atoms with their e.s.d.s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} / <i>U</i> ^a
Hg	0.29237(3)	0.19357(6)	0.04437(3)	61.6(2)
N(1)	0.2669(4)	0.331(1)	-0.0355(6)	59(3)
N(2)	0.3043(4)	0.410(1)	-0.0749(5)	52(1)
N(3)	0.3878(6)	0.174(1)	-0.0322(7)	80(4)
N(4)	0.4066(5)	0.297(1)	-0.0632(6)	63(4)
N(5)	0.3722(4)	0.481(1)	0.0205(5)	54(3)
N(6)	0.3393(5)	0.593(1)	0.0417(6)	69(4)
N(7)	0.3978(5)	0.553(1)	-0.0998(6)	61(4)
N(8)	0.3952(6)	0.542(1)	-0.1719(6)	84(5)
C(6)	0.2134(6)	0.335(1)	-0.0653(8)	72(5)
C(7)	0.2134(7)	0.421(2)	-0.1209(9)	110(7)
C(8)	0.2718(6)	0.466(2)	-0.1250(8)	78(6)
C(9)	0.4305(7)	0.083(2)	-0.0443(9)	95(6)
C(10)	0.4784(7)	0.142(2)	-0.0771(9)	110(7)
C(11)	0.4603(6)	0.277(2)	-0.0904(9)	86(6)
C(12)	0.4111(6)	0.442(2)	0.0702(8)	69(5)
C(13)	0.4030(7)	0.528(2)	0.1255(8)	81(6)
C(14)	0.3574(7)	0.623(2)	0.1047(8)	79(6)
C(15)	0.4299(6)	0.666(1)	-0.0799(8)	69(5)
C(16)	0.4487(7)	0.736(2)	-0.1386(9)	83(6)
C(17)	0.4264(7)	0.656(2)	-0.1926(9)	99(6)
B	0.3706(6)	0.438(2)	-0.0555(7)	53(5)
C(1)	0.3113(6)	0.072(2)	0.1256(8)	75(5)
S(1)	0.2677(4)	-0.045(1)	0.1700(7)	82
C(2)	0.3691(8)	0.060(4)	0.148(2)	82
C(3)	0.3733(9)	-0.013(4)	0.213(2)	89
C(4)	0.3249(9)	-0.105(3)	0.221(2)	89
C(5)	0.3145(9)	-0.214(4)	0.276(2)	114
S(1')	0.3813(5)	0.046(1)	0.1564(7)	82
C(2')	0.2724(6)	-0.015(5)	0.160(2)	82
C(3')	0.2994(7)	-0.094(4)	0.214(1)	89
C(4')	0.3592(7)	-0.076(2)	0.218(1)	89
C(5')	0.4031(9)	-0.142(4)	0.265(2)	114

Note: italicized atoms were given an occupancy factor equal to 0.5.
^a *U*_{eq} = (1/3)Σ_iΣ_j*U*_{ij}*a*_i^{*}*a*_j^{*}*a*_i·*a*_j

sure at below 10°C. The residue was redissolved in CH₂Cl₂ and reprecipitated by slowly adding a mixture of Et₂O-*n*-pentane (1:1 v/v). Compounds 2–6 and 10 were obtained similarly, controlling and limiting the reaction times in order to avoid incipient deposition of metallic mercury. In the case of 10, a ligand to organomercurial 2:1 molar ratio was used.

IR: 3120w cm⁻¹ (C–H stretching vibration), 1540s cm⁻¹ (ring 'breathing'), 2512m cm⁻¹ (B–H stretching), 480 m, 460 m, 365w.

3.2.2. [Tetrakis(1H-pyrazol-1-yl)borate](5-methyl-2-thienyl)mercury(II)] 8

A dichloromethane solution (30 ml) of 5-Me-2-thienylmercurychloride C₅H₅SHgCl [7] (333 mg, 1 mmol) was added to a stirred suspension of potassium tetrakis(pyrazol-1-yl)borate, KpzTp (318 mg; 1 mmol), in dichloromethane (50 ml). Since the ligand cannot be oxidized by mercury, and owing to its lower solubility,

the mixture was refluxed for ca. 5 h. After filtration and evaporation the residue was recrystallized from benzene–*n*-hexane. Suitable crystals for X-ray analysis were grown from slow evaporation of a dichloromethane–acetonitrile solution ca. 3:1 v/v. Compounds **7**, and **9** were obtained similarly.

IR: 3130w cm^{-1} (C–H stretching vibration), 1511s cm^{-1} (ring 'breathing'), 490m, 350w.

3.2.3. Attempted preparation of hydridotris(1*H*-pyrazol-1-yl)borato (Tp) complexes

Following the above procedure for Tp* or Tp^{3Me} complexes, a ready development of a black deposit of mercury was observed, and no Hg-containing compound could be isolated. This behaviour has already been noted for the ligand with either inorganic [6a,c] or organomercury halides [6b].

3.3. X-ray analysis of [(5Me)Thien-2-yl]Hg-(μ -Pz)₂-B(Pz)₂

Details of the structure analysis are listed in Table 7, final fractional atomic coordinates (with displacement parameters) in Table 8 and bond lengths and angles in Table 9. The compound was recrystallized as needles from a mixture of dichloromethane and acetonitrile. X-ray data were collected at room temperature on an Enraf–Nonius CAD4-F automatic diffractometer using Cu K α graphite-monochromated radiation operating in the ω – θ scan mode. The unit cell parameters were obtained by a least squares fitting of the setting values of 25 strong reflections in the θ range $23 \leq \theta \leq 27^\circ$. Three monitoring reflections, measured every 500, showed insignificant intensity fluctuations. The structure was solved by routine application of the Patterson and Fourier techniques. Scrutiny of the difference Fourier map showed the methyl-thienyl group to be disordered over two equally populated sites, related to each other by the Hg–C(1) bond as a twofold axis. A model of the disordered group was fitted on the electron density in the two alternative conformations with site occupancy factor of 0.5. The atoms of the model were included in a restrained refinement procedure, where reasonable values of isotropic thermal parameters were assigned to atoms and held fixed. All other non-hydrogen atoms were refined anisotropically.

The full-matrix least squares refinement minimised the quantity $\sum w(\Delta F)^2$ with $w^{-1} = [\sigma^2(F_o) + (0.02F_o)^2 + 0.2]$ where σ is derived from counting statistics. The H-atoms were placed in calculated positions with isotropic thermal parameters 1.2 times larger than the B_{eq} of the carrier atoms at the beginning of each least squares cycle and not refined. At the end of the isotropic refinement a correction for absorption effects was applied according to Walker and Stuart [16], by using the computer program DIFABS. (Max. and min.

Table 9

Bond lengths (Å) and valence angles (deg) with their e.s.d.s in parentheses

Hg–N(1)	2.09(1)	Hg–N(3)	2.62(1)
Hg–C(1)	1.98(2)	N(1)–N(2)	1.35(1)
N(1)–C(6)	1.34(2)	N(2)–C(8)	1.32(2)
N(2)–B	1.56(2)	N(3)–N(4)	1.36(2)
N(3)–C(9)	1.31(2)	N(4)–C(11)	1.33(2)
N(4)–B	1.56(2)	N(5)–N(6)	1.35(2)
N(5)–C(12)	1.35(2)	N(5)–B	1.52(2)
N(6)–C(14)	1.31(2)	N(7)–N(8)	1.40(2)
N(7)–C(15)	1.34(2)	N(7)–B	1.50(2)
N(8)–C(17)	1.34(2)	C(6)–C(7)	1.34(2)
C(7)–C(8)	1.39(2)	C(9)–C(10)	1.38(2)
C(10)–C(11)	1.35(2)	C(12)–C(13)	1.35(2)
C(13)–C(14)	1.42(2)	C(15)–C(16)	1.38(2)
C(16)–C(17)	1.38(2)	C(1)–S(1)	1.70(2)
C(1)–C(2)	1.38(3)	S(1)–C(4)	1.72(3)
C(2)–C(3)	1.43(5)	C(3)–C(4)	1.40(4)
C(4)–C(5)	1.48(5)	C(1)–S(1')	1.70(2)
C(1)–C(2')	1.37(4)	S(1')–C(4')	1.72(2)
C(2')–C(3')	1.42(4)	C(3')–C(4')	1.36(2)
C(4')–C(5')	1.49(4)		
N(3)–Hg–C(1)	103.3(5)	N(1)–Hg–C(1)	174.8(5)
N(1)–Hg–N(3)	81.5(4)	Hg–N(1)–C(6)	125.5(9)
Hg–N(1)–N(2)	125.3(7)	N(2)–N(1)–C(6)	108(1)
N(1)–N(2)–B	124(1)	N(1)–N(2)–C(8)	106(1)
C(8)–N(2)–B	129(1)	Hg–N(3)–C(9)	138(1)
Hg–N(3)–N(4)	116(1)	N(4)–N(3)–C(9)	104(1)
N(3)–N(4)–B	121(1)	N(3)–N(4)–C(11)	110(1)
C(11)–N(4)–B	129(1)	C(12)–N(5)–B	129(1)
N(6)–N(5)–B	119(1)	N(6)–N(5)–C(12)	111(1)
N(5)–N(6)–C(14)	106(1)	C(15)–N(7)–B	128(1)
N(8)–N(7)–B	120(1)	N(8)–N(7)–C(15)	111(1)
N(7)–N(8)–C(17)	103(1)	N(1)–C(6)–C(7)	111(1)
C(6)–C(7)–C(8)	103(1)	N(2)–C(8)–C(7)	111(1)
N(3)–C(9)–C(10)	113(1)	C(9)–C(10)–C(11)	103(1)
N(4)–C(11)–C(10)	109(1)	N(5)–C(12)–C(13)	108(1)
C(12)–C(13)–C(14)	104(1)	N(6)–C(14)–C(13)	111(1)
N(7)–C(15)–C(16)	108(1)	C(15)–C(16)–C(17)	105(1)
N(8)–C(17)–C(16)	113(1)	N(5)–B–N(7)	110(1)
N(4)–B–N(7)	110(1)	N(4)–B–N(5)	108(1)
N(2)–B–N(7)	112(1)	N(2)–B–N(5)	107(1)
N(2)–B–N(4)	109(1)	Hg–C(1)–C(2)	120(1)
Hg–C(1)–S(1)	130(1)	S(1)–C(1)–C(2)	109(2)
C(1)–S(1)–C(4)	94(1)	C(1)–C(2)–C(3)	112(2)
C(2)–C(3)–C(4)	110(2)	S(1)–C(4)–C(3)	109(2)
C(3)–C(4)–C(5)	129(2)	S(1)–C(4)–C(5)	121(1)
Hg–C(1)–C(2')	126(1)	Hg–C(1)–S(1')	124(1)
S(1')–C(1)–C(2')	110(2)	C(1)–S(1')–C(4')	94(1)
C(1)–C(2')–C(3')	113(1)	C(2')–C(3')–C(4')	114(2)
S(1')–C(4')–C(3')	109(1)	C(3')–C(4')–C(5')	130(2)
S(1')–C(4')–C(5')	121(1)		

values of the absorption correction were 1.33 and 0.59.) The final Fourier difference map showed no peaks greater than $1.58 \text{ e } \text{Å}^{-3}$.

Neutral atomic scattering factors were taken from literature [17]. All calculations, carried out on a Vax 750 at the Centro Interdipartimentale di Metodologie Chimico-fisiche of the University of Naples, were performed by using the Enraf–Nonius (SDP) set of pro-

grams [18] and the SHELX76 program [19]. Final atomic parameters are presented in Table 8.

Hydrogen atom parameters and anisotropic thermal parameters of the non-hydrogen atoms are available from the Cambridge Crystallographic Data Centre.

Acknowledgements

We thank Dr. Giovanni Rifaiani for recording the ^{199}Hg NMR spectra and Dr. Maura Pellei for technical assistance. Financial support was provided by the ‘‘Consiglio Nazionale delle Ricerche’’ and ‘‘Università degli Studi’’ Camerino.

References

- [1] S. Trofimenko, *J. Am. Chem. Soc.*, **89** (1967) 3170.
- [2] (a) S. Trofimenko, *Acc. Chem. Res.*, **4** (1971) 17; (b) S. Trofimenko, *Chem. Rev.*, **72** (1972) 497.
- [3] (a) S. Trofimenko, *Prog. Inorg. Chem.*, **34** (1986) 115; (b) K. Niedenzu and S. Trofimenko, *Top. Curr. Chem.*, **131** (1986) 1.
- [4] S. Trofimenko, *Chem. Rev.*, **93** (1993) 943.
- [5] (a) G. Gioia Lobbia, F. Bonati, P. Cecchi, A. Cingolani and A. Lorenzotti, *J. Organomet. Chem.*, **378** (1989) 139; (b) G. Gioia Lobbia, F. Bonati P. Cecchi and D. Leonesi, *J. Organomet. Chem.*, **391** (1990) 155; (c) G. Gioia Lobbia, F. Bonati P. Cecchi A. Lorenzotti and C. Pettinari, *J. Organomet. Chem.*, **403** (1991) 317; (d) G. Gioia Lobbia, P. Cecchi, R. Spagna, M. Colapietro, A. Pifferi and C. Pettinari, *J. Organomet. Chem.*, **485** (1995) 45; (e) G. Gioia Lobbia, P. Cecchi, S. Calogero, G. Valle, M. Chiarini and L. Stievano, *J. Organomet. Chem.*, **503** (1995) 297. (f) S. Calogero, L. Stievano, G. Gioia Lobbia, A. Cingolani, P. Cecchi and G. Valle, *Polyhedron*, **14** (1995) 1731.
- [6] (a) G. Gioia Lobbia, F. Bonati, P. Cecchi and C. Pettinari, *Gazz. Chim. Ital.*, **121** (1991) 355; (b) G. Gioia Lobbia, P. Cecchi, F. Bonati and G. Rifaiani, *Synth. React. Inorg. Met-Org. Chem.*, **22** (1992) 775; (c) G. Gioia Lobbia, P. Cecchi, S. Bartolini, C. Pettinari and A. Cingolani, *Gazz. Chim. Ital.*, **123** (1993) 641.
- [7] *Houben-Weyl: Methoden der organischen Chemie*, Georg Thieme, Stuttgart, 1974, pp. 52–54.
- [8] A.H. Cowley, C.J. Carrano, R.L. Geerts, R.A. Jones and C.M. Nunn, *Angew. Chem. Int. Ed. Engl.*, **27** (1988) 277.
- [9] A. Duatti, F. Tisato, F. Refosco, U. Mazzi and M. Nicolini, *Inorg. Chem.*, **28** (1989) 4564.
- [10] R.A. Kresinski, T.A. Hamor, L. Isam, C.J. Jones and J.A. McCleverty, *Polyhedron*, **8** (1989) 845.
- [11] A.J. Canty, B.W. Skelton and A.H. White, *Aust. J. Chem.*, **40** (1987) 1609.
- [12] C. Lopez, R.M. Claramunt, D. Sanz, C. Foces Foces, F.H. Cano, R. Faure, E. Cayon and J. Elguero, *Inorg. Chim. Acta*, **176** (1990) 195.
- [13] S. Aime, G. Digilio, R. Gobetto, P. Cecchi, G. Gioia Lobbia and M. Camalli, *Polyhedron*, **13** (1994) 2695.
- [14] A.J. Canty, C.V. Lee, N. Chaichit and B.M. Gatehouse, *Acta Crystallogr. Sect. B*; **38** (1982) 743.
- [15] A.J. Canty, N. Chaichit, B.M. Gatehouse, E.E. George and G. Hayhurst, *Inorg. Chem.*, **20** (1981) 2414.
- [16] N. Walker and D. Stuart, *Acta Crystallogr. Sect. A*; **39** (1983) 158.
- [17] *International Tables for X-ray Crystallography*, Vol. IV, Kynoch, Birmingham, UK, 1984.
- [18] Enraf–Nonius (1989) CAD-4 Software, Version 5.0, Enraf–Nonius, Delft, Netherlands.
- [19] G.M. Sheldrick, *SHELX76 Program for Crystal Structure Determination*, 1976, University of Cambridge, UK.