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## “Twisted” scorpionates: synthesis of a tris(2-pyridonyl)borate (Thp) ligand; lessons in the requirements for successful B(L<sub>2</sub>D)<sub>3</sub> type ligands \*\*

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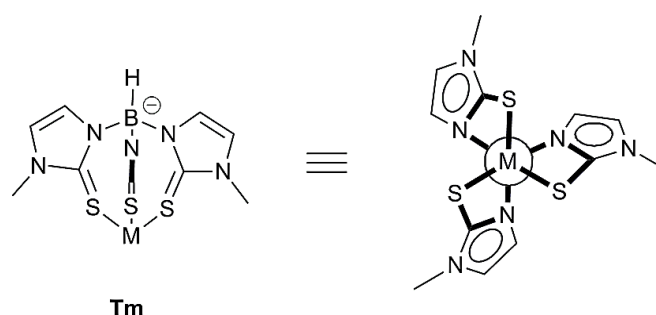
†Electronic Supplementary Information (ESI) available: full experimental and characterisation details; crystallographic details for compounds **2** and **3**. See <http://dx.doi.org/10.1039/C1CC14473A>. CCDC 829912 and 829913 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by e-mailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

## Abstract

The synthesis of a new charge-neutral zwitterionic tripodal borate ligand based on 2-hydroxypyridine is reported. (Dimethylaminopyridinium)tris(2-hydroxypyridine)borate, (DMAP)Thp, has been complexed to copper (I) chloride to give a pseudo- $C_3$  symmetric complex. The propensity for this ligand and other flexible scorpionates to exhibit such helical chirality upon complexation is discussed.

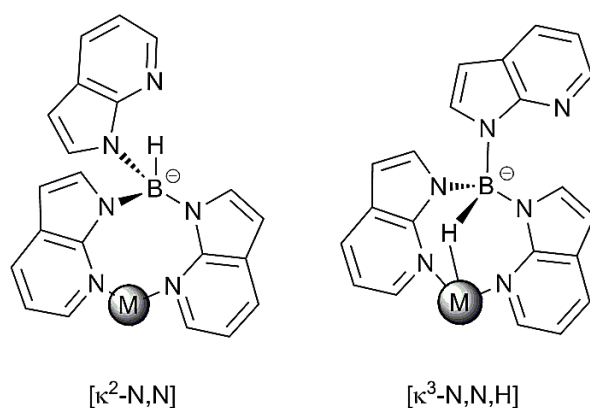
## Main text

The majority of trisubstituted borate ligands, the most common of which is the hydrotris(pyrazolyl)borate (Tp) ligand, coordinate in a tripodal ( $\kappa^3$ ) mode, utilising three ligand donor ‘arms’ and leaving one uncoordinated boron substituent.<sup>1,2</sup> The hydrotris(methimazolyl)borate (Tm) ligand differs from Tp in forming 8-membered chelate rings on metal complexation due to the presence of two atoms (N and C) linking the boron and sulfur donor atoms (*cf.* a single linking N atom in the Tp ligand).<sup>3</sup> Nevertheless, Tm also commonly coordinates in the  $\kappa^3$ -mode and such complexes exhibit  $C_3$ -helical chirality, which contrasts with the achiral  $C_{3v}$  symmetry provided by the  $\kappa^3$ -Tp ligand. This chirality arises due to ‘twisting’ of the bicyclo[3.3.3] metal-ligand cage structure, which forms upon  $\kappa^3$ -complexation, in order to relieve angle strain (Fig. 1).



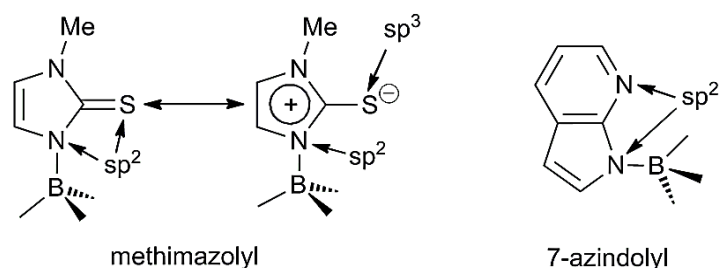
**Figure 1.** Hydrotris(methimazolyl)borate (Tm) exhibits  $C_3$ -helical chirality when coordinated to a metal.

The hydrotris(7-azindolyl)borate (Tai) ligand, which also forms 8-membered chelate rings on metal coordination, more commonly coordinates either in the  $\kappa^2$ -[N,N] or  $\kappa^3$ -[N,N,H] modes (Fig. 2).<sup>3,4</sup> The complex [(Tai)ZnCl] contains the only reported example of this ligand coordinated in the  $\kappa^3$ -[N,N,N] mode.<sup>4</sup> The coordination behavior of this ligand therefore contrast with that of Tm and its derivatives, despite the topological equivalence of their  $\kappa^3$ -[N,N,N] and  $\kappa^3$ -[S,S,S] coordination modes.



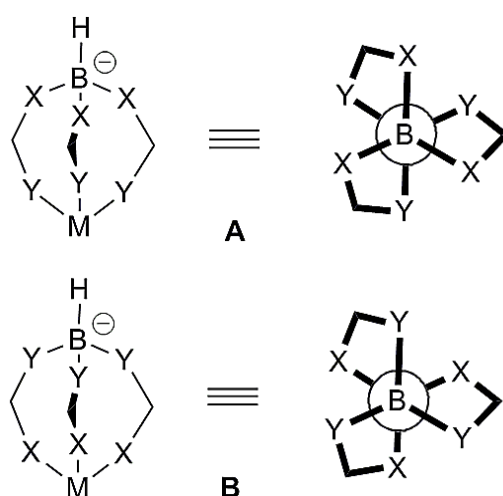
**Figure 2.** Common binding modes of the Tai ligand.

We have sought to understand the coordination modes of these ligands in our effort to develop the application of the chirality of  $C_3$ -symmetric complexes in asymmetric catalysis. Analysis of the torsion angles around the sulfur donors in Tm complexes clearly indicates them to be  $sp^3$  hybridised. The two lone pairs on an  $sp^2$  thione sulfur are necessarily coplanar with the attached imidazole ring which would provide an ideal M-S-C-N torsion angle of  $0^\circ$  on metal complexation, and a  $C_{3v}$  symmetric structure. However, torsion angles of between  $60$  and  $70^\circ$  are typically observed in Tm complexes of both octahedral and tetrahedral metal ions, and the M-S-C bond angles typically lay in the range  $100$ - $110^\circ$ ;<sup>7</sup> together being consistent only with  $sp^3$  sulfur. It should be noted that the presence of  $sp^3$  thiolate sulfur donors in the Tm ligand and its derivatives is also entirely consistent with the donor properties of this ligand system.<sup>8</sup> In contrast, the involvement of the N-donor atoms in the Tai ligand in pyridine rings means that they can only provide  $sp^2$  hybridised lone pairs in the plane of the pyridine rings (Fig. 3). The resulting  $\kappa^3$ -coordinated Tai ligand in [(Tai)ZnCl] provides a highly strained  $C_{3v}$ -symmetric system in which the mean Zn-N-C-N torsion angle is just  $3.6^\circ$  and the mean angle at each of the nine 7-azaindolyl atoms involved in the chelate rings is  $130.6^\circ$ .<sup>5</sup> The evident angle strain in this system thus generally results in complexes in which only two of the 7-azaindolyl arms are coordinated to give either of the common coordination modes shown in Fig. 2, although the structure of [(Tai)ZnCl] indicates that  $\kappa^3$ -coordination is not precluded.



**Figure 3.** Resonance forms of methimazole and 7-azindole.

On considering these hybridisation issues it becomes apparent that  $C_3$ -symmetric tripodal ( $\kappa^3$ ) coordination of this type of ligand requires that either the donor *or* the boron-bound atom of the donor group be  $sp^3$  hybridised, and thus an alternate hybridisation framework may be envisaged (**B**, Fig. 4). Seeking to design a ligand of this alternative type, with  $sp^3$  atoms bound to boron and  $sp^2$  donor atoms, we have explored the synthesis of a ligand incorporating 2-pyridonyl (derived from 2-hydroxypyridine) as the donor groups, rationalising that the hard  $sp^3$  oxygen centre would preferentially bind to boron, leaving the pyridine nitrogen atoms available for metal coordination. Accordingly, we describe here the synthesis of two novel ligands based on tris(2-pyridonyl)borate (Thp).

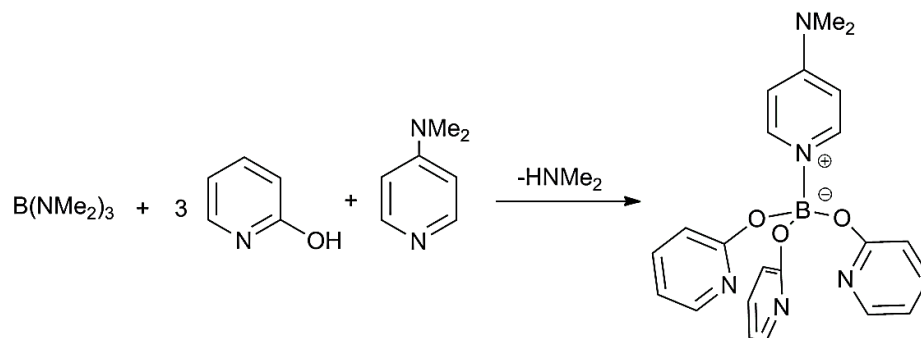


**Figure 4.** The two alternative hybridisation frameworks providing  $C_3$ -symmetric complexes. X =  $sp^2$  hybridised atom, Y =  $sp^3$  hybridised atom.

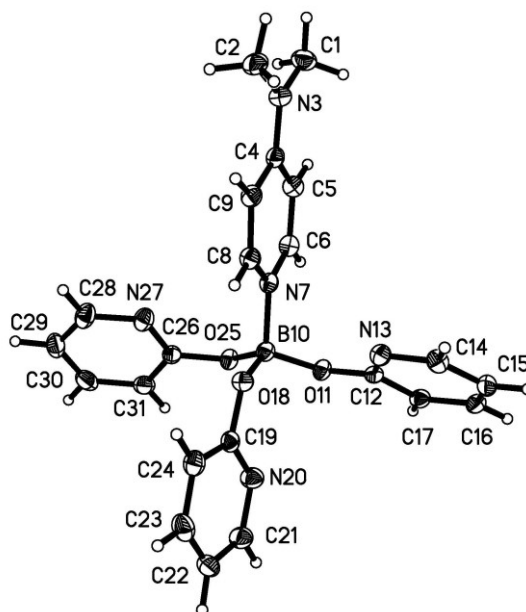
Following the methodology we have developed for the construction of charge-neutral analogues of tripodal borate ligands bearing a neutral donor in place of the usual hydride in Tp and Tm,<sup>8,9</sup> (HNMe<sub>2</sub>)tris(2-pyridonyl)borate [(HNMe<sub>2</sub>)Thp] (**1**) was obtained from the reaction of 2-hydroxypyridine with B(NMe<sub>2</sub>)<sub>3</sub> in toluene under reflux. Evolution of HNMe<sub>2</sub> ceased after 3 h and <sup>1</sup>H NMR spectroscopy showed no evidence of starting materials. Four new resonances corresponding to the target material were present in the aromatic region of the spectrum and a doublet at 2.84 ppm confirmed the retention of a single HNMe<sub>2</sub> group. EI mass spectrometry showed a molecular ion peak at  $m/z = 339.1$  consistent with the anticipated structure.

We have previously shown that it is possible to replace the HNMe<sub>2</sub> moiety in this type of zwitterionic borate ligand with alternative donors, the process being favoured by release of HNMe<sub>2</sub> gas.<sup>8,9</sup> The same outcome may be achieved *in situ* via a one-pot reaction starting from the three components (Scheme 1), and the HNMe<sub>2</sub> group in **1** was thus replaced with 4-dimethylaminopyridine (DMAP) by reaction of 2-hydroxypyridine,

$B(NMe_2)_3$  and DMAP (3:1:1) in toluene under reflux. The new adduct (**2**) was isolated as a colorless solid in 69% yield after workup. The X-ray crystal structure of **2** confirms the expected binding of the 2-pyridonyl groups to boron through oxygen (Fig. 5). The B-O-C angles are in the range 124-126° and the B-O-C-N torsion angles range from 7-28°.



**Scheme 1.** Synthesis of (dimethylaminopyridinium)tris(2-pyridonyl)-borate (**2**).

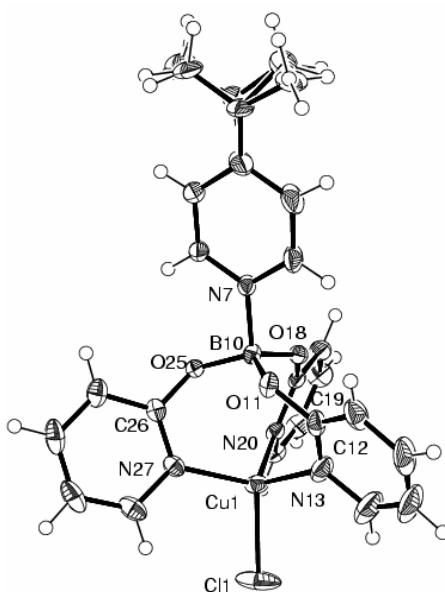


**Figure 5.** X-ray crystal structure of (DMAP)Thp (**2**).

Complexation of the ligand **2** to copper(I) chloride in  $CH_2Cl_2$  provided a yellow complex  $[(DMAP)Thp]CuCl$  (**3**). This was found to be insoluble in most common solvents, but  $^1H$ -NMR in  $d^6$ -DMSO showed three very broad resonances and a slightly sharper triplet for the pyridyl protons, each integrating for 3H. Two less broadened resonances corresponding to the DMAP ring protons are visible at 6.81 ppm and 8.51 ppm. A singlet appears at 3.10 ppm for the DMAP dimethylamino protons. The  $^{13}C$ -NMR

also shows broadened resonances for three of the pyridine ring carbon atoms. Cyclic voltammetry of this complex in DMF showed a reversible oxidation at  $E_{1/2} = 0.48$  V (vs NHE), corresponding to the Cu(I)/(II) couple, and the Cu(I)/(0) couple was observed as an irreversible process at  $E_{1/2} = -1.60$  V.

In pursuit of a more soluble Thp complex, **2** was reacted with  $[(PPh_3)CuCl]_4$  in an attempt to form the salt  $[(DMAP)ThpCu(PPh_3)]Cl$ . In order to test the viability of this route an initial test reaction was performed in a sealed NMR tube in  $CDCl_3$  solution. Crystals of the product of this reaction grew serendipitously upon standing overnight and X-ray crystallography showed these to be the previously prepared chloro complex **3**, thus demonstrating that the  $PPh_3$ , rather than the chloride, had been replaced by the Thp ligand. The structure of **3** (Fig. 6) confirms that the complex exhibits pseudo- $C_3$  symmetry by forming a helically-twisted complex of type **B** (Fig. 4), the unit cell containing a racemic mixture of two pairs of complexes with *M* and *P* helicity. The B-O-C-N torsion angles (range  $42.4 - 58.8^\circ$ ) clearly indicate  $sp^3$  hybridisation of the O atoms. There is some strain within the metal-ligand cage evidenced by small deviations of the planes of the pyridyl rings from their N-Cu bonds (range  $7.1 - 11.8^\circ$ ) leading to slight non-planarity at the N-atoms (sum of the angles at N range  $358.8 - 359.6^\circ$ ). No corresponding distortions are observed in Tm metal complexes, in which the methimazolyl rings are found to be coplanar with their B-N bonds, and their origin would appear to be a result of the small size of oxygen (*cf.* sulfur), which results in an increase of the O-B-O angles on formation of the metal-ligand cage, and this strain is partially relieved by the observed distortions. The sum of the O-B-O angles in complex **3** and the free ligand are  $342.4^\circ$  and  $333.0^\circ$  respectively, values which should be compared with  $329.0^\circ$  for the sum of the N-B-N angles in the complex  $TmCuPPh_3$  (i.e. almost ideal for tetrahedral boron).<sup>10</sup>



**Figure 6.** X-ray crystal structure of (DMAP)ThpCuCl (**3**).

It has been demonstrated that the replacement of the 2-pyridonyl donor groups of the Thp ligand by their mercapto analogue, through the conventional synthesis involving reaction of  $\text{LiBH}_4$  with 2-mercaptopyridine (mp), provides  $\text{HB}(\text{mp})_3$  (Tmp), a ligand in which the pyridine nitrogen preferentially binds to the boron leaving the sulfur atoms as the tripod donors.<sup>11</sup> This Tmp ligand is thought to exhibit a  $\kappa^3$ -[S,S,S] coordination to Cu(I) in the complex  $[(\text{Tmp})\text{Cu}(\text{PPh}_3)]$ , although no X-ray crystal structure has been reported; the helical twisting of the metal-ligand cage cannot therefore be assessed, and there is evidence to suggest that the hybridisation framework in this ligand is not clear-cut [i.e. neither purely type **A** or **B** (Fig. 4)].<sup>11</sup> Nevertheless, it is clear that the two ligands Thp and Tmp, which differ only in the identity of the pyridyl 2-substituent (O or S respectively) provide the two possible alternative architectures through ‘flipping’ of the donor groups.

In combination with the work of others on the Tai and Tmp ligands discussed above, the results reported here demonstrate that there is considerable flexibility in the choice of donor groups in tripodal borate centred ligands of the type  $\text{XB}(\text{L}_2\text{D})_3$  ( $X$  = hydride or neutral donor;  $L$  = linking atoms;  $D$  = donor atoms). However, the constraints of the bicyclo[3.3.3] cage architecture formed on  $\kappa^3$ -coordination of such ligands requires  $sp^3$  hybridisation of either the boron-bound or donor atoms in order to reduce angle strain by twisting to form a  $C_3$ -symmetric helical structure. It is also evident that the size of the atoms incorporated into the  $L_2D$  arms has an impact on the angle strain within the cage. The absence of distortions (of the type found in complex **3**) in complexes of the Tm ligand and its derivatives indicate that the combination of nitrogen and sulfur atoms in these roles provides the lowest angle strain of the systems so far studied. Whether their choice was serendipitous or by design when Reglinski and Spicer first conceived the Tm ligand is a moot point,<sup>12</sup> but it is increasingly clear that this is a tripod ligand whose flexibility is rivaled only by the Tp ligand system.



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