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A pentametallic Co₅L₄ architecture constructed from bis-substituted phosphate-based ligands†

Jas S. Ward * and Paul E. Kruger *

A pentametallic Co₅L₄ architecture has been constructed from the bis-substituted phosphoric acid pro-ligand P(O)(OH)(OC₆H₄NH₂-3)₂. The architecture, which is comprised of a metal centre embedded in a M₄L₄ square, was characterised in the solid state by X-ray diffraction, confirming cobalt atoms in two different coordination geometries.

The construction of supramolecular cages through self-assembling processes is well-established and has produced a myriad of interesting architectures with various topologies,^{1,2} many of which are capable of accommodating guest molecules within their internal voids.^{3–9} This host-guest behaviour has been utilised to selectively bind guests within the cavity,^{10,11} catalyse reactions,^{12–15} extend the lifetimes of fleeting species,^{16–18} and even shield highly reactive species.^{19,20}

Supramolecular squares have been reliably synthesised through the use of *cis*-blocked square planar Pd(II) and Pt(II) metal centres bearing 1,2-bis(diphenylphosphino)ethane (dppe) and 1,3-bis(diphenylphosphino)propane auxiliary ligands; this combination ensures a 90° ligand–metal–ligand configuration suitable for supramolecular square formation.^{21–23} The pre-organisation of the metal centres and their auxiliary diphosphine ligands greatly contributes to favouring discrete species over polymeric ones. Without this preorganisation, octahedrally coordinated metal nodes would generally favour the formation of 3D motifs, rather than 2D squares. The synthesis of supramolecular squares without such pre-organisation in the metal nodes is therefore less common and of interest for further studies.

Whilst phosphates ([PO₄]^{3–}) are ubiquitous in fields such as biochemistry, and simple cages derived from H₃PO₄ have been previously reported,²⁴ their utilisation in the field of supramolecular chemistry is still quite rare.²⁵ Nevertheless, examples of phosphorus-based ligands, beyond those of simply phosphine-coordinated ligands,^{26,27} being incorporated into supramolecular frameworks have begun to emerge in the recent years.^{28–31} Promisingly, applications like the selective anion extraction have also begun to be demonstrated for these phosphorus-based supramolecular complexes.³² Non-metallic supramolecular cages have also been demonstrated,^{33–35} which have been shown to possess improved properties over their non-supramolecular constituent parts,³⁵ and may offer advantages to fields for which their metallic analogues are not suited, for example in pharmaceuticals, akin to boron neutron capture therapy (BNCT).³⁶ Therefore, the investigation of multi-topic, phosphorus-based ligands with respect to their ability to construct new supramolecular architectures is of interest to a wide range of researchers across a variety of fields. With this in mind, the supramolecular potential of a ditopic phosphate-based ligand was explored.

The previously unknown phosphoric acid pro-ligand, P(O)(OH)(OC₆H₄NH₂-3)₂, was synthesised as the major product from P(O)(OC₆H₄NO₂-3)₃ *via* a Pd/C hydrogenation in MeOH under an atmosphere of hydrogen gas. The bis-substituted P(O)(OH)(OC₆H₄NH₂-3)₂ was found to be favoured over the tris-substituted product P(O)(OC₆H₄NH₂-3)₃ with prolonged reaction times (*via* the opportunistic interaction of the H₂O by-product of the hydrogenation reaction).³⁷

Characterisation with NMR spectroscopy unremarkably revealed a single resonance in the ³¹P NMR spectrum at –10.5 ppm and four peaks in the ¹H NMR spectrum at 6.35, 6.49, 6.51 and 6.88 ppm for the *meta*-substituted aminophenyl rings. Mass spectroscopy supported the identity of the product by observation of the [M + H]⁺ at *m/z* 281, further confirmed through an X-ray diffraction study which identified the bis-substituted phosphoric acid in its zwitterionic form (Fig. S1†). It should be noted that the bond lengths revealed that a formal

MacDiarmid Institute for Advanced Materials and Nanotechnology, School of Physical and Chemical Sciences, University of Canterbury, Christchurch, New Zealand. E-mail: james.s.ward@jyu.fi, paul.kruger@canterbury.ac.nz

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‡ Current address: University of Jyväskylä, Department of Chemistry, 40014 Jyväskylä, Finland.



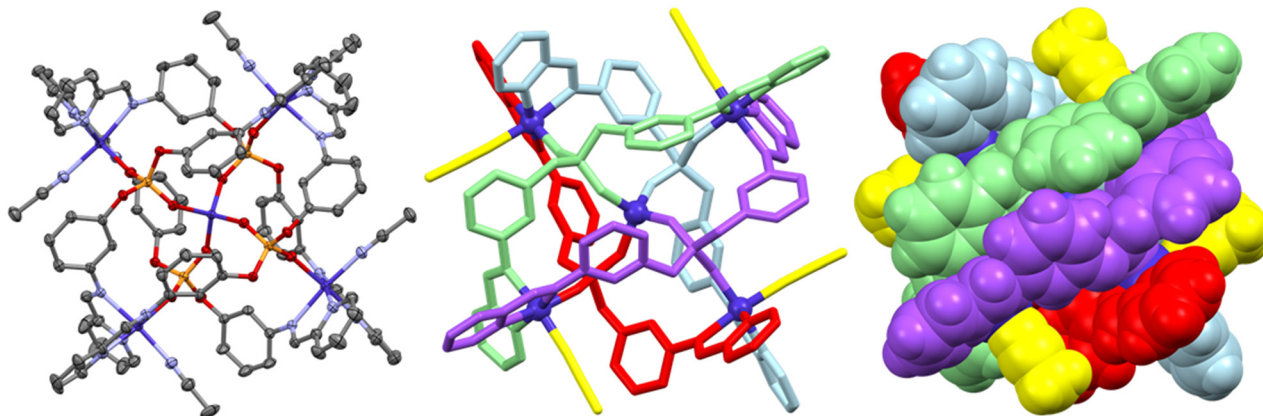


Fig. 1 The solid-state structure of $[\text{Co}_5\text{L}_4(\text{MeCN})_4]^{6+}$ coloured by element (left; hydrogen atoms omitted for clarity, thermal ellipsoids at 50% probability), with ligands block coloured to show connectivity (middle; hydrogen atoms omitted for clarity), and in a spacefill representation (right) to illustrate the complete encapsulation of the central Co^{2+} metal centre (in all cases anions and solvates were omitted for clarity).

single and double bond did not exist between each of the two unsubstituted oxygen atoms and the phosphorus centre, instead their crystallographic similarity indicated that the negative charge was delocalised over both terminal oxygen atoms. The phosphoric acid derivative was recognised as a potential pro-ligand for bis-bidentate self-assembly supramolecular chemistry and investigations with a suitable cobalt salt were conducted.

To explore the supramolecular potential of $\text{P}(\text{O})(\text{OH})(\text{OC}_6\text{H}_4\text{NH}_2)_2$, it was initially reacted in a 3:6:2 ratio with 2-pyridinecarboxaldehyde and $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, respectively, envisioning that the ligand (formed by metal-catalysed imine condensation of the pro-ligand) would effectively act as a linear bis-bidentate linker to form M_2L_3 or M_4L_6 species. However, when acetonitrile was used as the solvent, vapour diffusion of the crude reaction mixture (after filtration) with benzene as the anti-solvent yielded large green crystals of the supramolecular square $[\text{Co}_5\text{L}_4(\text{MeCN})_4][\text{BF}_4]_6$ (Fig. 1; $\text{L} = \text{bis}(3-((E)\text{-pyridin-2-ylmethylene})\text{amino})\text{phenyl})$ phosphate). The composition of this non-traditional nano-square revealed that in addition to the Co_5L_4 core, each of the corner Co^{2+} metal centres had also acquired an acetonitrile (MeCN) molecule to satisfy their coordination sphere, which was taken from the reaction solvent used during synthesis and crystallisation of the complex.

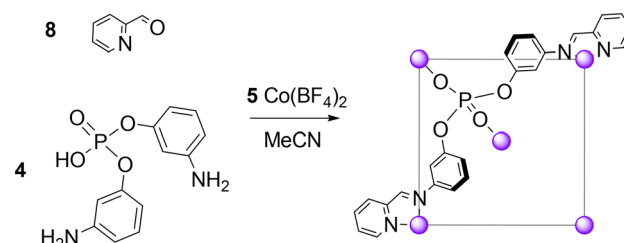
The reaction was repeated with the correct stoichiometry of 4:8:5 (phosphoric acid pro-ligand:aldehyde: Co^{2+}) to give the product in a recovered yield of 19% (Scheme 1). As a side note on the recovered yield of the desired product, a second product from reaction was isolated and found to be $[\text{Co}(\kappa^3\text{-N}(\text{C}(\text{O})\text{py-2})_2)_2][\text{BF}_4]$ (Fig. S3†), with the $[\text{BF}_4]^-$ anion confirming the presence of Co^{3+} rather than Co^{2+} . The rational synthesis of this cation (with various anions) has been previously described.^{38–40}

The paramagnetic Co^{2+} atoms of $[\text{Co}_5\text{L}_4(\text{MeCN})_4][\text{BF}_4]_6$ prevented NMR studies, however, a conclusive ($R_1/wR_2 = 6.1/16.5\%$) single crystal X-ray diffraction study confirmed the complex to be a pentametallic supramolecular nano-square incorporating a fifth centrally encapsulated Co^{2+} centre.

The architecture of the complex is unusual, especially when compared to conventional, edge-bridged supramolecular

squares,^{41–47} where nano square complexes can be straightforwardly synthesised using linear ditopic ligands or linkers and metal nodes (usually with a square planar coordination sphere, though they can also be of an octahedral geometry) with two vacant *cis*-coordination sites, combined in a 1:1 ratio, or more aptly a 4:4 stoichiometry. However, in $[\text{Co}_5\text{L}_4(\text{MeCN})_4][\text{BF}_4]_6$ the four phosphate ligands are nestled, though not interwoven (Fig. 2), diagonally into one another to each bridge two opposing corner Co^{2+} atoms, as well as to the central Co^{2+} and a third Co^{2+} atom of an adjacent corner *via* the two unsubstituted terminal oxygen atoms of the phosphate ligand (upon deprotonation of the acidic pro-ligand during self-assembly). The encapsulation of the central Co^{2+} is particularly striking, given that the terminal oxygen substituents of the phosphate ligands are non-innocent with respect to the overall supramolecular construction, in contrast to the $\text{P} = \text{X}$ ($\text{X} = \text{O}, \text{S}, \text{Se}$) groups of analogous *tris*-substituted phosphate-based supramolecular cages.^{30,31,34}

The $\text{Co}-\text{O}$ bond lengths for the corner (2.025(4), 2.026(4) Å) and central (1.934(4), 1.938(4) Å) cobalt dications were crystallographically independent for a $6\sigma^2$ tolerance, as would be expected for octahedral and tetrahedral geometries, respectively. The differences of $\text{Co}-\text{N}$ bond lengths for the imine (2.151(4)–2.172(4) Å) and pyridyl (2.114(4)–2.131(4) Å)



Scheme 1 The sub-component self-assembly of bis(3-aminophenyl) phosphoric acid, 2-pyridinecarboxaldehyde and $\text{Co}(\text{BF}_4)_2$ in acetonitrile to yield the pentametallic complex $[\text{Co}_5\text{L}_4(\text{MeCN})_4]^{6+}$. The purple circles represent $\text{Co}(\text{II})$ centres.



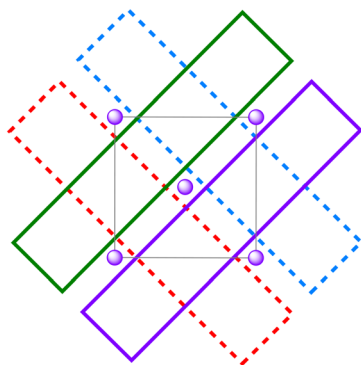


Fig. 2 A graphical representation of how the four phosphate ligands (L, coloured purple, green, red and blue) of $[\text{Co}_5\text{L}_4(\text{MeCN})_4]^{6+}$ are ordered within the supramolecular scaffold. The purple circles represent Co(II) centres and solid and dashed shapes indicate that objects are above and below the plane, respectively.

nitrogen atoms were crystallographically insignificant within the complex and corresponded to the expected values for a Co(X)(Y)(L)_2 coordination sphere (where L is a bis- N,N' -bidentate ligand).⁴⁸

Similarly, the bond length ranges of the P-O(Co) (1.475(4)–1.492(4) Å) and P-O(R) (1.586(4)–1.606(4) Å) were crystallographically indistinguishable from the free protonated ligand $\text{P(O)}_2(\text{OC}_6\text{H}_4\text{NH}_2\text{-}3)(\text{OC}_6\text{H}_4\text{NH}_3\text{-}3)$ (cf. P-O 1.474(1), 1.490(1) Å; P-O(R) 1.594(1), 1.610(1) Å). However, the bond angles for the phosphate nodes showed substantial strain with values for $(\text{R})\text{O-P-O(R)}$ of 100.5(2) and 100.9(2)° in the supramolecular complex to accommodate the Co_5L_4 motif (cf. 105.47(7)° in $\text{P(O)}_2(\text{OC}_6\text{H}_4\text{NH}_2\text{-}3)(\text{OC}_6\text{H}_4\text{NH}_3\text{-}3)$). To a lesser degree (though still crystallographically significant), the $(\text{Co})\text{O-P-O(Co)}$ bond angles of 117.1(2) and 117.5(2)° were also contracted to facilitate bridging two cobalt centres (cf. 118.89(7)° in $\text{P(O)}_2(\text{OC}_6\text{H}_4\text{NH}_2\text{-}3)(\text{OC}_6\text{H}_4\text{NH}_3\text{-}3)$). The Co^{2+} corner-corner distances were close to being square, with through space lengths of 8.018(2) and 8.128(2) Å, and the Co^{2+} centre-corner distances were found to be 5.672(2) and 5.699(2) Å.

The spacefill representation of $[\text{Co}_5\text{L}_4(\text{MeCN})_4][\text{BF}_4]_6$ (Fig. 1) demonstrates that the central Co^{2+} centre is completely encapsulated, suggesting that its incorporation into the supramolecular scaffold would almost certainly have to have been during assembly of the cation, and not after the Co_4L_4 square had been formed. This assumption supports the idea that the central Co^{2+} played a role in templating the $[\text{Co}_4\text{L}_4]^{4+}$ nano-square. This motif of total encapsulation is reminiscent of other oxygen-donor, metal binding species such as crown ethers and cryptands, where $[\text{Co}_5\text{L}_4(\text{MeCN})_4][\text{BF}_4]_6$ can be seen as a phosphorus-based variant of these fundamental overarching families of macrocycles and molecular capsules for which Cram, Lehn, and Pedersen shared the 1987 Nobel prize in chemistry.

In conclusion, a novel pentametalllic Co_5L_4 supramolecular architecture has been synthesised and characterised in the solid state. The supramolecular assembly involves a Co_4L_4 nano-

square comprised of bis(substituted)phosphate ligands, which encapsulates a fifth cobalt atom through the coordination of the phosphates' terminal oxygen atoms. The construction of this unusual supramolecular nano square through the non-innocent involvement of the terminal oxygen substituents of the phosphate ligands is an interesting caveat.

The results reported herein demonstrate that the incorporation of functional groups such as phosphates into supramolecular synthons enable unexpected and non-traditional connectivities and architectures to be observed, and therefore merit further studies to fully realise their potential.

Data availability statement

The data supporting this article have been included as part of the ESI†. Crystallographic data for bis(3-aminophenyl) phosphoric acid (**Pro_ligand**), $[\text{Co}_5\text{L}_4(\text{MeCN})_4][\text{BF}_4]_6$ (**Co₅L₄**), and $[\text{C}_{24}\text{H}_{16}\text{CoN}_6\text{O}_4][\text{BF}_4]$ (**Side_product**) have been deposited at the Cambridge Crystallographic Data Centre (CCDC 1569646–1569648).

Conflicts of interest

There are no conflicts to declare.

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