Uncovering the Hidden Landscape of Tris(4-pyridyl) Ligands: Topological Complexity Derived from the Bridgehead

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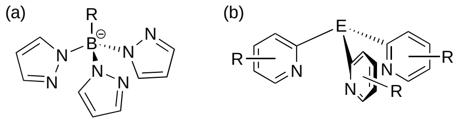
Supporting information for this article is given via a link at the end of the document. Contains full spectroscopic, analytical crystallographic data. Deposition Number(s) 2058021 (for **2**), 2058025 (for **3**), 2058022 (for **4**), 2058023 (for **5**), 2058026 (for **6**), 2058019 (for **7**) and 2058020 (for **8**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service https://www.ccdc.cam.ac.uk/structures.

Abstract: Supramolecular main group chemistry is a developing field which parallels the conventional domain of metallo-organic chemistry. Little explored building blocks in this area are main group metal-based ligands which have the appropriate donor symmetry to build desired molecular or extended arrangements. Tris(pyridyl) main group ligands ($E(py)_3$, E = main group metal) are potentially highly versatile building blocks since shifting the N-donor arms from the 2- to the 3-positions and 4-positions provides a very simple way of changing the ligand character from mononuclear/chelating to multidentate/metal-bridging. Here we explore the coordination behaviour of the first main group metal tris(4-pyridyl) ligands, $E(4\text{-}py)_3$ (E = Sb, Bi, Ph-Sn), and their ability to build metal organic frameworks (MOFs). The complicated topology of these MOFs shows a marked influence on the counter anion and on the ability of the $E(4\text{-}py)_3$ ligands to switch coordination mode, depending on the steric and donor character of the bridgehead. This structure-directing influence of the bridgehead provides a potential building strategy for future molecular and MOF design in this area.

The development of new classes of ligands is an important and ongoing challenge in modern chemistry, and a corner stone in advances in catalysis, supramolecular assembly and biomimetic chemistry.[1–7] Of the many new classes of ligands that have been introduced, C_3-symmetric tripodal ligands have emerged over the past few decades as one of the most important classes in catalysis.[8] Amongst these, tris(pyrazolyl)borate (Tp^-) ligands (Figure 1a)[9] are recognised as one of the most versatile families, stemming from the ability to tune their electronic and steric properties by modifying the substitution of the heterocyclic rings. Although less well studied, the closely related tris(2-pyridyl) family of tripodal ligands has also gained significant interest in recent years (Figure 1b).[10] In particular, because changing the bridgehead atom or group (E) introduces a further means of modifying donor/acceptor character and ligand bite angle.



E = CR', COR', SiR'
N, P, As, Sb, Bi

Figure 1. The tripodal ligand frameworks of (a) tris(pyrazolyl)borate,[8] and (b) neutral tris(2-pyridyl) (E = main group bridgehead).

Examples of tris(2-pyridyl) ligands containing lighter (non-metallic) bridgehead atoms or groups, such as N, P and CR, have been known for several decades.[11] However, analogues containing heavier, metallic or semi-metallic bridgehead atoms have only been introduced relatively recently,[10] with intensive work in this area in the past few decades establishing this class of ligands across the p-block.[12-16]

While the orientation of the donor-N atoms in tris(2-pyridyl) ligands leads to chelation of metal ions in the majority of complexes, changing the N-atom to the 3- or 4-positions introduces the prospect of forming supramolecular assemblies, as a result of bridging of the ligands between metal centers. Coordination studies in this area have, however, so far been limited to only a few $E(3\text{-}py)_3$ (E = P,[17] MeSi,[18] PhSn[19]) and $E(4\text{-}py)_3$ (E = CR,[20] P,[21] MeSi[22]) ligands. Significantly, the coordination chemistry of tris(4-pyridyl) ligands containing the heavier more metallic p-block bridgeheads is a totally unexplored area.

In the current work, our attention was drawn to the heavier Group 15 tris(4-pyridyl) ligands $E(4\text{-}py)_3$ (E = Sb and Bi) not just because of the scarcity of fundamental structural knowledge for the heavier congeners, but because of their obvious potential to act as building blocks for supramolecular, three-connected polyhedra (Figure 2a) and as tetrahedral nodes in MOFs (Figure 2b). Relevant to this idea is the use of organic N-donors[23] as well as main group elements as structure directing units in crystal engineering and supramolecular chemistry.[24] However, the potential to build new MOFs has not been explored systematically in tris(pyridyl) systems even for the phosphorus counterpart, P(4-py)$_3$, which has been known for a number of years.[25] In addition, a distinct feature of the heavier homologues is the far greater Lewis acidity of the bridgehead atoms, resulting in the prospect of the bridgehead atoms to act not only as donors but also as acceptors to counter anions and Lewis base donors. All of these considerations suggested that the metal-based Group 15 ligands should have a rich and multi-faceted coordination chemistry.

In this paper we explore the topologically rich world of tris(4-pyridyl) ligands of heavier main group elements (beyond Period 3), revealing the effects of the bridgehead atom and counter anion on the structure of metal organic frameworks for the first time.

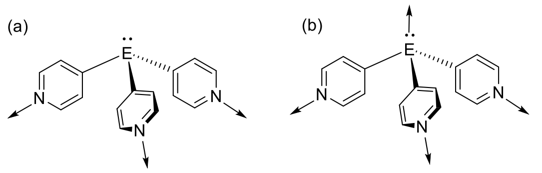
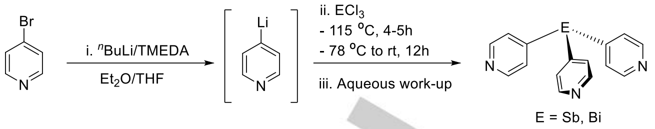


Figure 2 (a) An N,N,N-coordination mode and (b) an N,N,N/E coordination mode.

The initial hurdle proved to be finding a reliable way to generate the 4-lithio-pyridine intermediate (4-Li-py) used in the synthesis of the 4-pyridyl ligands. Previous syntheses of P(4-py)$_3$ have mainly used 4-iodo-pyridine as a precursor, which is lithiated under various conditions.[25] However, 4-iodo-pyridine is thermally and photolytically unstable and commercially supplied material proved to be highly impure. To circumvent this issue, we used 4-bromo-pyridine hydrochloride as the precursor, which is stable indefinitely under ambient conditions and much cheaper. Free 4-bromo-pyridine is readily obtained from the hydrochloride by reaction with $NaHCO_3$ in H_2O and can be stored for up to a week at −14 ºC in the dark.[26] Using D_2O quenching experiments, we optimised the metalation conditions using a range of organometallic reagents, solvents and reaction times (see Supporting Information). Using ^{n}BuLi/TMEDA in THF at −115 ºC with a reaction time of 4–5 min produced the maximum conversion to 4-Li-py. These conditions were used to prepare the new ligands Sb(4-py)$_3$ (**1**) and Bi(4-py)$_3$ (**2**) in isolated yields of 20 and 55%, respectively (Scheme 1). The identities of both ligands were confirmed by ^{1}H NMR spectroscopy and elemental analysis, with the X-ray crystal structure also being obtained for **2** (see Supporting Information). Reflecting the Lewis acidity of the Bi(III) atom, molecules of ligand **2** are associated in the crystal lattice *via* intermolecular N•••Bi and π-arene•••Bi interactions (unlike the discrete arrangement found in P(4-py)$_3$[25]).



Scheme 1. Synthesis of heavier Group 15 E(4-py)$_3$ ligands (E = Sb (**1**), Bi (**2**)).

In order to explore the coordination landscape of ligands **1** and **2**, we selected Ag^I salts containing a range of weakly-coordinating anions (AgX, X = $CF_3SO_3^-$, PF_6^-, SbF_6^-). The softness of Ag^I, we reasoned, would encourage the N,N,N/E coordination mode (Figure 2b) and lead to condensed MOF arrangements. At the same time, the presence of weakly-coordinating anions should limit competing anion-bridgehead (E) interactions. For comparison, Ag^I networks containing the nitrogen homologue N(4-py)$_3$ have been described recently,[27] with both trifluoroacetate (CF_3COO^-) and PF_6^- anions. In both, the pyridyl-N atoms of the ligand adopt an approximately planar geometry and the Ag^I atoms also act as 3-coordinate nodes, producing simple planar 2-D honeycomb nets (topology descriptor **hcb**). By contrast, the networks $\{Ag^I_2(\mathbf{2})_3\}_n(CF_3SO_3)_{2n}$ (**3**) and $\{Ag^I_2(\mathbf{2})_3\}_n(SbF_6)_{2n}$ (**4**), show a more complex arrangement on account of the approximately orthogonal coordination vectors within ligand **2**. The structures consist of identical (although not fully isostructural) 2-D nets (Figure 3) in which the Ag^I centres have (see-saw) 4- and (square-pyramidal) 5-coordinate environments. The Ag^I cations are coordinated solely by pyridyl-N atoms of **2**, which adopts the N,N,N-coordination mode. The result is a complicated, undulating sheet network consisting of interlocked Bi_3Ag_3 and Bi_2Ag_2 ring units. The $CF_3SO_3^-$ or SbF_6^- anions (and some DCM solvent) are also present in the structures, but they do not form any clear interaction with Ag^I. Like the crystal structure of **2**, the overall Bi coordination environment can be viewed as pseudo-octahedral, with two sites being capped by long-range, face-on pyridyl rings and one site being capped by either a F atom of SbF_6^- or an O atom from triflate, in addition to the three bonds made with the 4-py groups (Supporting Information).

The network topology of **3** and **4** can be rationalised by referring to an idealised NaCl-type structure comprising Bi and Ag atoms, with an Ag–Bi distance of 7.6 Å (lattice dimension = 15.2 Å; Figure 4a). Since the Bi(4-py)$_3$ ligands act as 3-coordinate nodes, three edges must be removed from the NaCl lattice around each Bi atom. Appropriate removal of edges produces both 5-coordinate (square-pyramidal, after removal of one edge) and 4-coordinate ("see-saw", after removal of two adjacent edges) environments for Ag^I, as seen in the network structures. The overlay of the observed Ag/Bi positions in the 2-D network in **3** and **4** and the hypothetical net derived from the NaCl lattice is almost exact (Figure 4b). The topology of the resulting network is based on the **hcb** net, but with every other row of hexagons capped by a further tripodal Bi(4-py)$_3$ ligand to produce rows with a rhombus tiling. In this way, the net can be viewed as a hybrid of the **hcb** and kagome dual (**kgd**) nets.

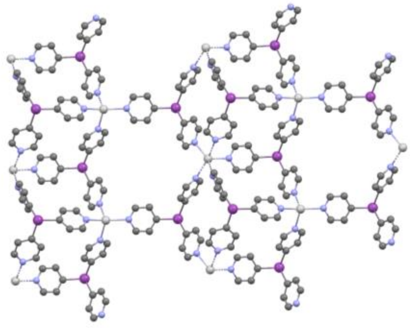


Figure 3 The 2-D network structure of **3** (the network formed in **4** has the same connectivity). $CF_3SO_3^-$ anions and CH_2Cl_2 solvent molecules are omitted for clarity. Colour code, Bi (magenta), N (lilac), Ag (silver), C (grey).

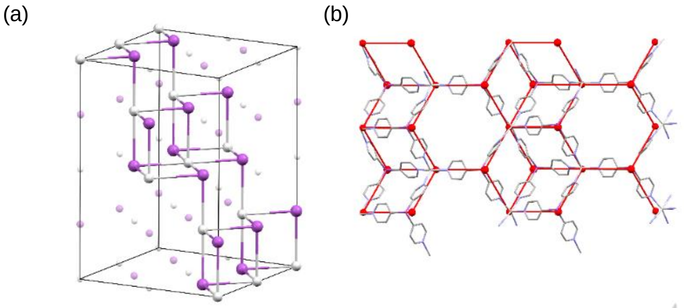


Figure 4 (a) A model of the lattice of **3** and **4** as an extruded segment of the NaCl lattice, and (b) overlay of the lattices of **3** and **4** with an idealised NaCl lattice (with Ag-Bi 7.6 Å, red), Colour code, Bi (magenta), Ag (silver).

Employing the same chemistry with $AgPF_6$ produces the coordination compound $\{Ag^I_2(\mathbf{2})_3\}_n(PF_6)_{2n}$ (**5**), which shows a remarkable 3-D network structure (Figure 5a). This is based on building units of corner-sharing cubes extracted from the parent NaCl lattice, in which the shared corner comprises a six-coordinate Ag^I atom and the exposed Ag^I atoms are all four-coordinate (inset to Figure 5a). In a regular NaCl lattice of Ag and Bi atoms, the cube corners opposite to six-coordinate Ag would each comprise a six-coordinate Bi. Since ligand **2** acts as a 3-coordinate (N,N,N-coordination) node, however, the structure diverges from the parent lattice of NaCl in this region. The body diagonals of the cube units are aligned with the long *c* axis (*i.e.* the 3-fold axis) of the *R*-centred unit cell. Looking down the *c*-axis (Figure 5b), the three connected corner-sharing cubes within the next layer along the *c* axis are offset and rotated by *ca* 30°. The next layer along *c* induces a further rotation of 30°, which brings the corner-sharing cubes back to a translational relationship.

The large change in the lattice compared to that of **3** and **4** can be traced to the structure-directing effect of the PF_6^- anion in **5**. As shown in Figure 5a, some of the PF_6^- anions are encapsulated within the cubane units and potentially act as templates. Similar templating using PF_6^- has recently been observed for discrete molecular cages formed from the PhSn(3-py)$_3$ ligand,[19] and the influence of counter anions in supramolecular chemistry and crystal engineering is a well-documented field.[28]

A glimpse at the effect of changing the bridgehead atom is provided by the structure of the complex of the Sb^{III} ligand **1** with $AgSbF_6$, $\{Ag^I(\mathbf{1})\}_n(SbF_6)_n$ (**6**). The result is a completely different lattice to that of the complex of **2** with $AgSbF_6$ (complex **4**). Complex **6** forms a 3-D network structure in which the ligands **1** adopt an N,N,N/E coordination mode, which is unprecedented for any Group 15 E(4-py)$_3$ complex (Figure 2b).[29] The adoption of this mode stems from the greater Lewis basicity of Sb^{III} compared to Bi^{III}, and provides the key reason for the difference in structure between these complexes of **1** and **2**. Earlier reports have also noted the poor donor properties of triorgano-Bi ligands compared to Sb counterparts.[30] The structure of **6** is composed of honeycomb layers of interlocked Sb_3Ag_3 puckered ring units (Figure 6) which stack vertically into a porous network *solely* by Sb-Ag bonds, involving all of the Ag and Sb atoms within the layers (Sb-Ag 2.6029(9) Å).[31] Both Ag and Sb form 4-coordinate tetrahedral nodes, and the resulting network is topologically identical to the zinc imidazolate framework, ZIF-64 (CSD:GITTEJ).[32] An interesting comparison can be made between the structure of **6** and the $AgCF_3SO_3$ complex of the novel ligand PhSn(4-py)$_3$ (**7**), which was also prepared as part of the current work. The blocking of the metal-donor site by the Ph-group in **7** and the replacement of interlayer interactions by $CF_3SO_3^-$ coordination of the Ag^I cations in the resulting complex $\{Ag^I(\mathbf{7})\}_n(CF_3SO_3)_n$ (**8**) leads to the formation of a lattice composed of discrete honeycomb layers (Supporting Information, Figure S21).

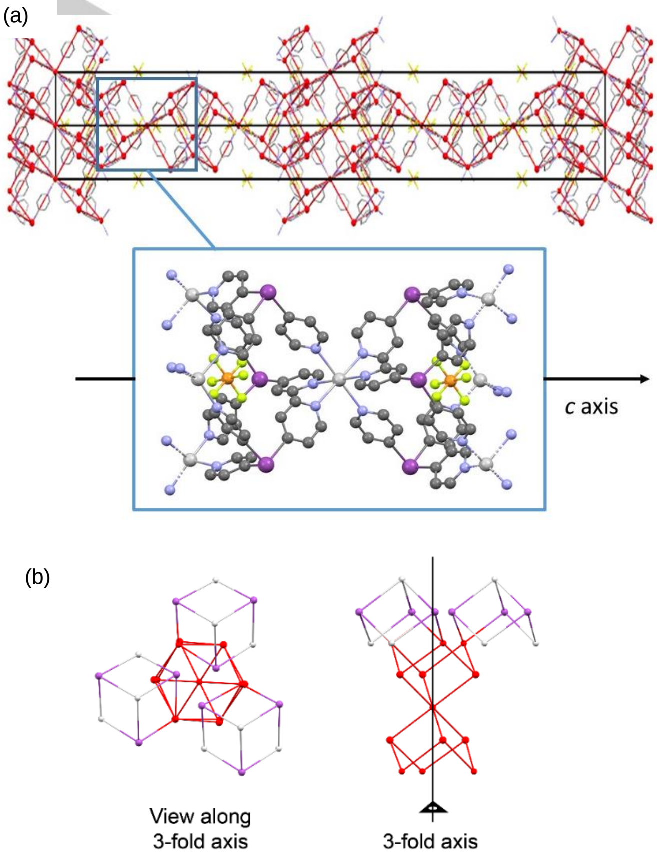


Figure 5 (a) The complicated 3-D network of **5**, and (b) built up from cube fragments, which aggregate into the lattice along the 3-fold, *c*-axis. Colour code, Bi (magenta), N (lilac), Ag (silver), C (grey), F (yellow), P (orange).

In conclusion, we have reported the first examples of tris-4-pyridyl ligands of heavier p-block elements, allowing systematic exploration of the structure-directing effects of the bridgehead and anion on the formation of MOFs. The Ag^I frameworks show rich topological complexity, ranging from 2-D to 3-D networks, which in the cases of **3**, **4** and **5** can be neatly related to a parent NaCl-type structure based on the Group 15 and Ag atoms. Perhaps the most important conclusion on the basis of this work and previous studies of the N(4-py)$_3$ ligand[27] is that the coordination mode can be modulated by descending Group 15 (planar N,N,N-, to tetrahedral N,N,N/E-, to pyramidal N,N,N-) as a result of the dual periodic effects of the decrease in s/p-mixing and Lewis basicity. This transition provides a potentially important tool in the future targeted assembly of specific molecular and extended lattice arrangements.

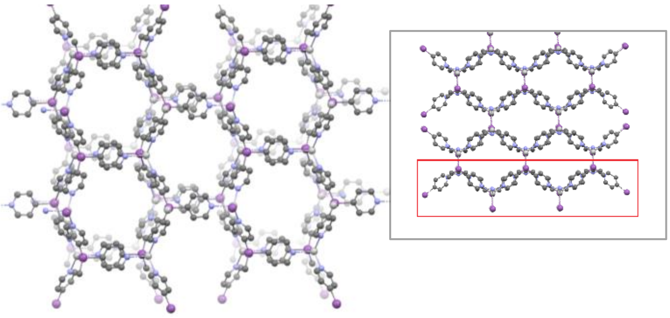


Figure 6 The honeycomb layers of **6**, formed from Sb$_3$Ag$_3$ ring units (viewed approximately along crystallograpic *a* axis), The inset shows the connection of the layers (highlighted by the red rectangle) via Sb-Ag bonding (viewed approximately along the crystallographic *b* axis). The pores created are occupied by SbF$_6^-$ anions, which are omitted for clarity. The pores measure ca. 11.1 Å in diameter, Colour code, Sb (magenta), N (lilac), Ag (silver), C (grey).

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Keywords: pnictogens • tripodal ligands • main-group synthesis • coordination networks • topology

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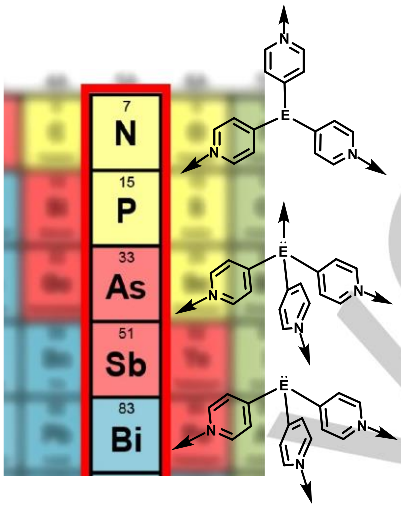
Entry for the Table of Contents

The power to change: the new heavy main group metal tris(4-pyridyl) ligands E(4-py)$_3$ (E= Sb, Bi) build into topologically complex MOFs with Ag^{I}, in which the bridgehead atom plays an important role in structure direction. The E(4-py)$_3$ ligands can function as pyramidal or tetrahedral nodes, an ability that is modulated by the Lewis basicity (stereochemical activity) of the Group 15 element.		**Uncovering the Hidden Landscape of Tris(4-pyridyl) Ligands: Topological Complexity Derived from the Bridgehead** J. E. Waters, G. Berger, A. J. Peel, R. García-Rodríguez,* A. D. Bond,* D. S. Wright*