

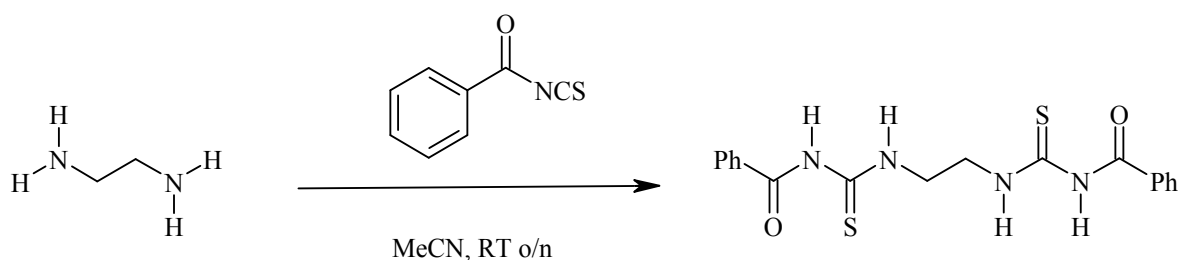
Dihydrogen Phosphate-containing Dinuclear Double Assemblies that Demonstrate Phosphate Reactivity to the Tetrafluoroborate Anion.

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Electronic Supplementary Information.

Chemicals were purchased and used without further purification. ^1H and ^{13}C NMR spectra were recorded on a 400MHz Bruker Avance DP X400. Mass spectra were obtained on an Agilent 6210 TOF MS for the organic species with the metal complexes run on a Bruker MicroQTOF LC.

Synthesis of L¹



To a 250 mL RBF was charged with ethylenediamine (1 mL, 0.9 g, 15 mmol) and MeCN (50 mL) was added a solution of benzoyl isothiocyanate (5 mL, 6.1 g, 37.5 mmol) in MeCN (50 mL) slowly over 30 mins with constant stirring. The reaction mixture was then stirred at RT for a further 12hrs during this time a heavy white precipitate was formed. The resulting mixture was then added dropwise whilst stirring to deionised water (300 mL) to yield a white/yellow precipitate which was then isolated via vacuum filtration. The solid was then suspended in MeOH (50 mL) in a 100 mL conical flask and sonicated (5 mins). The white/yellow suspension was then once again filtered under vacuum to yield a fine white solid which was washed with further portions of MeOH (3 x 10 mL) to give the dibenzoylated dithiourea as a fine white powder (3.5 g, 60 %). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$) δ (ppm) 11.39 (s, 2H, PhCONH), 10.97 (s, 2H, -CH₂CONH), 7.95 (d, J = 7.5, 4H, H-2 Ph), 7.63 (t, J = 7.5, 2H, H-4 Ph), 7.51 (t, J = 7.5 Hz, 4H, H-3 Ph), 4.04 (s, 4H, -CH₂-). ^{13}C NMR [400 MHz, $(\text{CD}_3)_2\text{SO}$]: δ_{C} = 183.5 (C=S), 168.4 (C=O), 133.4 (CH), 132.7 (Q), 129.0 (CH), 128.7 (CH), 44.8 (CH₂). ESI-MS m/z 387 ($\text{M} + \text{H}^+$), HR ESI-MS found 387.0927 $\text{C}_{18}\text{H}_{19}\text{N}_4\text{S}_2\text{O}_2$ requires 387.0944 (error 4.5 ppm). Whilst the ESI-MS analysis did give an accurate ion the compound did decompose rapidly in the ESI MS process and only a small M^+ ion was observed. This behaviour is common to all the aliphatic bridged dithioamines and their derivatives.

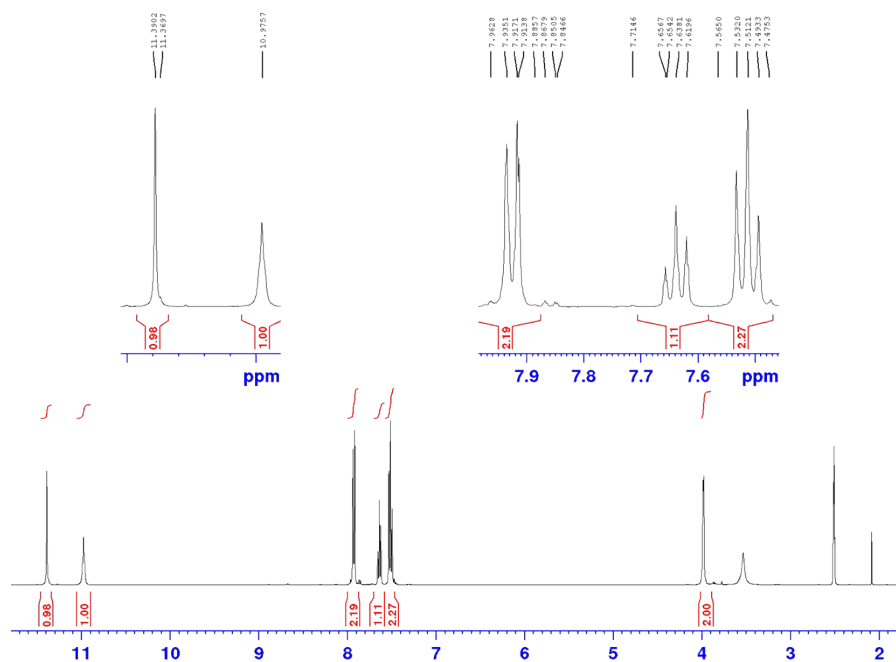
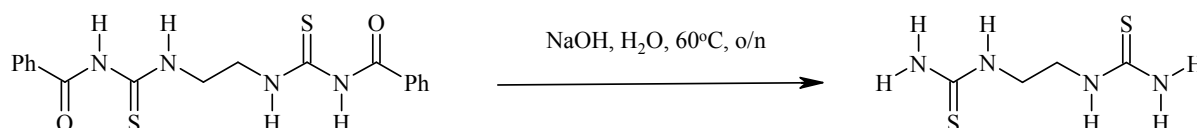


Figure 1. ¹H NMR ((CD₃)₂SO) of dibenzoylated dithiourea derivative.



In a 100 ml RBF was combined the benzoylated dithiourea (1 g, 2.6 mmol), deionised water (30 mL) and a magnetic stir bar. A solution of NaOH (0.63 g, 15.8 mmol) in H₂O (15 mL) was then added to the reaction mixture whilst stirring at 60°C. After 12hrs the resulting colourless solution was then cooled to RT during which time a fine white precipitate was formed. The precipitate was then collected via vacuum filtration and then washed with deionised water (3 x 5 mL) giving the thiourea as a fine white powder (0.43 g, 93 %). The ¹H NMR gives four broad signals in the aromatic region and two broad signals at ~ 3.5 ppm. It is suspected that intra-molecular hydrogen bonding is inducing broad peaks in the ¹H NMR. However, both the ¹³C and ESI-MS are exactly as expected. ¹³C NMR [400 MHz, (CD₃)₂SO]: δ_C = 183.9 (C=S), 43.7 (CH₂). ESI-MS *m/z* 179 (M + H⁺). HR ESI-MS found 179.0415 C₄H₁₁N₄S₂ requires 179.042 (error 2.61 ppm).

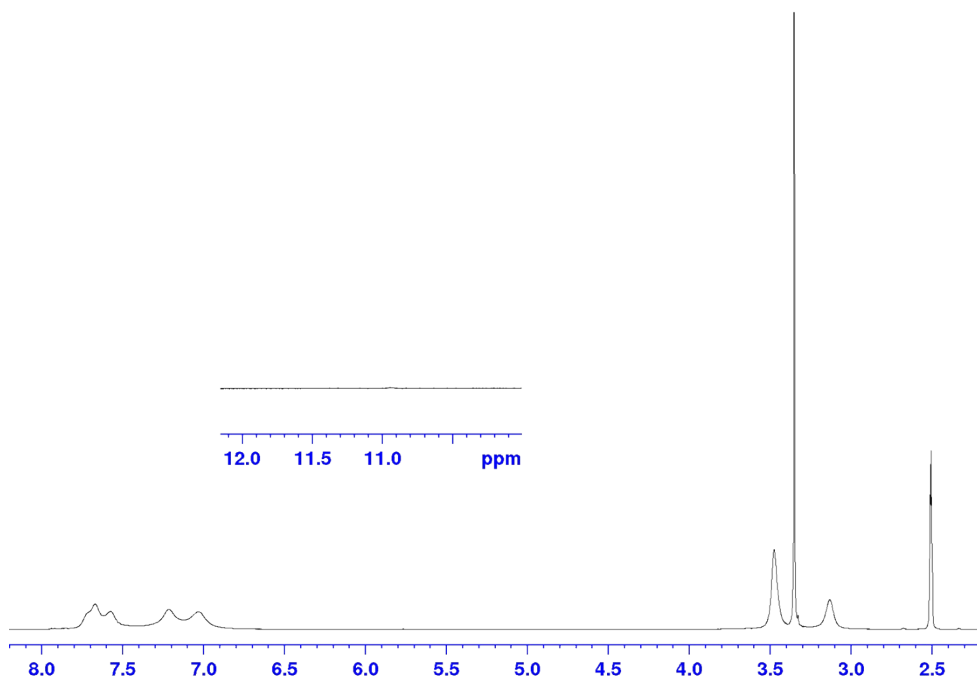
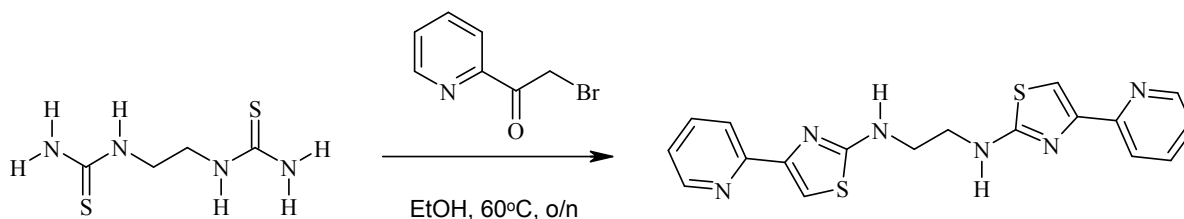


Figure 2. ^1H NMR ($(\text{CD}_3)_2\text{SO}$) of the dithiourea derivative.



Synthesis of L^1 . A 25 mL RBF was charged with dithiourea derivative (228 mg, 1.3 mmol), EtOH (10 mL) and magnetic stir bar and the mixture was then heated to 60 °C and to this added α -bromoacetyl pyridine (540 mg, 2.7 mmol) in a solution in EtOH (2 mL) solution whilst stirring. Heating was continued for a further 8 h during which time a heavy yellow precipitate was formed. This was then isolated via vacuum filtration and the filtrand was then washed with portions of EtOH (3 x 2 mL) to give the protonated product. The free-base ligand was then isolated by suspending in concentrated ammonia (15 mL) for 24 h. The resulting colourless suspension was then sonicated (5mins) and was filtered under vacco and the filtrand washed with portions of deionised water (5 x 2 mL) and EtOH (2 x 2 mL) giving the product as a fine off white powder (402 mg 81 %). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$) δ (ppm) 8.55 (d, $J = 4$, 2H, H-6 py), 7.91-7.89 (m, overlapping, 4H, H-3 py and -NH), 7.79 (dt, $J = 7.6, 1.6$, 2H, H-4 py), 7.31 (s, 2H, tz), 7.26 (ddd, $J = 7.4, 2.6, 1.2$, 2H, H-5 py), 3.60 (d, $J = 2.5$ Hz, 4H, $-\text{CH}_2-$). ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{SO}$) δ 169.0, 152.9, 150.7, 149.7, 137.4, 122.8, 120.8, 105.4 and 44.1 ppm. ESI-MS m/z 381 ($\text{M} + \text{H}^+$). HR ESI-MS found 381.0934 $\text{C}_{18}\text{H}_{17}\text{N}_6\text{S}_2$ requires 381.0951 (error 4.79 ppm). IR (ATR) ν/cm^{-1} 3206 (s, -NH), 3001 (s, CH), 1590 (s, N=CH) and 1531 (s, CH).

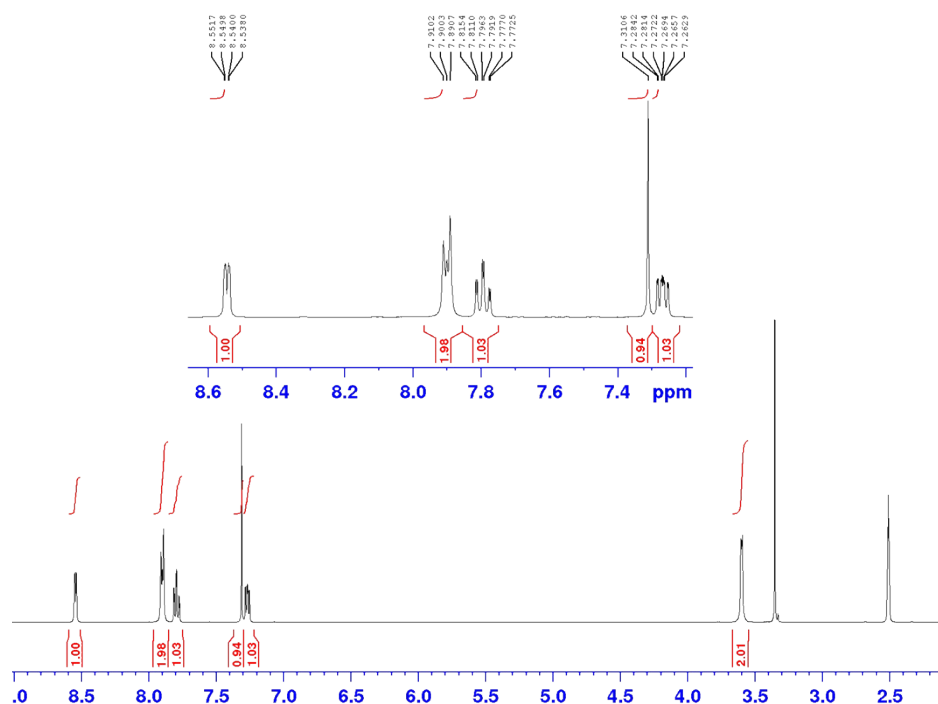
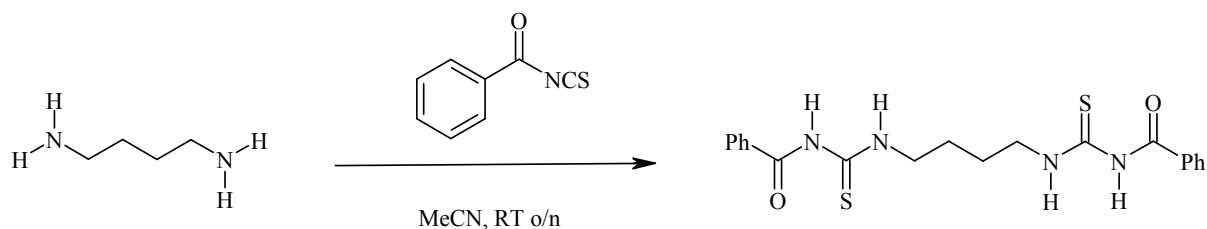


Figure 3. ^1H NMR ($(\text{CD}_3)_2\text{SO}$) of ligand L^1 .



To a 100 mL RBF was charged with putrescine (0.35 g, 3.9 mmol) and MeCN (25 mL) was added a solution of benzoyl isothiocyanate (1.3 mL, 1.59 g, 9.8 mmol) in MeCN (25 mL) slowly over 30 mins with constant stirring. The reaction mixture was then stirred at RT for a further 12hrs during this time a heavy white precipitate was formed. The resulting mixture was then added dropwise, whilst stirring, to deionised water (100 mL) to yield a cream precipitate which was then isolated via vacuum filtration. The solid was then suspended in MeOH (20 mL) in a 50 mL conical flask and sonicated (5 mins). The cream suspension was then once again filtered under vacuum to yield a fine white solid which was washed with further portions of MeOH (3 x 5 mL) to give the dibenzoylated thiourea as a fine white powder (0.90 g, 55 %). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$) δ (ppm) 11.30 (s, 2H, PhCONH), 10.92 (t, $J = 5.4$, 2H, $-\text{CH}_2\text{NH}-$), 7.92 (d, $J = 7.2$, 4H, H-2 Ph), 7.64 (t, $J = 7.4$, 2H, H-4 Ph), 7.51 (t, $J = 7.8$, 4H, H-3 Ph), 3.68 (d, $J = 5.4$ Hz, 4H, $-\text{CH}_2\text{NH}-$), 1.72 (brs, 4H, $-\text{CH}_2\text{CH}_2\text{NH}-$). ^{13}C NMR [400 MHz, $(\text{CD}_3)_2\text{SO}$]: $\delta_{\text{C}} = 183.5$ (C=S), 168.4 (C=O), 133.4 (CH), 132.7 (Q), 129.0 (CH), 128.7 (CH), 44.8 (CH_2), 25.6 (CH_2). ESI-MS m/z 415 ($\text{M} + \text{H}^+$), HR ESI-MS found 415.1257 $\text{C}_{20}\text{H}_{23}\text{N}_4\text{S}_2\text{O}_2$ requires 415.1268 (error 2.65 ppm). Whilst the ESI-MS analysis did give an accurate

ion the compound did decompose rapidly in the ESI MS process and only a small M^+ ion was observed. This behaviour is common to all of the aliphatic bridged dithioamines and their derivatives.

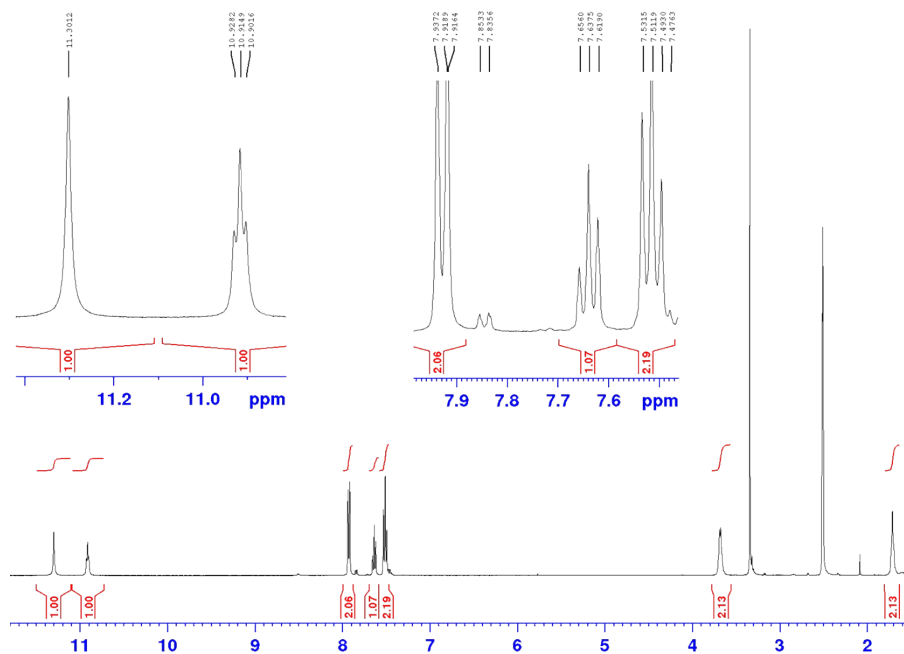
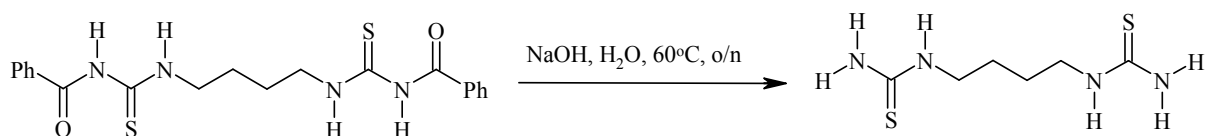


Figure 4. ^1H NMR $(\text{CD}_3)_2\text{SO}$ of the dibenzoylated dithiourea derivative.



In a 50 ml RBF was combined the dibenzoylated dithiourea (510 mg, 1.23 mmol), deionised water (10 mL) and a magnetic stir bar. A solution of NaOH (290 mg, 7.4 mmol) in H_2O (10 mL) was then added to the reaction mixture whilst stirring at 60°C . After 12hrs the resulting colourless solution was then cooled to RT during which time a fine white precipitate was formed. The precipitate was then collected via vacuum filtration and then washed with deionised water (3 x 3 mL). To give the dithiourea as a fine white powder (210 mg, 83 %). The ^1H NMR gives three broad signals in the aromatic region and two broad signals at 3.0 and 1.4 ppm. As has been mentioned previously is suspected that intra-molecular hydrogen bonding is inducing broad peaks in the ^1H NMR. However, the ^{13}C and ESI-MS is exactly as expected. ^{13}C NMR [400 MHz, $\text{DMSO}-d_6$]: $\delta_{\text{C}} = 183.5$ (C=S), 44.1 (CH_2), 26.9 (CH_2). ESI-MS m/z 207 ($M + \text{H}^+$). HR ESI-MS found 207.0735 $\text{C}_6\text{H}_{15}\text{N}_4\text{S}_2$ requires 207.0733 (error 1.48 ppm).

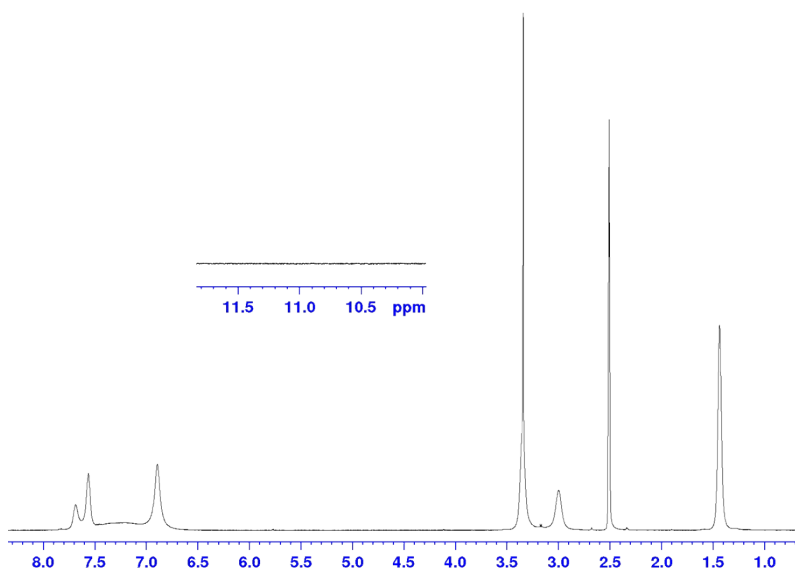
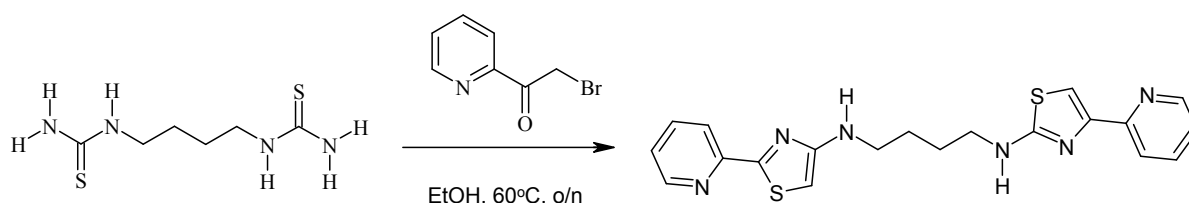


Figure 5. ^1H NMR ($(\text{CD}_3)_2\text{SO}$) of the dithiourea derivative.



Synthesis of L^2 . A 25 mL RBF was charged with the dithiourea derivative (150 mg, 0.73 mmol), EtOH (10 mL) and magnetic stir bar and the mixture was then heated to 60 °C and to this added α -bromoacetyl pyridine (0.30 mg, 1.5 mmol) in a solution in EtOH (2 mL) solution whilst stirring. Heating was continued for a further 8 h during which time a heavy yellow precipitate was formed. This was then isolated via vacuum filtration and the filtrand was then washed with portions of EtOH (3 x 2 mL) to give the protonated product. The free-base ligand was then isolated by suspending in concentrated ammonia (15 mL) for 24 h. The resulting colourless suspension was then sonicated (5 mins) and was filtered under vacuum and the filtrand washed with portions of deionised water (5 x 2 mL) and EtOH (2 x 2 mL), giving the product as a fine off white powder (180 mg 60 %). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$) δ (ppm) 8.53 (d, $J = 4$, 2H, H-6 py), 7.88 (d, $J = 7.8$, 2H, H-3 py), 7.79 (dt, 7.6, $J = 1.7$, 2H, H-4 py), 7.75 (t, $J = 5.4$, 2H, -NH), 7.28 (s, 2H, tz), 7.25 (dd, $J = 5.7$, 2H, H-5 py), 3.33 (brs, 4H, - CH_2NH -, overlapping with H_2O), 1.71 (brs, 4H, - $\text{CH}_2\text{CH}_2\text{NH}$ -). ^{13}C NMR (400 MHz $(\text{CD}_3)_2\text{SO}$) δ 169.2, 153.0, 150.7, 149.7, 137.5, 122.8, 120.7, 104.9, 44.6 and 26.7 ppm. ESI-MS m/z 409 ($\text{M} + \text{H}^+$), HR ESI-MS found 409.1261 $\text{C}_{20}\text{H}_{21}\text{N}_6\text{S}_2$ requires 409.1264 (error 0.97 ppm). IR (ATR) ν/cm^{-1} 3216 (m, -NH), 2870 (w, CH), 1574 (s, N=CH) and 1516 (w, CH).

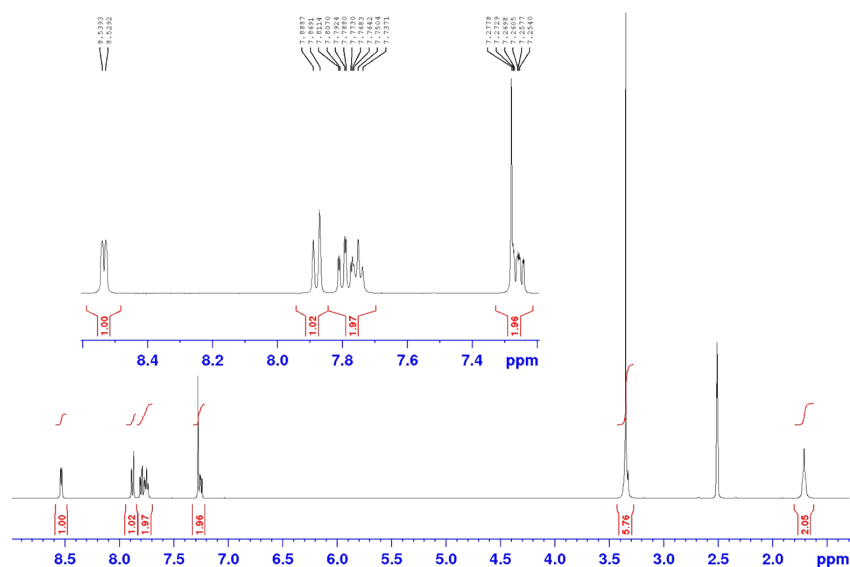


Figure 6. ^1H NMR ($(\text{CD}_3)_2\text{SO}$) of ligand L^2 .

Synthesis of $[\text{Cu}_2(\text{L}^1)_2](\text{trif})_4$. To a solution of $\text{Cu}(\text{trif})_2$ (10 mg, 0.028 mmol) in MeNO_2 (1 ml) was added a suspension of ligand L^1 (10 mg, 0.026 mmol) in MeNO_2 and the reaction warmed and sonicated until a clear dark blue solution had formed. Diethyl ether was slowly allowed to diffuse into the solution resulting in dark blue block-like crystals after several days. Filtration and washing with Et_2O (1 ml) and diethyl ether (1 ml) gave dark blue crystals which lost solvent rapidly (yield = 46%). $[\text{Cu}_2(\text{L}^1)_2](\text{trif})_4$. Found: C, 32.0; H, 1.7 N, 10.91%; $\text{C}_{40}\text{H}_{32}\text{N}_{12}\text{S}_8\text{Cu}_2\text{F}_{12}\text{O}_{12}$ requires C, 32.37; H, 2.17; N, 11.32%.

Synthesis of $[\text{Cu}_2(\text{L}^1)_2(\text{H}_2\text{PO}_4)](\text{trif})_3$. To a solution of $\text{Cu}(\text{trif})_2$ (10 mg, 0.028 mmol) in MeNO_2 (1 ml) was added a suspension of ligand L^1 (10 mg, 0.026 mmol) in MeNO_2 and the reaction warmed and sonicated until a clear dark blue solution had formed. To this was added a solution of $\text{Bu}_4\text{NH}_2\text{PO}_4$ (4.5 mg, 0.013 mmol) in MeNO_2 (0.5 ml) during which the colour changed from dark blue to lime green. Di-isopropyl ether was slowly allowed to diffuse into the solution resulting in lime green needle-like crystals after several days. Filtration and washing with diisopropyl ether (1 ml) and diethyl ether (1 ml) gave lime green crystals which lost solvent rapidly (yield = 39%).

Synthesis of $[\text{Cu}_3(\text{L}^1)_3(\text{O}_3\text{POBF}_3)](\text{BF}_4)_3$. To a solution of $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (10 mg, 0.029 mmol) in MeNO_2 (1 ml) was added a suspension of ligand L^1 (11 mg, 0.029 mmol) in MeNO_2 and the reaction warmed and sonicated until a clear dark blue solution had formed. To this was added a solution of $\text{Bu}_4\text{NH}_2\text{PO}_4$ (4.9 mg, 0.014 mmol) in MeNO_2 (0.5 ml) during which the colour changed from dark blue to lime green. Di-isopropyl ether was slowly allowed to diffuse into the solution resulting in lime green needle-like crystals after several days. Filtration and washing with diisopropyl ether (1 ml) and diethyl ether (1 ml) gave lime green crystals which lost solvent rapidly (yield = 37%). $[\text{Cu}_3(\text{L}^1)_3(\text{O}_3\text{POBF}_3)](\text{BF}_4)_3$. Found: C, 36.25; H, 1.73; N, 13.44%; $\text{C}_{54}\text{H}_{48}\text{N}_{18}\text{S}_6\text{Cu}_3\text{B}_4\text{F}_{15}\text{PO}_4 \cdot 2\text{H}_2\text{O}$ requires C, 36.21; H, 2.93; N, 14.07%.

Synthesis of $[\text{Cu}_2(\text{L}^2)_2(\text{H}_2\text{PO}_4)](\text{trif})_3$. To a solution of $\text{Cu}(\text{trif})_2$ (10 mg, 0.028 mmol) in MeNO_2 (1 ml) was added a suspension of ligand L^2 (11 mg, 0.027 mmol) in MeNO_2 and the reaction warmed and sonicated until a clear dark blue solution had formed. To this was added a solution of $\text{Bu}_4\text{NH}_2\text{PO}_4$ (4.7 mg, 0.014 mmol) in MeNO_2 (0.5 ml) during which the colour changed from dark blue to lime green. Di-isopropyl ether was slowly allowed to diffuse into the solution resulting in lime green needle-like crystals after several days. Filtration and washing with diisopropyl ether (1 ml) and diethyl ether (1 ml) gave lime green crystals which lost solvent rapidly (yield = 41%).

Synthesis of $[\text{Cu}_2(\text{L}^2)_2(\text{O}_2\text{P}(\text{OBF}_3)_2)](\text{BF}_4)$. To a solution of $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (10 mg, 0.028 mmol) in MeNO_2 (1 ml) was added a suspension of ligand L^2 (11 mg, 0.027 mmol) in MeNO_2 and the reaction warmed and sonicated until a clear dark blue solution had formed. To this was added a solution of $\text{Bu}_4\text{NH}_2\text{PO}_4$ (4.7 mg, 0.014 mmol) in MeNO_2 (0.5 ml) during which the colour changed from dark blue to lime green. Di-isopropyl ether was slowly allowed to diffuse into the solution resulting in lime green needle-like crystals after several days. Filtration and washing with diisopropyl ether (1 ml) and diethyl ether (1 ml) gave lime green crystals which lost solvent rapidly (yield = 38%). $[\text{Cu}_2(\text{L}^2)_2(\text{O}_2\text{P}(\text{OBF}_3)_2)](\text{BF}_4)$. Found: C, 36.35; H, 2.91; N, 12.61%; $\text{C}_{40}\text{H}_{40}\text{N}_{12}\text{S}_4\text{B}_3\text{Cu}_2\text{F}_{10}\text{PO}_4 \cdot 3\text{H}_2\text{O}$ requires C, 36.52; H, 3.52; N, 12.78%.

In all cases the solutions gave a homogeneous mass of crystalline product. X-ray analysis was carried out several times (either a whole data collection or unit cell parameters) in an effort to assure homogeneity and repeatability. However, this was often accompanied by small amounts of an intractable fine powder (especially upon addition of dihydrogen phosphate for $[\text{Cu}_2(\text{L}^1)_2(\text{H}_2\text{PO}_4)](\text{trif})_3$ and $[\text{Cu}_2(\text{L}^2)_2(\text{H}_2\text{PO}_4)](\text{trif})_3$) and this precluded elemental analysis in these cases.

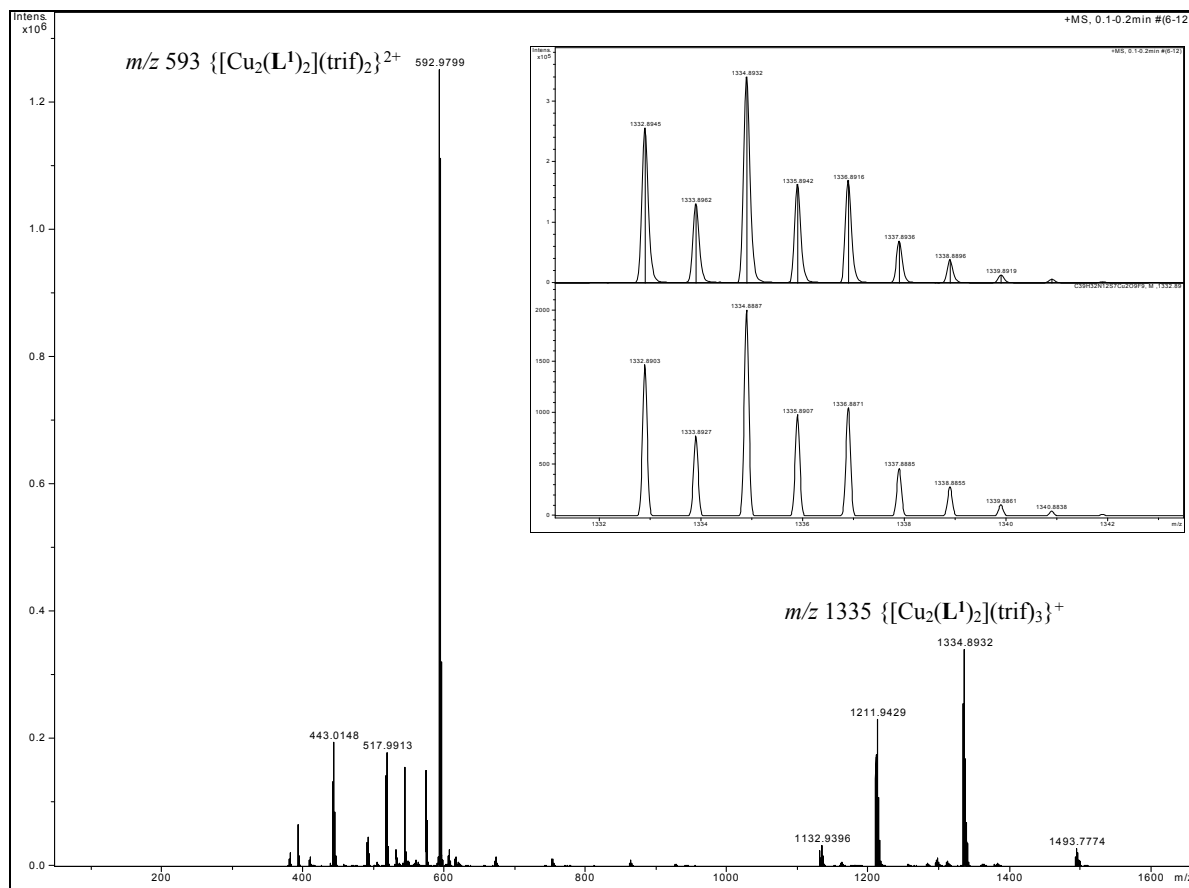


Figure 7. ESI-MS of $[\text{Cu}_2(\text{L}^1)_2](\text{trif})_4$ with the obtained isotope pattern (inset top) and calculated (inset bottom) for m/z 1335 $[\text{Cu}_2(\text{L}^1)_2](\text{trif})_3^+$.

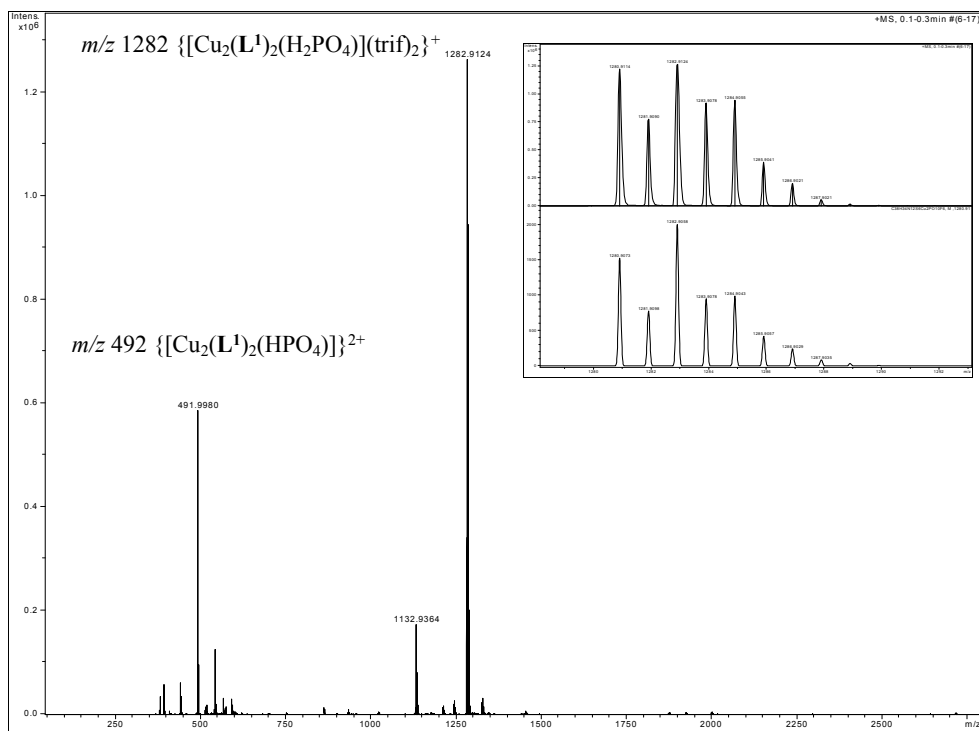


Figure 8. ESI-MS of $[\text{Cu}_2(\text{L}^1)_2(\text{H}_2\text{PO}_4)](\text{trif})_3$ with the obtained isotope pattern (inset top) and calculated (inset bottom) for m/z 1282 $[\text{Cu}_2(\text{L}^1)_2(\text{H}_2\text{PO}_4)](\text{trif})_2^+$.

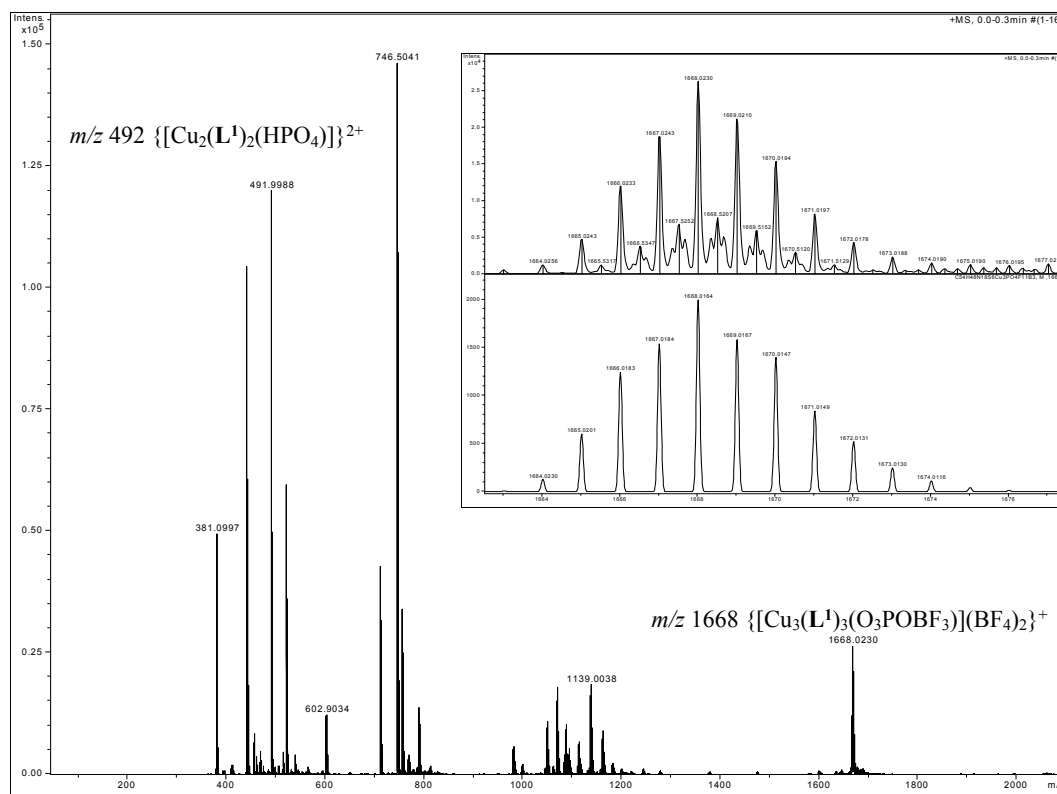


Figure 9. ESI-MS of $[Cu_3(L^1)_3(O_3POBF_3)](BF_4)_3$ with the obtained isotope pattern (inset top) and calculated (inset bottom) for m/z 1668 $\{[Cu_3(L^1)_3(O_3POBF_3)](BF_4)_2\}^+$.

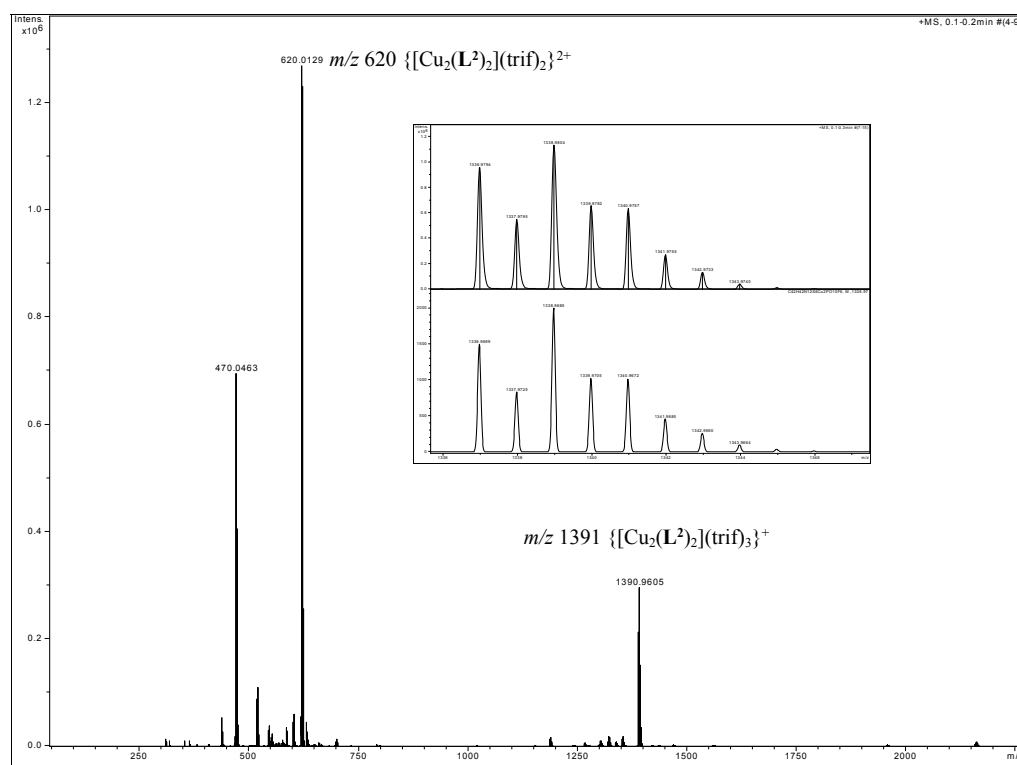


Figure 10. ESI-MS of $[Cu_2(L^2)_2](trif)_4$ with the obtained isotope pattern (inset top) and calculated (inset bottom) for m/z 1391 $\{[Cu_2(L^2)_2](trif)_3\}^+$.

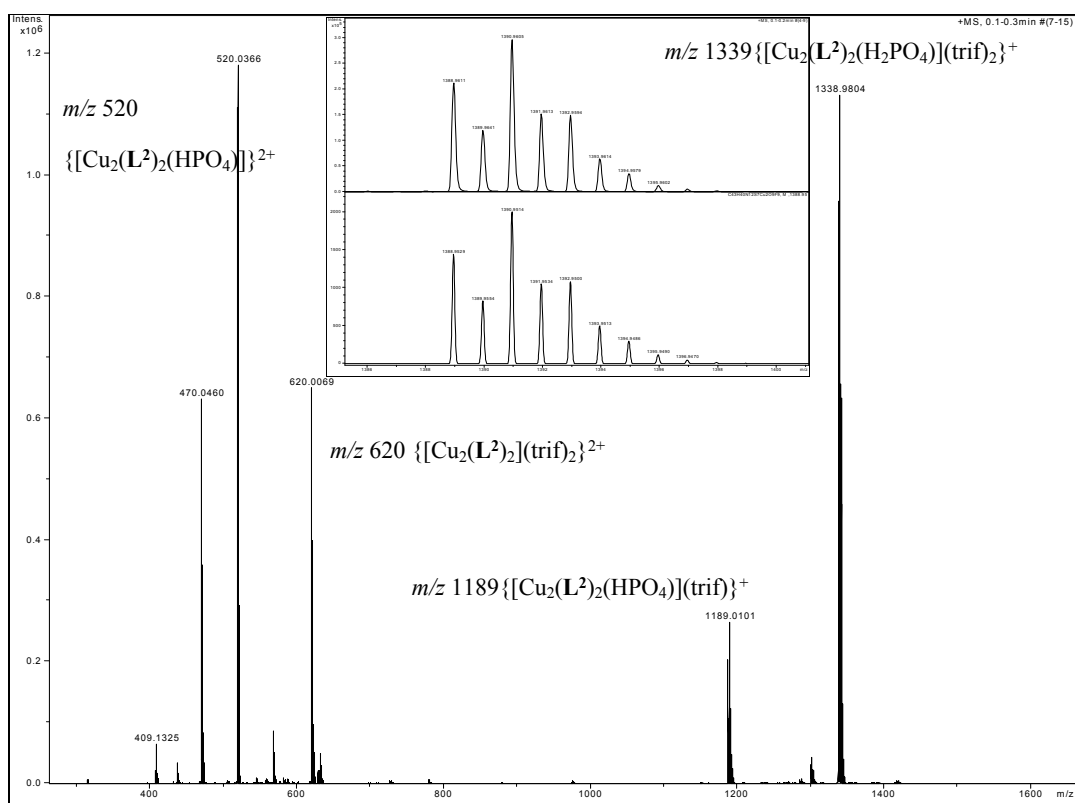


Figure 11. ESI-MS of $[\text{Cu}_2(\text{L}^2)_2(\text{H}_2\text{PO}_4)](\text{trif})_3$ with the obtained isotope pattern (inset top) and calculated (inset bottom) for m/z 1339 $[\text{Cu}_2(\text{L}^2)_2(\text{H}_2\text{PO}_4)](\text{trif})_2^+$.

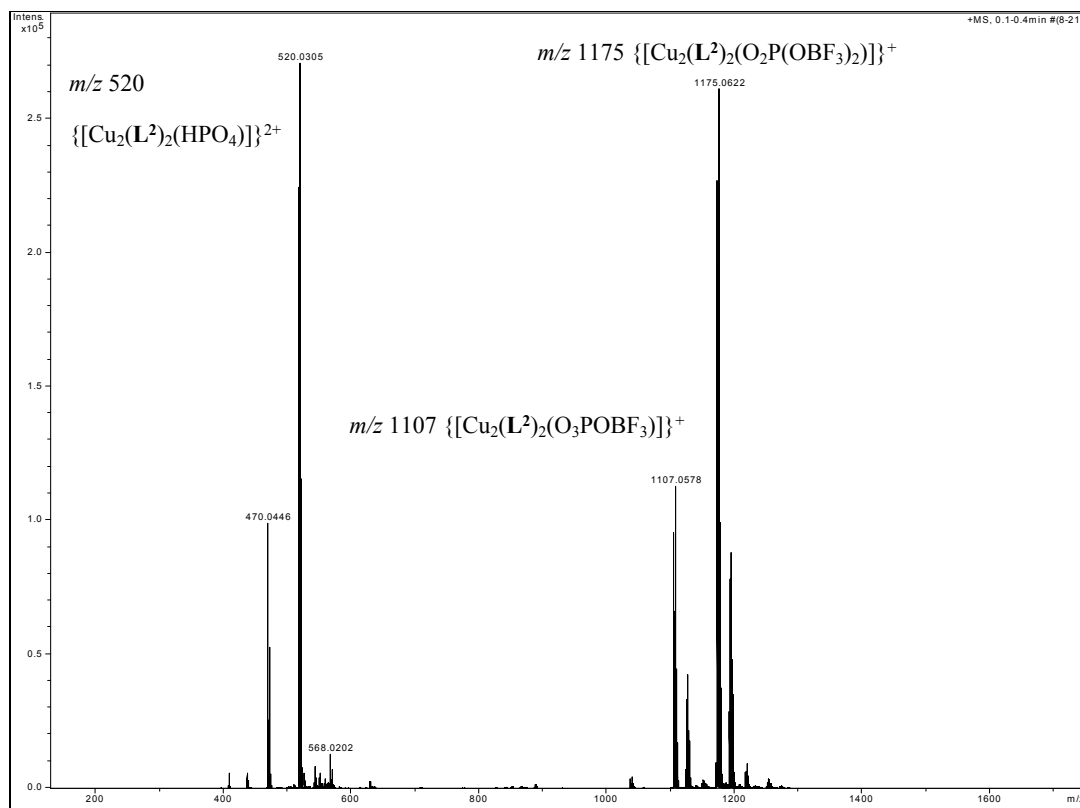


Figure 12. ESI-MS of $[\text{Cu}_2(\text{L}^2)_2(\text{O}_2\text{P}(\text{OBF}_3)_2)](\text{BF}_4)$. Peaks (unlabelled) at m/z 1127 and 1195 correspond to $[\text{Cu}_2(\text{L}^2)_2(\text{HPO}_4)](\text{BF}_4)^+$ and $[\text{Cu}_2(\text{L}^2)_2(\text{HO}_3\text{P}(\text{OBF}_4))](\text{BF}_4)^+$ respectively.

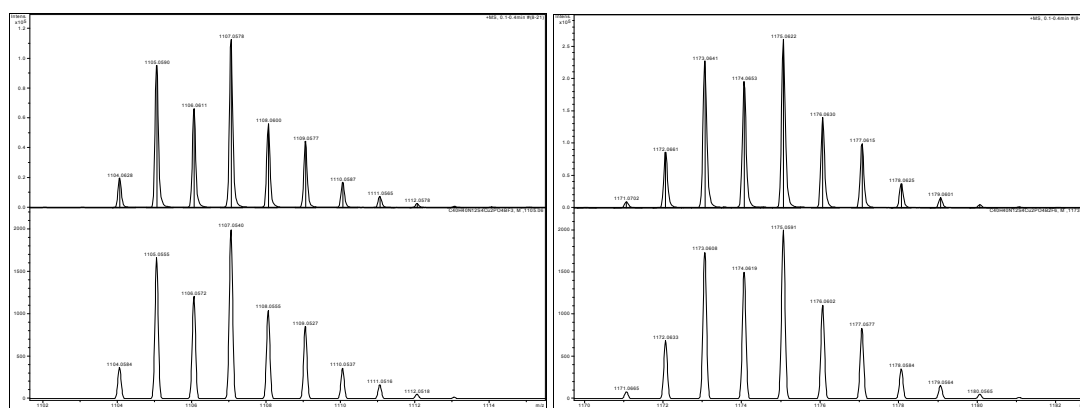


Figure 13. ESI-MS isotope pattern for a) m/z 1107 $\{[\text{Cu}_2(\text{L}^2)_2(\text{O}_3\text{POBF}_3)]\}^+$ (LHS observed top and calculated bottom) and b) m/z 1175 $\{[\text{Cu}_2(\text{L}^2)_2(\text{O}_2\text{P}(\text{OBF}_3)_2)]\}^+$ (RHS observed top and calculated bottom).

Crystallography

Single crystal X-ray diffraction data was collected at 150(2) K on a Bruker D8 Venture diffractometer equipped with a graphite monochromated $\text{Mo}(\text{K}\alpha)$ (or $\text{Cu}(\text{K}\alpha)$ for $\text{Cu}_3[(\text{L}^1)_3(\text{O}_3\text{P}(\text{OBF}_3))](\text{BF}_4)_3$) radiation source and a cold stream of N_2 gas. Solutions were generated by conventional heavy atom Patterson or direct methods and refined by full-matrix least squares on all F^2 data, using SHELXS-97 and SHELXL software respectively.¹ Absorption corrections were applied based on multiple and symmetry-equivalent measurements using SADABS.² For all five species the crystallisations were repeated several times and either a full data set or unit cell collected, each time giving the same cell parameters as those observed for the structures reported.

$[\text{Cu}_2(\text{L}^1)_2](\text{trif})_4$ this crystal structure was treated as standard.

$[\text{Cu}_2(\text{L}^1)_2(\text{H}_2\text{PO}_4)(\text{trif})_3]$ contained both a positionally disordered triflate counter anion and nitromethane solvent molecules. These were modelled over two positions using the *PART* instruction and assigned their own free variable. In most cases *DELU*, *SIMU* and *ISOR* were used to constrain the adp's in the least-squares refinement.

$[\text{Cu}_3(\text{L}^1)_3(\text{O}_3\text{P}(\text{OBF}_3))](\text{BF}_4)_3$ contained two molecules of the trinuclear assembly in the asymmetric unit and disorder that could not be successfully modelled. As a result the diffuse electron density was removed using

the solvent mask facility in Olex2, resulting in voids of 2515 Å³ (629 Å³ or 227 electrons per circular helicate) in the crystal structure.³ This corresponds to one BF₄ anion and 6 MeNO₂ molecules per helicate.

[Cu₂(L¹)₂(H₂PO₄)](trif)₃ contained a positionally disordered triflate counter anion and this was modelled over two positions using the *PART* instruction and assigned its own free variable. In most cases *DELU*, *SIMU* and *ISOR* were used to constrain the adp's of the disordered fragments in the least-squares refinement. Furthermore, the structure contained disorder that could not be successfully modelled and as a result the diffuse electron density was removed using the solvent mask facility in Olex2, resulting in voids of 1176 Å³ which corresponds to 545 electrons.³ This accounts for 5 molecules of DIPE per asymmetric unit.

[Cu₂(L²)₂(O₂P(OBF₃)₂)](BF₄) contained a rotationally disordered tetrafluoroborate counter anion and as a result the fluorine atoms were modelled over two sites using the *PART* instruction. The resulting B-F bond lengths had to be restrained using the *SADI* instruction and the anisotropic thermal parameters had to be restrained using *DELU*, *SIMU* and *ISOR* in the l.s. refinement. The structure also contains a relatively poorly defined water oxygen atom on a special position and as a result the hydrogen atoms were not added.

In the above two structures attempts at growing crystals containing less disorder was tried numerous times, coupled with numerous attempts at modelling the resultant disorder. The solvent mask was only applied once the gross structure had been determined, refined, made anisotropic and hydrogen atoms added. Despite the removal of diffuse electron density the gross molecular connectivity can be established and the structures (and their hosts) are also confirmed by ESI-MS.

Compound	[Cu ₂ (L ¹) ₂](trif) ₄	[Cu ₂ (L ¹) ₂ (H ₂ PO ₄)](trif) ₃	[Cu ₃ (L ¹) ₃ (PO ₄ BF ₃)](BF ₄) ₃
Formula	C ₄₀ H ₃₂ Cu ₂ F ₁₂ N ₁₂ O ₁₂ S ₈	C ₄₀ H ₃₄ Cu ₂ F ₉ N _{13.858} O _{15.743} PS ₇	C ₁₁₄ H ₁₁₄ B ₅ Cu ₆ F ₁₈ N ₄₂ O ₂₀ P ₂ S ₁₂
<i>M</i>	1484.33	1514.22	3616.55
Crystal system	triclinic	triclinic	triclinic
Space group	P -1	P -1	P -1
a (Å)	9.7479(10)	11.358(4)	12.3871(8)
b (Å)	10.8987(11)	16.280(5)	24.199(2)
c (Å)	14.1786(14)	16.681(7)	32.271(4)
α (°)	67.525(3)	99.030(16)	78.661(7)
β (°)	73.066(3)	108.218(16)	85.813(9)
γ (°)	83.669(3)	92.693(12)	78.326(7)
<i>V</i> (Å ³)	1331.6(2)	2878.4(18)	9283.1(15)
<i>Z</i>	1	2	2
ρ _{calc} (Mg cm ⁻³)	1.851	1.7470	1.2937
<i>F</i> (000)	746	1530.0797	3666.8836

Crystal dimensions (mm)	0.15, 0.1, 0.1	0.25, 0.2, 0.1	0.1, 0.1, 0.1
Reflections measured	22989	80975	132190
Range	$2.072 \leq \theta \leq 30.578$	$1.92 \leq \theta \leq 30.69$	$2.56 \leq \theta \leq 68.72$
<i>hkl</i> range indices	$-13 \leq h \leq 13, -15 \leq k \leq 15, -20 \leq l \leq 15$	$-16 \leq h \leq 16, -23 \leq k \leq 23, -23 \leq l \leq 23$	$-14 \leq h \leq 14, -28 \leq k \leq 29, 0 \leq l \leq 38$
N° independent reflections	8122	17674	33538
Reflections with $I > 2\sigma(I)$	5735	11284	23849
R_{int}	0.0692	0.0829	0.1127
Final R_I values	0.0498	0.0744	0.0997
Final $wR(F^2)$ values	0.1146	0.1587	0.2929
Final R_I values (all data)	0.0846	0.1299	0.1337
Final $wR(F^2)$ values (all data)	0.1288	0.1923	0.3299
GOF	1.034	1.0732	1.2535
Refined parameters	388	886	2014
Restraints	0	48	121
Largest peak and hole ($e \text{ \AA}^{-3}$)	0.942, -0.779	1.6254, -2.0257	1.8506, -1.6788
CCDC Number	1849997	1849998	1849999

Compound	$[\text{Cu}_2(\text{L}^2)_2(\text{H}_2\text{PO}_4)](\text{trif})_3$	$[\text{Cu}_2(\text{L}^2)_2(\text{O}_2\text{P}(\text{OBF}_3)_2)](\text{BF}_4)$
Formula	$\text{C}_{43}\text{H}_{42}\text{Cu}_2\text{F}_9\text{N}_{12}\text{O}_{13}\text{PS}_7$	$\text{C}_{40}\text{H}_{40}\text{B}_4\text{Cu}_2\text{F}_{14}\text{N}_{12}\text{O}_{4.5}\text{PS}_4$
<i>M</i>	1488.40	1356.37
Crystal system	triclinic	tetragonal
Space group	P -1	I -4 2 d
<i>a</i> (Å)	14.629(5)	22.4423(11)
<i>b</i> (Å)	15.453(6)	22.4423(11)
<i>c</i> (Å)	17.397(6)	20.6438(10)
α (°)	93.102(18)	90
β (°)	103.018(14)	90
γ (°)	95.287(15)	90
<i>V</i> (Å ³)	3804(2)	10397.4(9)
<i>Z</i>	2	8

ρ_{calc} (Mg cm ⁻³)	1.2994	1.733
$F(000)$	1512.1201	5464
Crystal dimensions (mm)	0.2, 0.1, 0.1	0.25, 0.2, 0.2
Reflections measured	114289	27338
Range	$1.85 \leq \theta \leq 30.44$	$2.26 \leq \theta \leq 30.55$
hkl range indices	$-20 \leq h \leq 20, -21 \leq k \leq 21, -24 \leq l \leq 24$	$-32 \leq h \leq 32, -22 \leq k \leq 22, -29 \leq l \leq 29$
N° independent reflections	22936	7906
Reflections with $I > 2\sigma(I)$	13386	4758
R_{int}	0.0777	0.0675
Final R_i values	0.0762	0.0804
Final $wR(F^2)$ values	0.1957	0.2190
Final R_i values (all data)	0.1334	0.1445
Final $wR(F^2)$ values (all data)	0.2317	0.2635
GOF	1.1000	1.026
Refined parameters	858	384
Restraints	87	62
Largest peak and hole (e Å ⁻³)	2.6065, -2.0660	1.657, -1.360
CCDC Number	1850000	1850001

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3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* (2009). **42**, 339-341.