Letter

# Chiral coordination polymers based on thallium(I) complexes of new bis- and tris(pyrazolyl)borate ligands with externally-directed 4-pyridyl groups

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**The new ligands dihydro-bis[3-(4-pyridyl)pyrazol-1-yl]borate ($Bp^{4py}$) and hydro-tris[3-(4-pyridyl)pyrazol-1-yl]borate ($Tp^{4py}$) are derivatives of the well known bis- and tris(pyrazolyl)borate cores, bearing 4-pyridyl substituents attached to the pyrazolyl $C^3$ positions; crystal structures of the Tl(I) complexes show that both are infinite one-dimensional polymeric chains, in which the Tl(I) centre within each bis-pyrazolyl or tris-pyrazolyl cavity is also connected to a pendant 4-pyridyl residue from an adjacent complex unit to build up the chain.**

## Introduction

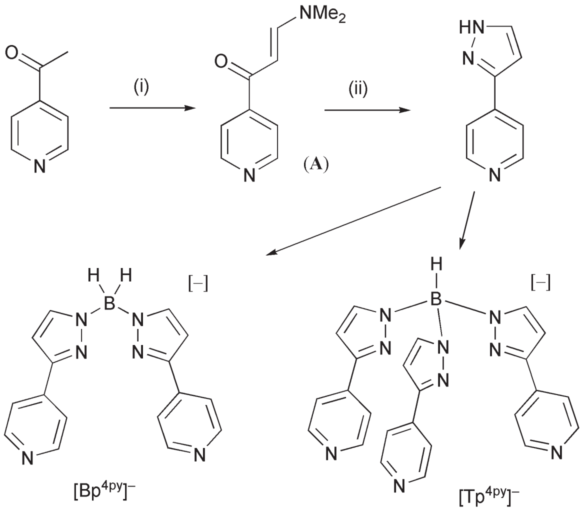
Since their introduction by Trofimenko, poly(pyrazolyl)borate ligands have proven to be extremely popular. Initial development of the ligands concentrated on controlling their steric properties using substituents at the $C^3$ position of each pyrazolyl ring, in order to provide a protecting environment around a metal ion.[1] More recently, a new generation of poly(pyrazolyl)borate derivatives has been developed in which additional coordinating groups have been attached to the pyrazolyl rings. Prominent among these is the ligand $[Tp^{2py}]^-$ in which the attachment of a 2-pyridyl substituent to each of the three pyrazolyl rings at the $C^3$ position makes each 'arm' of the ligand a bidentate chelate.[2] This completely changes the coordination behaviour, as the ligand is now hexadentate and shows behaviour such as encapsulation of lanthanide(III) or actinide(III) ions in 12-coordinate species $[M(Tp^{2py})_2]^+$,[3] and triply-bridging coordination modes in tetrahedral cage complexes such as $[Mn_4(Tp^{2py})_4]^{4+}$.[4] Other coordinating substituents which have been appended to the pyrazolyl $C^3$ positions of poly(pyrazolyl)borates in a similar vein have included bipyridyl,[5] thioanisyl,[6] pyrazinyl,[7] and carboxamide[8] units.

In this communication we report the synthesis and structural characterisation of the ligands $[Bp^{4py}]^-$ and $[Tp^{4py}]^-$, in which 4-pyridyl units (instead of 2-pyridyl) are used as the pyrazolyl $C^3$ substituents. Again this changes the character of the ligands. The central cavity now reverts to the bidentate or terdentate character of the simple bis- and tris(pyrazolyl)borates respectively, with the modification that the externally-directed 4-pyridyl groups cannot chelate to the central metal ion but instead are 'exodentate' and capable of binding to additional metal centres to form, in principle, multinuclear assemblies; or, if they are used to complete the coordination sphere around a metal ion in a different complex unit, coordination polymers will result. An exactly similar principle has been used by Champness and co-workers to prepare structurally elaborate multinuclear assemblies,[9] and we note that the 3-pyridyl substituted Tp analogue, described recently by Vahrenkamp, formed coordination polymers with $K^+$.[10]

## Results and discussion

The key intermediate for formation of $[Bp^{4py}]^-$ and $[Tp^{4py}]^-$ is 3-(4-pyridyl)pyrazole, which was prepared from 4-acetylpyridine in the usual two-step procedure (Scheme 1) for conversion of acetyl groups to pyrazole groups.[5–7] Reaction of 4-acetylpyridine with $KBH_4$ in a melt was then used to prepare the ligands; as reported by Trofimenko, control of stoichiometry and temperature allows selective formation of the bis- or tris-(pyrazolyl)borate in moderate yields.[1] Thus, reaction of $KBH_4$ with 3-(4-pyridyl)pyrazole in a 1 : 2.5 ratio at 175–180°C for 30 minutes afforded $KBp^{4py}$ after workup; use of 3.3 equivalents of 3-(4-pyridyl)pyrazole at 230°C for 3.5 hours afforded $KTp^{4py}$. For the purposes of purification and easier characterisation, these were converted to their Tl(I) salts (which were more crystalline) by reaction with one equivalent of Tl(I) acetate in MeOH. The resulting white solid in each case was filtered off, dried, and crystallised from $CH_2Cl_2$–MeOH (for $TlTp^{4py}$) or DMF–ether (for $TlBp^{4py}$). Analytical and mass spectrometric data for both complexes are in agreement with the formulations; the crystal structures are shown in Figs. 1 and 2.

The structure of $TlBp^{4py}$ (Fig. 1) shows that the complex is a coordination polymer, with one pendant 4-pyridyl group on each $TlBp^{4py}$ monomer unit being used to complete the coordination environment about the adjacent Tl(I) centre, resulting in helical one-dimensional chains. This behaviour is what we hoped to achieve by using externally-directed 4-pyridyl



**Scheme 1** Synthesis of the ligands $[Bp^{4py}]^-$ and $[Tp^{4py}]^-$. *Reagents and conditions*: (i) *N*,*N*-Dimethylformamide–dimethyl acetal, reflux; (ii) hydrazine hydrate, EtOH, reflux.

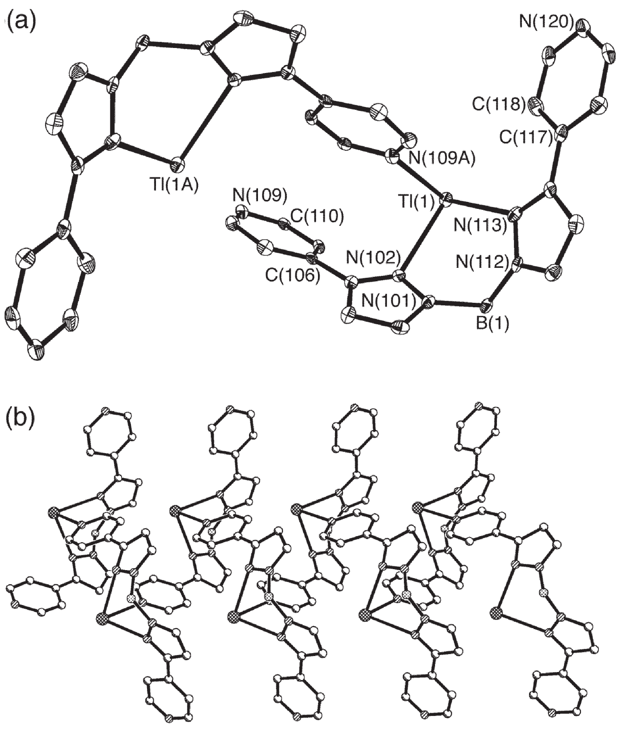


**Fig. 1** Two views of the crystal structure of $TlBp^{4py}$: (a) two monomer units (shown with 40% thermal ellipsoids) illustrating the labelling scheme; (b) a view showing how several monomer units form a helical chain. Selected bond distances (Å) and angles (deg): Tl(1)–N(102) 2.641(6), Tl(1)–N(113) 2.751(7), Tl(1)–N(109A) 2.678(7), N(102)–Tl(1)–N(109A) 77.4(2), N(102)–Tl(1)–N(113) 84.5(2), N(109A)–Tl(1)–N(113) 82.1(2), N(101)–B(1)–N(112) 110.5(6).

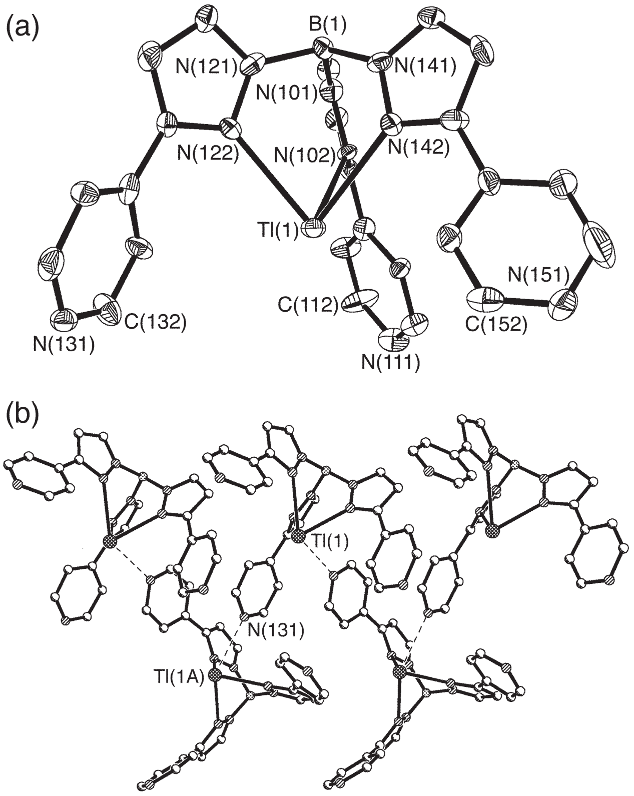


**Fig. 2** Two views of the crystal structure of $TlTp^{4py}$: (a) the monomer unit (shown with 40% thermal ellipsoids) illustrating the labelling scheme; (b) a view showing how several monomer units form a helical chain. Selected bond distances (Å) and angles (deg): Tl(1)–N(122) 2.577(8), Tl(1)–N(142) 2.609(9), Tl(1)–N(102) 2.791(7), Tl(1)–N(131A) 2.978(8), N(122)–Tl(1)–N(142) 77.9(3), N(122)–Tl(1)–N(102) 72.3(2), N(142)–Tl(1)–N(102) 67.3(2), N(131 A)–Tl(1)–N(102) 131.7(3), N(131 A)–Tl(1)–N(122) 71.3(2), N(131 A)–Tl(1)–N(142) 74.9(2), N(141)–B(1)–N(101) 111.4(10), N(141)–B(1)–N(121) 109.5(8), N(101)–B(1)–N(121) 107.9(9).

substituents on the ligand core. Each Tl(I) centre is in a pyramidal three-coordinate environment, arising from the two chelating pyrazolyl donors from one ligand and a 4-pyridyl donor from an adjacent complex unit. The pyramidal geometry implies that the lone pair is stereochemically active and occupying the vacant site which would therefore complete an approximately tetrahedral array of electron pairs around the metal.[11,12] The N–Tl–N angles are however considerably compressed compared to the tetrahedral ideal, a consequence of the length of the Tl–N bonds. In each ligand the pyridyl groups are slightly twisted out of the plane of the attached pyrazolyl ring, with the torsion angles being 4° and 26° for the pyridyl rings containing N(12) and N(109) respectively.

The structure of $TlTp^{4py}$ is shown in Fig. 2; again, a chiral one-dimensional polymeric chain results by virtue of a bridging interaction between a pendant 4-pyridyl donor on one complex unit and the Tl(I) centre of another. The monomer unit looks structurally similar to the complex $TlTp^{tol}$, in which the Tl(I) centre is coordinated by the three pyrazolyl donors in a pyramidal geometry with a stereochemically active lone pair in the apical position, and the three aromatic substituents (*p*-tolyl groups) arrayed in a cone-like conformation protecting the Tl(I) centre.[11] Replacement of tolyl substituents by 4-pyridyl units does not affect this basic structure, but the diverging cone-like array of 4-pyridyl units is reminiscent of tris(4-pyridyl)-functionalised bowl-shaped ligands prepared recently by Fujita and co-workers which were used as the basis for assembling capsule-like structures.[13] The pyridyl substituents are in each case twisted away from the mean plane of the attached pyrazolyl ring, with torsion angles of 29, 35 and 27° for the pyridyl rings containing N(151), N(131) and N(111) respectively. A packing diagram of $TlTp^{4py}$ reveals an additional bridging interaction which results in formation of a one-dimensional coordination polymer; the pyridyl donor N(131) on one complex unit is directed between the ligating arms of an adjacent $TlTp^{4py}$ unit to form a rather long Tl···N bond [2.978 Å, compared to an average value of 2.66 Å for the three Tl···N(pyrazolyl) bonds]. The longest of the Tl···N(pyrazolyl) interactions [2.791 Å, to N(102)] is the one that is approximately *trans* to the additional pyridyl ligand; the insertion of this pyridyl ring between two of the arms [involving the pyrazolyl donors N(122) and N(142)] results in the angle N(122)–Tl(1)–N(142) being the largest of the three bite angles at 77.9°.

It is noteworthy that both crystals have chiral space groups [*P*2(1) for $TlBp^{4py}$, *Pc* for $TlTp^{4py}$] despite being composed of achiral components. Crystalline materials in chiral space groups have been of interest recently for their second-order non-linear optical properties.[14,15] Accordingly these new complexes are likely to be of interest in this respect, in addition to the possibilities available for assembly of polynuclear complexes by attachment of additional metal ions at the peripheral 4-pyridyl sites of the monomer units.[13]

## Experimental

### Preparations

**3-(4-Pyridyl)pyrazole.** This was prepared in two steps from 4-acetylpyridine as shown in Scheme 1. In the first step, a mixture of 4-acetylpyridine (24.2 g, 0.2 mol) and *N*,*N*-dimethylformamide–dimethyl acetal (40 $cm^3$) was heated to reflux for 2 h. After concentration *in vacuo*, recrystallisation of the orange residue from $CHCl_3$–hexane afforded an orange/yellow powder (intermediate **A**) in 58% yield. Chemical ionization MS: $m/z$ 177 $(M+H)^+$. $^1H$ NMR ($CDCl_3$): $\delta$ 8.64 (2H, d, $J$ 5.9;

pyridyl H$^2$/H$^6$), 7.79 (1H, d, *J* 12.5; alkene CH), 7.63 (2H, d, *J* 5.9; pyridyl H$^3$/H$^5$), 5.60 (1H, d, *J* 12.5 Hz; alkene CH), 3.12 (3H, s, Me), 2.89 (3H, s, Me). Found: C, 64.5; H, 6.8; N, 15.2. Required for [$C_{10}H_{12}N_2O\cdot0.5H_2O$]: C, 64.8; H, 7.0; N, 15.1%. A mixture of **A** (20.3 g, 0.115 mmol), ethanol (30 cm$^3$) and hydrazine hydrate (30 cm$^3$) was then heated to 60°C with stirring for 30 min. After addition to cold water (130 cm$^3$) and overnight refrigeration, the resulting off-white precipitate was filtered off, washed with copious amounts of water, and dried to give 3-(4-pyridyl)pyrazole in 77% yield. Although characterisation data were satisfactory at this stage, the material could be further purified by vigorous washing with toluene (ultrasound cleaning bath) followed by recrystallisation from water. EI-MS: 145 ($M^+$). $^1$H NMR ($CDCl_3$): $\delta$ 11.68 (1H, br s, N*H*), 8.65 (2H, d, *J* 6.2, pyridyl H$^2$/H$^6$), 7.72 (2H, d, *J* 5.9, pyridyl H$^3$/H$^5$), 7.68 (1H, d, *J* 2.6; pyrazolyl), 6.76 (1H, d, *J* 2.2 Hz; pyrazolyl). Found: C, 66.3; H, 5.1; N, 29.2. Required for $C_8H_7N_3$: C, 66.2; H, 4.9; N, 29.0%.

**KBp$^{4py}$.** 3-(4-Pyridyl)pyrazole (1.44 g, 9.9 mmol) and $KBH_4$ (0.215 g, 4 mmol) were ground together thoroughly in a pestle and mortar and heated for 30 min in a Schlenk tube at 175–180°C under $N_2$. The mixture was stirred throughout, although this was hindered once melting occurred at 150°C. After cooling to rt, toluene (30 cm$^3$) was added and the mixture was agitated in an ultrasound cleaning bath for 20 min. The suspension was filtered, and the solid was washed with hot toluene and hot hexane and then dried gave KBp$^{4py}$ as a white powder in 80% yield. Negative-ion electrospray MS: $m/z$ 301 [$C_{16}H_{14}N_6B$]$^-$. $^1$H NMR (MeOD): $\delta$ 8.43 (4H, d, *J* 6.2; pyridyl H$^2$/H$^6$), 7.82 (4H, d, *J* 6.6; pyridyl H$^3$/H$^5$), 7.61 (2H, d, *J* 2.2; pyrazolyl), 6.64 (2H, d, *J* 1.9; pyrazolyl). $^{11}$B NMR (MeOD): $\delta$ −7.59. Found: C, 53.9; H, 4.9; N, 23.7. Required for [$C_{16}H_{14}N_6BK\cdot H_2O$]: C, 53.6; H, 4.5; N, 23.5%. IR: $\nu_{B-H}$ 2380, 2263 cm$^{-1}$.

**TlBp$^{4py}$.** Methanolic solutions of thallium(I) acetate (0.18 mmol) and KBp$^{4py}$ (0.18 mmol), both in 5 cm$^3$ MeOH, were combined and stirred at rt for 40 min, during which time a white precipitate formed. The solution was concentrated *in vacuo* and refrigerated for several hours before being filtered off and washed with MeOH to give a white powder. Recrystallisation by diffusion of $Et_2O$ vapour into a solution of the complex in DMF afforded colourless crystals suitable for X-ray diffraction studies. These were filtered off and washed with $Et_2O$ to give pure TlBp$^{4py}$ in 42% yield. FAB-MS: $m/z$ 507 [$M^+$] 358 [M$^+$ − pyridylpyrazole unit]. Found: C, 37.8; H, 2.5; N, 16.5. Required for [$C_{16}H_{14}N_6BTl$]: C, 38.0; H, 2.8; N, 16.6%. IR: $\nu_{B-H}$ 2412, 2389, 2264 cm$^{-1}$.

**KTp$^{4py}$.** 3-(4-Pyridyl)pyrazole (0.96 g, 6.6 mmol) and $KBH_4$ (0.108 g, 2 mmol) were ground together thoroughly in a pestle and mortar, and heated under $N_2$ in a Schlenk tube, with stirring, at 230°C for 3.5 h. After cooling to rt, 30 cm$^3$ of toluene were added and the mixture was agitated in an ultrasound cleaning bath for 20 min. The suspension was filtered, and the solid was washed with hot toluene and hot hexane and then dried gave KTp$^{4py}$ as a white powder in 25% yield. Negative-ion ES MS: $m/z$ 444 [$C_{24}H_{19}N_9B$]$^-$. $^1$H NMR (MeOD): $\delta$ 8.50 (6H, d, *J* 6.2, pyridyl H$^2$/H$^6$), 7.88 (6H, d, *J* 6.2, pyridyl H$^3$/H$^5$), 7.41 (3H, d, *J* 2.2, pyrazolyl), 6.80 (3H, d, *J* 2.4 Hz, pyrazolyl). $^{11}$B NMR (MeOD): $\delta$ 0.37. Found: C, 57.8; H, 4.0; N, 25.0. Required for [$C_{24}H_{19}N_9BK\cdot H_2O$]: C, 57.5; H, 4.2; N, 25.1%. IR: $\nu_{B-H}$ 2418.

**TlTp$^{4py}$.** Methanolic solutions of thallium(I) acetate (0.346 g, 1.33 mmol) and KTp$^{4py}$ (0.59 g, 1.33 mmol), were combined and stirred at r.t. After 30 min. a white precipitate had started to evolve. Diethyl ether (20 cm$^3$) was added and stirring continued for an additional 15 min; this procedure was repeated once more. The reaction mixture was refrigerated (5°C) for several hours before filtration of the precipitate which was washed with ether to give TlTp$^{4py}$ as a white powder in 51% yield. Colourless crystals, suitable for X-ray diffraction studies, were grown from slow evaporation of a $CH_2Cl_2$–MeOH solution of the complex. FAB-MS: $m/z$ 650 [$M + H$]$^+$; 505 [MH$^+$ − pyridylpyrazole unit]. Found: C, 43.2; H, 2.9; N, 18.8. Required for [$C_{24}H_{19}N_9BTl$]: C, 43.2; H, 3.2; N, 18.9%. IR: $\nu_{B-H}$ 2441 cm$^{-1}$.

### X-Ray crystallography

Data for TlBp$^{4py}$, $C_{16}H_{14}BN_6Tl$: monoclinic, space group $P2_1$, $a = 10.454(2)$, $b = 6.3740(13)$, $c = 12.338(3)$ Å, $\beta = 98.96(3)°$, $U = 812.1(3)$ Å$^3$, $Z = 2$, $M_r = 505.51$ g mol$^{-1}$, $\rho_{calc} = 2.067$ g cm$^{-3}$, $\mu = 9.954$ mm$^{-1}$ (Mo-K$\alpha$ radiation). Refinement on $F^2$ of 3693 independent reflections ($R_{int} = 0.0455$; $2\theta_{max} = 55°$) converged at $R1 = 0.0370$ [based on selected data with $F \geq 4\sigma(F)$], $wR2 = 0.0785$ (for all data), using 225 parameters. Flack parameter: −0.020(14).

Data for TlTp$^{4py}$, $C_{24}H_{19}BN_9Tl$: monoclinic, space group $Pc$, $a = 8.7477(9)$, $b = 16.5928(17)$, $c = 8.3841(9)$ Å, $\beta = 96.281(2)°$, $U = 1209.6(2)$ Å$^3$, $Z = 2$, $M_r = 648.66$ g mol$^{-1}$, $\rho_{calc} = 1.781$ g cm$^{-3}$, $\mu = 6.708$ mm$^{-1}$ (Mo-K$\alpha$ radiation). Refinement on $F^2$ of 5428 independent reflections ($R_{int} = 0.0636$; $2\theta_{max} = 55°$) converged at $R1 = 0.0337$ [based on selected data with $F \geq 4\sigma(F)$], $wR2 = 0.0838$ (for all data), using 316 parameters. Flack parameter: 0.031(10).

In both cases a suitable crystal was mounted on a Bruker APEX diffractometer at 100 K and the data collection covered a full sphere of reciprocal space. After integration data were corrected for Lorentz and polarisation effects, and for absorption effects using an empirical method (SADABS).[16] Data reduction, structure solution and refinement were performed with the SHELX suite of programs.[17]

Crystallographic data for the two structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference nos. 212496 and 212497. See http://www.rsc.org/suppdata/nj/b3/b306659b/ for crystallographic data in .cif or other electronic format.

## Acknowledgements

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