

Dihydrogen Phosphate-containing Dinuclear Double Assemblies that Demonstrate Phosphate Reactivity to the Tetrafluoroborate Anion.

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Robert A. Faulkner, Nathan J. Patmore, Craig R. Rice* and Christopher Slater.

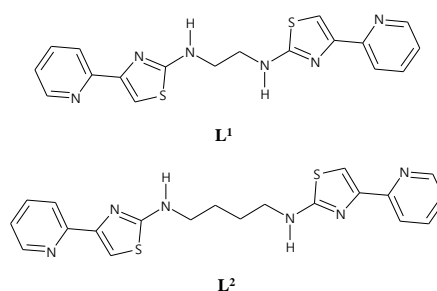
www.rsc.org/

The ligands **L**¹ and **L**² both form dinuclear assemblies with Cu(II) and these react with dihydrogen phosphate so that the anion is incorporated within the assembly (e.g. [Cu₂L₂(H₂PO₄)]³⁺). However, in the presence of tetrafluoroborate anions the phosphate undergoes reaction with the anion forming [Cu₃(L¹)₃(O₃POBF₃)]³⁺ and [Cu₂(L²)₂(O₂P(OBF₃)₂)]⁺.

Metallo-supramolecular chemistry is the self-assembly of structurally complex architectures from the coordination of suitably instructed ligand strands and metal ions.¹ In the helicate form a ligand is employed that can partition into two donor domains, each of which coordinates a different metal ion and a further ligand coordinates the remaining metal sites on the cation giving a dinuclear double helicate [M₂L₂]ⁿ⁺.² Whilst the linear helicate is arguably the simplest form of assembly there are many different species that can be formed such as circular helicates, grids, ladders and cages.³ One application of metallo-supramolecular chemistry is the self-assembly of anion receptors. Anions are chemically important species and their detection and sequestering is an important area of study. Whilst there has been a great deal of effort in this area, many anion receptors are often complex to prepare and often require multi-step synthesis.⁴ One method to circumvent complex synthetic procedures is to generate anion receptors from self-assembly, where the receptor is not synthesized in the conventional sense but is rather assembled in solution, generating a complex architecture from smaller pre-programmed chemical fragments.⁵ As a result the self-assembly of metallo-supramolecular species can produce suitably functionalised architectures that bind anions, forming receptors that are capable of sensing and sequestering these important chemical species. For example, we have shown that a bis-bidentate ligand containing a 1,3-diaminophenylene

spacer forms dinuclear double helicates with Cu(II) and contained within this species is a cavity which binds perchlorate and tetrafluoroborate anions. Reaction of this with dihydrogen phosphate changes the dinuclear structure to a trinuclear circular helicate that forms phosphate-phosphate hydrogen bonded dimers in the solid state.⁵ⁱ

In this work we show how two ligands that contain two bidentate pyridyl-thiazole domains, separated by either a 1,2-diaminoethyl (**L**¹) or 1,4-diaminobutyl (**L**²) spacer, form dinuclear assemblies upon coordination with Cu(trif)₂ (e.g. [Cu₂L₂](trif)₄) and upon reaction with H₂PO₄⁻ the dihydrogen phosphate anion is incorporated within the assembly. However, reaction of **L**¹ or **L**² with Cu(BF₄)₂ and H₂PO₄⁻ results in the reaction of dihydrogen phosphate with the tetrafluoroborate anion forming a {(POBF₃)⁻} moiety. In the case of [Cu₂(L²)₂(H₂PO₄)]²⁺ this reacts with two BF₄⁻ anions forming [Cu₂(L²)₂(O₂P(OBF₃)₂)]⁺ whereas [Cu₂(L¹)₂(H₂PO₄)]³⁺ only reacts once and forms a trinuclear circular helicate [Cu₃(L¹)₃(O₃P(OBF₃))]³⁺.



Scheme 1. Bis-bidentate ligands **L**¹ and **L**².

The ligand **L**¹ was prepared by reaction of ethylenediamine with benzoyl isothiocyanate to give the dibenzoylated dithiourea derivative. Hydrolysis of this with NaOH gave the bis-thiourea and reaction with α -bromoacetylpyridine gave the ligand **L**¹. Ligand **L**² was made in a similar fashion using 1,4-diaminobutane.

Reaction of **L**¹ with Cu(trif)₂ in MeNO₂ gives a tan-coloured solution and analysis by ESI-MS gave an ion at *m/z* 1335

^a Department of Chemical Sciences, School of Applied Sciences, University of Huddersfield, Huddersfield HD1 3DH (UK). E-mail: c.r.rice@hud.ac.uk.

[†] Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: [Synthetic and characterisation of ligands **L**¹ and **L**², ESI-MS and Crystallographic details of the metal complexes]. See DOI: 10.1039/x0xx00000x

corresponding to $\{[\text{Cu}_2(\text{L}^1)_2](\text{trif})_3\}^+$ as well as an ion at m/z 593 corresponding to $\{[\text{Cu}_2(\text{L}^1)_2](\text{trif})_2\}^{2+}$ indicating the formation of a dinuclear assembly. Exposure of the solution to diethyl ether gave a crystalline material which was analysed by X-ray crystallography. In the solid-state the ligand partitions into two separate bidentate binding domains each of which coordinates a different Cu(II) ion and both of these ions are coordinated by two bidentate pyridyl-thiazole domains one from each ligand (Fig. 1). The metal ions coordination sphere is supplemented by coordination by a triflate counter anion which itself forms a series of hydrogen bonding interactions to two -NH atoms on the same ligand strand (Cu-N range 1.948(2) – 2.126(2) Å, Cu-O 2.1693(19) Å). There is no twist about the ligand strand giving rise to a dinuclear double mesocate.

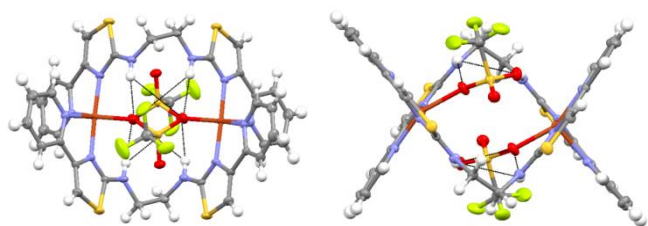


Figure 1. Two views of the X-ray structure of $[\text{Cu}_2(\text{L}^1)_2](\text{trif})_4$. The complex has crystallographically-imposed inversion symmetry. Thermal ellipsoids shown at the 30% probability level. Remaining anions are omitted for clarity. Colour code: orange, Cu(II); red, O; blue, N; yellow, S; lime F; grey, C.

Reaction of the mesocate assembly $[\text{Cu}_2(\text{L}^1)_2](\text{trif})_4$ in MeNO_2 with half an equivalent of $\text{Bu}_4\text{NH}_2\text{PO}_4$ results in a lime-green coloured solution from which a crystalline material was deposited upon slow diffusion of diisopropyl ether. In the solid state the dinuclear structure persists and each of the Cu(II) ions are again coordinated by two bidentate pyridyl-thiazole domains from the two different ligands (Fig 2). However, in this structure a dihydrogen phosphate anion is incorporated within the assembly which bridges the two Cu(II) ions via coordination of the oxygen atoms e.g. $[\text{Cu}_2(\text{L}^1)_2(\text{H}_2\text{PO}_4)]^{3+}$ (Cu-N range 1.974(3) - 2.231(3) Å, Cu-O 1.976(3) and 1.996(3) Å). The H_2PO_4 anion is also held within the ligand strand via -NH...anion interactions with the phosphate oxygen atoms interacting with a single amine hydrogen atom on each strand. The remaining amine hydrogen atom forms intermolecular hydrogen bonding interactions with the triflate counter anions. There are a total of three triflate anions present within the anion structure (i.e. $[\text{Cu}_2(\text{L}^1)_2(\text{H}_2\text{PO}_4)](\text{trif})_3$) indicating that dihydrogen phosphate is present and has not undergone further deprotonation. This is further supported by the hydrogen bonding interaction between both the $\text{O}_2\text{P}(\text{OH})_2$ units and an anion. The dinuclear structure persists in the gas phase with ESI-MS analysis giving ions at m/z 1282 and 492 corresponding to $\{[\text{Cu}_2(\text{L}^1)_2(\text{H}_2\text{PO}_4)](\text{trif})_2\}^+$ and $\{[\text{Cu}_2(\text{L}^1)_2(\text{HPO}_4)]\}^{2+}$.

Reaction of $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ with L^1 and half an equivalent of dihydrogen phosphate in MeNO_2 also gives a lime-green solution from which crystals are deposited from slow diffusion of diisopropyl ether. However, analysis by X-ray diffraction

showed that, unlike the dinuclear assembly formed with $\text{Cu}(\text{trif})_2$, with the BF_4^- counter anion a trinuclear structure is formed e.g. $[\text{Cu}_3(\text{L}^1)_3]^{6+}$.

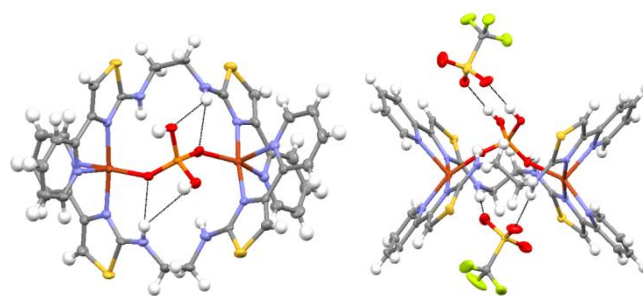


Figure 2. Two views of the X-ray structure of $[\text{Cu}_2(\text{L}^1)_2(\text{H}_2\text{PO}_4)](\text{trif})_3$. Thermal ellipsoids shown at the 30% probability level. Remaining triflate anions are omitted for clarity. Colour code: orange, Cu(II); red, O; blue, N; yellow, S; lime F; grey, C; light orange, P.

In the solid-state the assembly contains three metal ions and three ligands with each metal ion coordinated by two bidentate thiazole-pyridyl domains (Cu-N range 1.956(5) - 2.504(5) Å) from two different ligands (Fig 3a – 3c). The phosphate anion sits in the core of the assembly and coordinates all three Cu(II) ions via three Cu...O coordination bonds (Cu-O range 1.905(4) - 2.013(4) Å) and this is supplemented by a multitude of -NH...anion interactions (Fig 3d). The most unusual feature of the assembly is one of the phosphate oxygen atoms is bonded to a $-\text{BF}_3$ unit, which presumably arises from reaction with the BF_4^- counter anion. The species is also present in the ESI-MS which gave an ion at m/z 1668 corresponding to $\{[\text{Cu}_3(\text{L}^1)_3(\text{O}_3\text{POBF}_3)](\text{BF}_4)_2\}^+$.

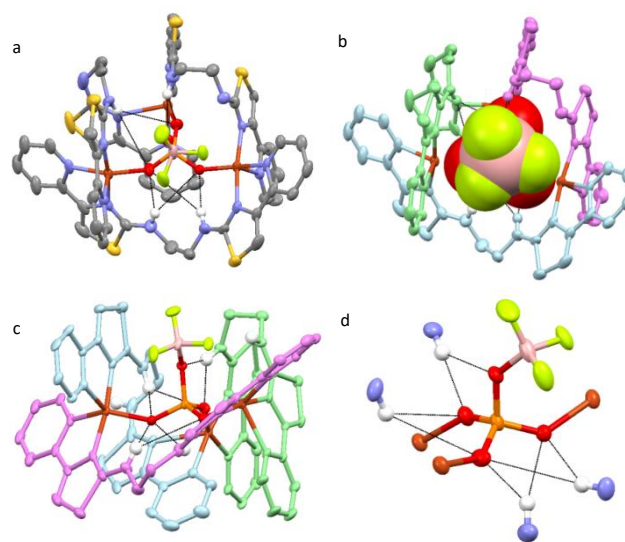


Figure 3. X-ray structure of $[\text{Cu}_3(\text{L}^1)_3(\text{O}_3\text{POBF}_3)](\text{BF}_4)_3$ a - d showing the trinuclear assembly and d) partial view of the $\{[\text{Cu}_3(\text{O}_3\text{P}-\text{OBF}_3)]^{3+}$ core and the hydrogen bonding to -NH atoms. Thermal ellipsoids shown at the 30% probability level. Remaining tetrafluoroborate anions are omitted for clarity. Colour code: orange, Cu(II); red, O; blue, N; yellow, S; lime F; grey, C; light orange, P; pink, B (apart from 3b and 3c where the ligand strands have been coloured for clarity).

The ligand L^2 is similar to L^1 but contains a butyl spacer between the two amine-bidentate domains. Reaction of L^2 with $Cu(trif)_2$ in $MeNO_2$ gives a tan coloured solution which analysis by ESI-MS gives an ion at m/z 1391 and 620 which corresponds to $\{[Cu_2(L^2)_2](trif)_3\}^+$ and $\{[Cu_2(L^2)_2](trif)_2\}^{2+}$ respectively. Although we were unable to successfully grow crystals of this species the ESI-MS data, coupled with comparison with L^1 , it seems likely a dinuclear species has been formed. Reaction of this species with $Bu_4NH_2PO_4$ gives a lime-green coloured solution from which a crystalline material was deposited upon slow diffusion of diisopropyl ether. Analysis by X-ray crystallography showed the expected dinuclear structure with two Cu(II) metal ions coordinated by two bidentate pyridyl-thiazole units from two different ligand strands (Fig. 4). The phosphate anion bridges the two metal ions coordinating each via two oxygen atoms and the $Cu\cdots O$ coordination is supplemented by a single $-NH\cdots$ anion from each ligand strand (Cu-N range 1.969(3) - 2.178(4) Å, Cu-O 2.010(2) - 2.033(3) Å). The remaining amine and the phosphate -OH units form hydrogen bonding interactions with the triflate counter anions. Again, in a similar fashion to the complex with L^1 , the number of counter anions present shows that the dihydrogen phosphate has not undergone further deprotonation. ESI-MS analysis is consistent with the solid-state with ions observed at m/z 1339 $\{[Cu_2(L^2)_2(H_2PO_4)](trif)_2\}^+$, m/z 1189 $\{[Cu_2(L^2)_2(HPO_4)](trif)\}^+$ and m/z 520 $\{[Cu_2(L^2)_2(HPO_4)]\}^{2+}$ as well as lower molecular weight species such as m/z 620 $\{[Cu(L^2)](trif)\}^+$.

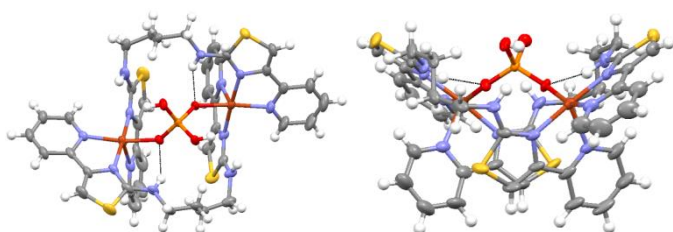


Figure 4. Two views of the X-ray structure of $[Cu_2(L^2)_2(H_2PO_4)](trif)_3$. Thermal ellipsoids shown at the 30% probability level. Remaining triflate anions are omitted for clarity. Colour code: orange, Cu(II); red, O; blue, N; yellow, S; lime F; grey, C; light orange, P.

Reaction of $Cu(BF_4)_2 \cdot 6H_2O$ with L^2 and half an equivalent of dihydrogen phosphate in $MeNO_2$ also gives a lime-green solution from which crystals are deposited by slow diffusion of diisopropyl ether. In the solid-state the dinuclear structure is observed as expected. Each of the ligands partition into two bidentate domains and coordinate different metal ions and the phosphate anion bridges the two metal ions (Cu-N range 1.974(5) - 2.204(6) Å, Cu-O 2.006(4) Å) in an identical manner to the previously described triflate structure (Fig 5a - 5c). However, in this structure the phosphate has reacted with two tetrafluoroborate anions to give a molecule of $\{BF_3O-PO_2-OBF_3\}^{3-}$. This molecule is held within the self-assembly by two $Cu\cdots O$ coordination bonds and a hydrogen bonding interaction between one of the amine units on the ligand strand and a phosphate oxygen atom. The remaining amine unit on each

ligand strand forms a hydrogen bond to one of the fluoride atoms on the $-BF_3$ unit and the same fluoride coordinates the Cu(II) metal ion (Fig. 5d). Examination of this material by ESI-MS showed ions at m/z 1175 and m/z 1107 corresponding to $\{[Cu_2(L^2)_2(O_2P(OBF_3)_2)]\}^+$ and $\{[Cu_2(L^2)_2(O_3POBF_3)]\}^+$ respectively. Also present were smaller ions at 19 mass units higher at m/z 1194 and 1126 corresponding to $\{[Cu_2(L^2)_2(HO_3P(OBF_3))](BF_4)\}^+$ and $\{[Cu_2(L^2)_2(HPO_4)](BF_4)\}^+$, which we attribute to artefacts of the mass spectrometry process.

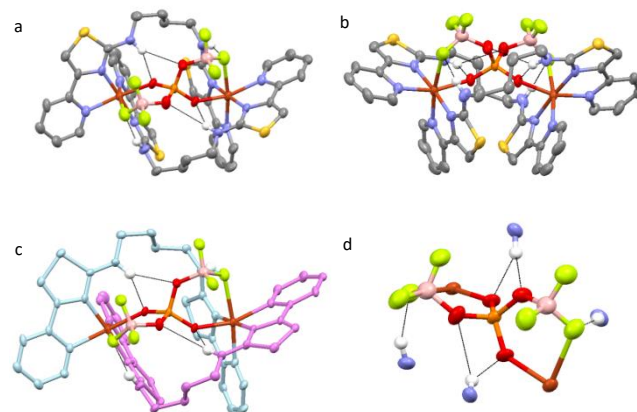


Figure 5. X-ray structure of $[Cu_2(L^2)_2(O_2P(OBF_3)_2)](BF_3)_3$ a - c) showing the dinuclear assembly and d) partial view of the $\{Cu_2(O_2P(OBF_3)_2)\}$ core and the hydrogen bonding to $-NH$ atoms. The complex has crystallographically-imposed inversion symmetry. Thermal ellipsoids shown at the 30% probability level. Remaining tetrafluoroborate anions are omitted for clarity. Colour code: orange, Cu(II); red, O; blue, N; yellow, S; lime F; grey, C; light orange, P; pink, B (apart from 4c where the ligands have been coloured for clarity).

The reaction in this manner is somewhat surprising as tetrafluoroborate is a common anion for numerous applications and is well-known for its chemical stability. Reactions can occur at elevated temperatures and at high or low pH and there is evidence that decomposition of this anion can occur in ionic liquids and in the presence of reactive main group compounds.⁶ However, decomposition of the BF_4^- anion and reaction with phosphate is unprecedented, especially considering the mild conditions.⁷ Furthermore, examination of the CCDC shows that the phosphate-borane adducts (e.g. $(RO)_3PO-BR_3$) are very rare and not derived from the reaction of phosphate and tetrafluoroborate.^{8,9}

Quite why the BF_4^- anion reacts with phosphate in this manner isn't entirely clear. However, examination of the structure of $[Cu_2(L^2)_2(H_2PO_4)](trif)_3$ shows that two of the triflate counter ions are held close to the encapsulated phosphate anion by a series of $-POH\cdots trif$ and $-NH\cdots trif$ interactions coupled with $Cu\cdots O_3SCF_3$ interactions (ave. $Cu\cdots O$ 3.2 Å). It is possible that in the case of the analogous tetrafluoroborate salt the resulting close proximity induces a reaction of the anion with dihydrogen phosphate via either a dissociative (via a BF_3 intermediate) or concerted mechanism, eliminating HF. It is worth noting that, due to the more sterically demanding environment imposed by the shorter ethylene spacer, in $[Cu_2(L^1)_2(H_2PO_4)](trif)_3$ only one phosphate is held close to the

dihydrogen phosphate and correspondingly the phosphate unit can only react with one of the tetrafluoroborate anions. The formation of different structures upon reaction of BF_4^- (e.g. trinuclear in the case of L^1 and dinuclear with L^2) is a consequence of the differing lengths of the aliphatic spacer. Reaction of $[\text{Cu}_2(\text{L}^1)_2(\text{H}_2\text{PO}_4)]^{3+}$ results in one of the $(\text{HO}_3\text{P-OH})^-$ bonds reacting with BF_4^- giving initially $(\text{HO}_3\text{P-OBF}_3)^{2-}$ and the inclusion of the electronegative group (e.g. $-\text{OBF}_3$) increases the acidity of the phosphate unit. This increased acidity will allow full deprotonation of the $(\text{HO}_3\text{P-OBF}_3)^{2-}$ unit and subsequently form three $\text{Cu}\cdots\text{O}$ coordination bonds, acting as a central template for the formation of the trinuclear assembly. However, because of the larger length of the butyl unit in $[\text{Cu}_2(\text{L}^2)_2(\text{H}_2\text{PO}_4)]^{3+}$ the less sterically demanding environment allows reaction between two of the P-OH bonds and BF_4^- , precluding the potential templation effect of the $(\text{O}_3\text{P-OBF}_3)^{3-}$ unit.

We have shown that ligands that contain two bidentate pyridyl-thiazole domains, separated by either a 1,2-diaminoethyl (L^1) or 1,4-diaminobutyl (L^2) spacer, form dinuclear assemblies upon coordination with $\text{Cu}(\text{trif})_2$ (e.g. $[\text{Cu}_2\text{L}_2](\text{trif})_4$) and these can bind dihydrogen phosphate anions. In the presence of BF_4^- the dihydrogen phosphate reacts with this anion and forms a $\{(\text{PO-BF}_3)^-\}$ fragment. In the case of L^2 this reaction occurs twice to form the helicate species $[\text{Cu}_2(\text{L}^2)_2(\text{O}_2\text{P}(\text{OBF}_3)_2)]^+$. With L^1 , which contains the shorter ethylene spacer, the phosphate only reacts once but the structure reassembles to form a trinuclear circular helicate $[\text{Cu}_3(\text{L}^1)_3(\text{O}_3\text{POBF}_3)]^{3+}$.

Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

- §
§§
etc.
- J. -M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995; J.W. Steed, J. L. Atwood, *Supramolecular Chemistry*, John Wiley and Sons, Chichester, 2000.
 - (a) M.J. Hannon, L.J. Childs, *Supramol. Chem.*, 2004, 167; (b) M. Albrecht, *Chem. Rev.* 2001, **101**, 3547; (c) M. Albrecht, *Chem. Soc. Rev.*, 1998, **27**, 281; (d) C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005; (e) E.C. Constable, in *Comprehensive Supramolecular Chemistry*, vol. 9; Polynuclear Transition Metal Helicates, ed J.-P. Sauvage, Elsevier, Oxford, 1996, pp. 213; (f) B. Jana, L. Cera, B. Akhuli, S. Naskar, C. A. Schalley and P. Ghosh, *Inorg. Chem.*, 2017, **56**, 12505; (g) S. J. Allison, D. Cooke, F. S. Davidson, P. I. P. Elliott, R. A. Faulkner, H. B. S. Griffiths, O. J. Harper, O. Hussain, P. J. Owen-Lynch, R. M. Phillips, C. R. Rice, S. L. Shepherd and R. T. Wheelhouse, *Angew. Chem. Int. Ed.*, 2018, DOI: 10.1002/anie.201805510.
 - (a) B. Hasenknopf, J.-M. Lehn, N. Boumediene, E. Leize, and A. Van Dorsselaer, *Angew. Chem. Int. Ed.*, 1998, **37**, 3265; (b) B. Hasenknopf, J.-M. Lehn, N. Boumediene, A. Dupont-Gervais, A. Van Dorsselaer, B. Kneisel, and D. Fenske, *J. Am. Chem. Soc.*, 1997, **119**, 10956; (c) J. S. Wright, A. J. Metherell, W. M. Cullen, J. R. Piper, R. Dawson and M. D. Ward, *Chem. Commun.*, 2017, **53**, 4398; (d) W. Cullen, M. C. Misuraca, C. A. Hunter, N. H. Williams and M. D. Ward, *Nature Chem.*, 2016, **8**, 231; (e) D. Fujita, Y. Ueda, S. Sato, N. Mizuno, T. Kumasaka and M. Fujita, *Nature*, 2016, **540**, 563.
 - (a) J. W. Steed, *Chem. Soc. Rev.* 2009, **38**, 506; (b) S. O. Kang, J. M. Llinares, V. W. Day and K. Bowman-James, *Chem. Soc. Rev.* 2010, **39**, 3980; (c) P. A. Gale, E. N. W. Howe and X. Wu, *Chem.* 2016, **1**, 351; (d) N. Busschaert, S. Park, K. Baek, Y. Choi, J. Park, E. Howe, J. Hiscock, L. Karagiannidis, I. Marques, V. Felix, W. Namkung, J. L. Sessler, P. A. Gale and I. Shin, *Nature Chemistry*, 2017, **9**, 667; (e) P. Gale, J. Davis and R. Quesada, *Chem. Soc. Rev.*, 2017, **46**, 2497; (f) P. Gale and C. Caltagirone, *Chem. Soc. Rev.*, 2015, **44**, 4212; (g) N. Busschaert, C. Caltagirone, W. Van Rossom and P. A. Gale, *Chem. Rev.*, 2015, **115**, 8038; (h) J. Hiscock, M. Sambrook, N. Wells and P. Gale, *Chem. Sci.*, 2015, **6**, 5680; (i) M. J. Langton, C. J. Serpell and P. Beer, *Angew. Chem. Int. Ed.* 2016, **55**, 1974; (j) J. L. Sessler, P. A. Gale and W.-S. Cho, *Anion Receptor Chemistry*, RSC, Cambridge, 2006. N. H. Evans and P. D. Beer, *Angew. Chem. Int. Ed.*, 2014, **53**, 11716. A. Bessette, S. Nag, A. K. Pal, S. Derossi and G. S. Hanan, *Supramolecular Chemistry*, 2012, **24**, 595. A. L. Blackburn, N. C. A. Baker and N. C. Fletcher, *RSC Adv.*, 2014, **4**, 18442.
 - (a) R. Custelcean, *Chem. Soc. Rev.* 2014, **43**, 1813; (b) P. Ballester, *Chem. Soc. Rev.* 2010, **39**, 3810; (c) H. Amouri, C. Desmarests and J. Moussa, *Chem. Rev.* 2012, **112**, 2015; (d) C. R. Rice, *Coord. Chem. Rev.* 2006, **250**, 3190; (e) D. Zhang, T. K. Ronson, J. Mosquera, A. Martinez, L. Guy and J. R. Nitschke, *J. Am. Chem. Soc.* 2017, **139**, 6574; (f) J.-F. Ayme, J. E. Beves, C. J. Campbell, G. Gil-Ramirez, D. A. Leigh and A. J. Stephens, *J. Am. Chem. Soc.* 2015, **137**, 9812; (g) R. Custelcean, P. V. Bonnesen, N. C. Duncan, X. Zhang, L. A. Watson, G. V. Berkel, W. B. Parson and B. P. Hay, *J. Am. Chem. Soc.* 2012, **134**, 8525; (h) R. Custelcean, A. Bock and B. A. Moyer, *J. Am. Chem. Soc.* 2010, **132**, 7177; (i) R. A. Faulkner, L. P. Harding, J. Higginson, C. R. Rice and C. Slater *Angew. Chem. Int. Ed. Engl.* 2014, **126**, 13540; (j) L. P. Harding, J. C. Jeffery, T. Riis-Johannessen, C. R. Rice and Z. Zeng, *Chem. Commun.* 2004, 654; (k) L. P. Harding, J. C. Jeffery, T. Riis-Johannessen, C. R. Rice and Z. Zeng, *J. Chem. Soc., Dalton Trans.* 2004, 2396.
 - For hydrolysis of tetrafluoroborate in ionic liquids see: M. G. Freire, C. M. S. Neves, I. M. Marrucho, J. A. P. Coutinho, and A. M. Fernandes *J. Phys. Chem. A* 2010, **114**, 3744. For reactions with $(\text{SiMe}_3)_2$ see: J. M. Larsson and K. J. Szabó, *J. Am. Chem. Soc.* 2013, **135**, 443. S. Radosavljević, V. Šćepanović, S. Stević and D. Milojković, *J. Fluorine Chem.*, 1979, **13**, 465.
 - Hydrolysis of BF_4^- to $(\text{BF}_3\text{OH})^-$ has been observed with $\text{Cu}(\text{II})$ see: J. C. Dewan and L. K. Thompson, *Can. J. Chem.*, 1982, **60**, 121.
 - Whilst adducts between phosphine oxides and borates are known (e.g. $\text{R}_3\text{P-O-BR}_3$) to the best of our knowledge there is only one report of compounds containing the $(\text{RO})_3\text{PO-BR}_3$ unit see: A. Styskalik, M. Babiak, P. Machac, B. Relichova and J. Pinkas, *Inorg. Chem.* 2017, **56**, 10699
 - Reactions between phosphate and boric acid are well established and boron phosphate (BPO_4) is known from the reaction of phosphoric acid with boric acid see: F. Mylius and A. Meusser, *Berichte der deutschen chemischen Gesellschaft*. 1904, **37**, 397.