Supporting Information for:

Mutual Stabilisation between $M^{II}_4L_6$ Tetrahedra and $M^{II}X_4^{2-}$ Metallate Guests

Imogen A. Riddell,^{a,b} Tanya K. Ronson,^a Jonathan R. Nitschke ^{a*}

^a University of Cambridge, Department of Chemistry, Lensfield Road, Cambridge, CB2 1EW, UK.
^bCurrent Address: Massachusetts Institute of Technology, Department of Chemistry, 77 Massachusetts Avenue, Cambridge, MA 02139, US.

**E-mail:* jrn34@cam.ac.uk

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1. Experimental

Unless otherwise specified, all starting materials were purchased from commercial sources and used as supplied. 6,6'-diformyl-3,3'-bipyridine was synthesised as previously reported.^{S1} NMR spectra were recorded on a Bruker DRX-400, Bruker Avance 500 Cryo and Bruker TXI 700 Cryo. ¹H Chemical shifts (δ) are reported in parts per million (ppm) and are reported relative to the solvent residual peak. Low resolution electrospray ionization mass spectra (ESI-MS) were obtained on a Micromass Quattro LC (cone voltage: 3-6 eV; desolvation temp. 313 K; ionisation temp. 313 K), infused from a Harvard Syringe Pump at a rate of 10 μ L per minute. High resolution mass spectra acquired using a Thermofisher LTQ Orbitrap XL (Capillary temp 303 K; Tube Lens 40 V).

1.1. Preparation of cobalt (II) species

Preparation of cobalt triflimide and Co-DL as previously reported.^{S2}

1.1.1. Preparation of [CoBr_4]^{2-} \subset Co-1: KBr (0.6 mg, 5.0 µmol) was added to a J-Young NMR tube containing Co-**DL** (2.0 mg 6,6'-diformyl-3,3'-bipyridine, 9.4 µmol). The tube was sealed and the solution was purified of dioxygen by three vacuum/nitrogen fill cycles. The solution was then sonicated and heated at 323 K for 24 hours. Suitable X-ray quality crystals of $[CoBr_4]^{2-} \subset Co-1$ were grown by slow diffusion of diethyl ether into an acetonitrile solution containing BF₄⁻ and NTf₂⁻ anions. ¹H NMR (400 MHz, 298 K, CD₃CN): $\delta = 233.4$ (s, 12H, imine), 81.9 (br. s, 12H, 2,2'-bipyridine), 69.5 (s, 12H, 5,5'-bipyridine), 16.3 (s, 12H, 4,4'-bipyridine), 10.5 (s, 36H, methyl), 10.0 (s, 24H, 3-aniline), -24.6 (s, 24H, 2-aniline); ESI-MS: m/z: ({ $[CoBr_4]^{2-} \subset Co-1$ }⁶⁺) = 492.9, ({ $[CoBr_4]^{2-} \subset Co-1 + NTf_2^{-}$)⁵⁺) = 647.4, ({ $[CoBr_4]^{2-} \subset Co-1 + 2NTf_2^{-}$)⁴⁺) = 879.3, ({ $[CoBr_4]^{2-} \subset Co-1 + 3NTf_2^{-}$)³⁺) = 1265.7.



Figure S1: ¹H NMR spectrum (400 MHz, 298 K, CD₃CN) of $[CoBr_4]^{2-} \subset Co-1$.





UV-Vis analysis: Samples were prepared at 22 mM concentration and analysed at 0.5 mM metal ion concentrations, using a 1 cm pathlength cuvette. The absorbance of the $[CoBr_4]^{2-}$ sample was divided by five to normalise the data relative to $[CoBr_4]^{2-} \subset Co-1$ where, ideally, only one in five metal centres would be contribute to the $[CoBr_4]^{2-}$ absorbance band, the other four constitute the Co_4L_6 tetrahedron.



Figure S3: UV-vis spectrum showing absorbance bands within the 550-800 nm wavelength range for acetonitrile solutions of $[Et_4N]_2[CoBr_4]^2$ (black), $[CoBr_4]^2 \subset Co-1$ (blue) and $SbF_6 \subset Co-1$ (red). Absorbance normalised for the number of metal centres.

1.1.2. Preparation of $[Co(NCO)_4]^{2-} \subset Co-1$: KOCN (0.3 mg, 3.7 µmol) was added to a J-Young NMR tube containing Co-DL (2.0 mg 6,6'-diformyl-3,3'-bipyridine, 9.4 µmol). The tube was sealed and the solution was purified of dioxygen by three vacuum/nitrogen fill cycles. The solution was then sonicated and heated at 323 K for 24 hours. ¹H NMR (400 MHz, 298 K, CD₃CN): $\delta = 240.7$ (s, 12H, imine), 83.7 (br. s, 12H, 2,2'-bipyridine), 68.5 (s, 12H, 5,5'-bipyridine), 15.6 (s, 12H, 4,4'-bipyridine), 10.3 (s, 36H, methyl), 9.9 (s, 24H, 3-aniline), -24.3 (s, 24H, 2-aniline); ESI-MS: m/z: ({[Co(NCO)_4]^2- \subset Co-1 + NTf₂-}⁵⁺) = 617.0, ({[Co(NCO)_4]^2- \subset Co-1 + 2NTf₂-}⁴⁺) = 841.2, ({[Co(NCO)_4]^2- \subset Co-1 + 3NTf₂-}³⁺) = 1215.0.



Figure S4: ¹H NMR spectrum (400 MHz, 298 K, CD₃CN) of [Co(NCO)₄]^{2−}⊂ Co-1.



Figure S5: ESI-MS of complex $[Co(NCO)_4]^{2-} \subset Co-1$.

1.1.3. Preparation of [CoCl₄]²⁻ \subset Co-1: NaCl (0.6 mg, 10.3 µmol) was added to a J-Young NMR tube containing Co-DL (2.0 mg 6,6'-diformyl-3,3'-bipyridine, 9.4 µmol). The tube was sealed and the solution was purified of dioxygen by three vacuum/nitrogen fill cycles. The solution was then sonicated and heated at 323 K for 24 hours. ¹H NMR (400 MHz, 298 K, CD₃CN): complex spectra recorded consistent with formation of a mixture of species, see Figure S1, major peaks assigned to complex [CoCl₄]²⁻ \subset Co-1 display very similar chemical shifts to those of other Co₄L₆ tetrahedra especially [CoBr₄]²⁻ \subset Co-1.



Figure S6:¹H NMR spectrum (400 MHz, 298 K, CD₃CN) of the reaction mixture generating by heating NaCl with Co-**DL**, major peaks assigned through their similar chemical shifts to the related $[CoBr_4]^2$, SbF₆⁻ and $[Co(OCN)_4]^2$ - inclusion complexes.

A mixture was also observed by mass spectrometry however peaks attributed to the formation of the desired divalent anion encapsulation complex were present. ESI-MS: m/z: ({[CoCl₄]²⁻ \subset Co-1}⁶⁺) =

462.9, $(\{[CoCl_4]^{2-} \subset Co-1 + NTf_2^{-}\}^{5+}) = 611.6$, $(\{[CoCl_4]^{2-} \subset Co-1 + 2NTf_2^{-}\}^{4+}) = 834.8$, $(\{[CoCl_4]^{2-} \subset Co-1 + 3NTf_2^{-}\}^{3+}) = 1206.3$.



Figure S7: ESI-MS of $[CoCl_4]^{2-} \subset Co-1$.

1.1.4. Preparation of SbF₆[−] ⊂ **Co-1**: NaSbF₆ (2.0 mg, 7.4 μmol) was added to a J-Young NMR tube containing Co-**DL** (3.0 mg 6,6'-diformyl-3,3'-bipyridine, 13.7 μmol). The tube was sealed and the solution was purified of dioxygen by three vacuum/nitrogen fill cycles. The solution was then sonicated and heated at 363 K for 24 hours. Suitable crystals for X-ray diffraction were grown by slow diffusion of diethyl ether into an acetonitrile solution of SbF₆[−] ⊂ Co-**1** containing NTf₂[−], SbF₆[−] and PF₆[−] anions. ¹H NMR (400 MHz, 298 K, CD₃CN): δ = 240.0 (s, 12H, imine), 83.6 (br. s, 12H, 2,2'-bipyridine), 68.2 (s, 12H, 5,5'-bipyridine), 15.4 (s, 12H, 4,4'-bipyridine), 10.3 (s, 36H, methyl), 9.9 (s, 24H, 3-aniline), -24.4 (s, 24H, 2-aniline); ¹⁹F NMR (376 MHz, 298 K, CD₃CN): δ = -79.0 (s, NTf₂[−]), -117.0 (br. m, SbF₆[−]), -219.0 (br. m, SbF₆[−] ⊂ Co-**1**); ESI-MS: *m/z*: ({[Co-**1**](NTf₂[−])(SbF₆[−])}⁶⁺) = 515.7, ({[Co-**1**](SbF₆[−])}⁵⁺) = 656.6, ({[Co-**1**](NTf₂[−])(SbF₆[−])}⁵⁺) = 674.8, ({[Co-**1**](SbF₆[−])}⁴⁺) = 879.8, ({[Co-**1**](NTf₂[−])(SbF₆[−])}⁵⁺) = 674.8, ({[Co-**1**](NTf₂[−])₃(SbF₆[−])}⁴⁺) = 913.5, ({[Co-**1**](NTf₂[−])(SbF₆[−])}³⁺) = 1266.4, ({[Co-**1**](NTf₂[−])₂(SbF₆[−])}³⁺) = 1281.9, ({[Co-**1**](NTf₂[−])₃(SbF₆[−])2³⁺) = 1296.3, ({[Co-**1**](NTf₂[−])₄(SbF₆[−])³⁺) = 1311.6.



Figure S8: ¹H NMR spectrum (400 MHz, 298 K, CD₃CN) of $SbF_6^- \subset$ Co-1. Even after prolonged heating, 363 K for 7 days no alternative architectures were observed to form in the presence of SbF_6^- .



Figure S9: ESI-MS of $SbF_6^- \subset$ Co-1. Each charge state is represented by a series of peaks corresponding to the Co-1 complex with different numbers of NTf_2^- and SbF_6^- counteranions. At least one SbF_6^- anion is associated with each m/z peak.

1.2. Zinc (II) species

1.2.1 Complex [ZnCl_4]^{2-} \subset Zn-1: NaCl (0.2 mg, 3.4 µmol) was added to a J-Young NMR tube containing Zn-**DL** (4.0 mg 6,6'-diformyl-3,3'-bipyridine, 18.9 µmol). The tube was sealed and the solution was sonicated then heated at 323 K for 24 hours. ¹H NMR (500 MHz, 298 K, CD₃CN): δ =8.62 (s, 12H, imine), 8.35 (d, J = 2.1 Hz, 12H, 2,2'-bipyridine), 8.14 (dd, J = 2.2, 8.1 Hz, 12H, 4,4'-bipyridine), 8.07 (d, J = 8.1 Hz, 12H, 5,5'-bipyridine), 7.14 (d, J = 10.0 Hz, 24H, 3-aniline), 6.40 (d, J = 8.9 Hz, 24H, 2-aniline), 2.37 (s, 36H, methyl); ¹³C NMR (126 MHz, 298 K, CD₃CN): $\delta = 163.4$, 149.8, 147.2, 144.9, 143.8, 140.6, 131.1, 129.9, 122.6, 122.2, 21.1; ESI-MS: m/z: ({[ZnCl₄]²⁻ \subset Zn-1 + NTf₂-}⁵⁺) = 617.8, ({[ZnCl₄]²⁻ \subset Zn-1 + 2NTf₂-}⁴⁺) = 842.7, ({[ZnCl₄]²⁻ \subset Zn-1 + 3NTf₂-}³⁺) = 1217.2.



Figure S10: ESI-MS of $[ZnCl_4]^{2-} \subset Zn-1$.

1.2.2 Complex $[ZnBr_4]^{2-} \subset Zn-1$: KBr (0.7 mg, 5.9 µmol) was added to a J-Young NMR tube containing Zn-DL (4.0 mg 6,6'-diformyl-3,3'-bipyridine, 18.9 µmol). The tube was sealed and the solution was sonicated then heated at 323 K for 24 hours. ¹H NMR (500 MHz, 298 K, CD₃CN): $\delta = 8.65$ (s, 12H, imine), 8.40 (d, J = 1.0 Hz, 12H, 2,2'-bipyridine), 8.15 (dd, J = 2.0, 8.0 Hz, 12H, 4,4'-bipyridine), 8.09 (d, J = 8.1 Hz, 12H, 5,5'-bipyridine), 7.13 (d, J = 8.4 Hz, 24H, 3-aniline), 6.43 (d, J = 8.4 Hz, 24H, 2-aniline), 2.33 (s, 36H, methyl); ¹³C NMR (126 MHz, 298 K, CD₃CN): $\delta = 163.2$,

149.9, 147.1, 144.9, 143.8, 140.6, 140.6, 131.1, 129.8, 122.1, 21.0; ESI-MS: m/z: ({[ZnBr₄]²⁻ \subset Zn-1})⁶⁺) = 498.1, ({[ZnBr₄]²⁻ \subset Zn-1 + NTf₂-}⁵⁺)= 653.8, ({[ZnBr₄]²⁻ \subset Zn-1 + 2NTf₂-}⁴⁺) = 887.5, ({[ZnBr₄]²⁻ \subset Zn-1 + 3NTf₂-}³⁺) = 1276.2.



Figure S11: ESI-MS of $[ZnBr_4]^2 \subset Zn-1$.

1.2.3 Complex [ZnI₄]²⁻ \subset Zn-1: KI (1.0 mg, 6.1 µmol) was added to a J-Young NMR tube containing Zn-DL (4.0 mg 6,6'-diformyl-3,3'-bipyridine, 18.9 µmol). The tube was sealed and was sonicated then heated at 323 K for 24 hours. ¹H NMR (500 MHz, 298 K, CD₃CN): \delta = 8.68 (s, 12H, imine), 8.59 (d, *J* **= 2.2 Hz, 12H, 2,2'-bipyridine), 8.18 (dd,** *J* **= 2.2, 8.0 Hz, 12H, 4,4'-bipyridine), 8.11 (d,** *J* **= 7.9Hz, 12H, 5,5'-bipyridine), 7.13 (d,** *J* **= 8.9 Hz, 24H, 3-aniline), 6.45 (d,** *J* **= 8.1 Hz, 24H, 2-aniline), 2.34 (s, 36H, methyl), in addition many small peaks were observed in the baseline; ¹³C NMR (126 MHz, 298 K, CD₃CN): \delta = 163.2, 150.2, 147.2, 145.1, 144.4, 140.6, 140.5, 131.2, 130.0, 122.6, 21.1; ESI-MS:** *m/z***: ({[ZnI₄]²⁻ \subset Zn-1 }⁶⁺) = 529.5, ({[ZnI₄]²⁻ \subset Zn-1 + NTf₂⁻)⁵⁺) = 691.3, ({[ZnI₄]²⁻ \subset Zn-1 + 2NTf₂⁻)⁴⁺)= 934.2, ({[ZnI₄]²⁻ \subset Zn-1 + 3NTf₂⁻)³⁺) = 1338.8.**



Figure S12: ESI-MS of $[ZnI_4]^2 \subset Zn-1$.

1.2.4 Complex $[Zn(NCO)_4]^{2-} \subset Zn-1$: KOCN (0.4 mg, 4.4 µmol) was added to a J-Young NMR tube containing Zn-DL (4.0 mg 6,6'-diformyl-3,3'-bipyridine, 18.9 µmol). The tube was sealed and was sonicated then heated at 323 K for 24 hours. ¹H NMR (500 MHz, 298 K, CD₃CN): δ =8.73 (s, 12H, imine), 8.24 (dd, J = 2.0, 8.0 Hz, 12H, 4,4'-bipyridine), 8.15 (d, J = 8.2 Hz, 12H, 5,5'-bipyridine), 7.90 (d, J = 1.9Hz, 12H, 2,2'-bipyridine), 7.13 (d, J = 7.9 Hz, 24H, 3-aniline), 6.51 (d, J = 7.9 Hz, 24H, 2-aniline), 2.33 (s, 36H, methyl); ¹³C NMR (126 MHz, 298 K, CD₃CN): δ = 163.3, 148.2, 147.4, 144.9, 143.9, 140.9, 140.0, 131.2, 130.5, 122.8, 21.0; ESI-MS: m/z: ({[Zn(OCN)₄]²⁻ \subset Zn-1 + NTf₂⁻}⁵⁺) = 623.6, ({[Zn(OCN)₄]²⁻ \subset Zn-1 + 2NTf₂⁻}³⁺) = 1225.7.



Figure S13: ESI-MS of $[Zn(NCO)_4]^2 \subset Zn-1$. Significant fragmentation was observed in the gas phase with this sample, however, peaks corresponding to the desired complex were also observed.

1.2.5 Complex [Zn(NCS)₄]²⁻ \subset Zn-1: KSCN (0.4 mg, 4.1 µmol) was added to a J-Young NMR tube containing Zn-DL (2.0 mg 6,6'-diformyl-3,3'-bipyridine, 9.4 µmol) in CD₃CN (0.6 mL). The tube was sealed and was sonicated then heated at 343 K for 24 hours. ¹H NMR (500 MHz, 298 K, CD₃CN): \delta =8.69 (s, 12H, imine), 8.36 (dd, J = 2.1, 8.0 Hz, 12H, 4,4'-bipyridine), 8.15 (d, J = 8.0 Hz, 12H, 5,5'-bipyridine), 8.0 (d, J = 2.0Hz, 12H, 2,2'-bipyridine), 7.14 (d, J = 8.1 Hz, 24H, 3-aniline), 6.43 (d, J = 8.4 Hz, 24H, 2-aniline), 2.34 (s, 36H, methyl); ¹³C NMR (126 MHz, 298 K, CD₃CN): \delta = 163.4, 147.7, 147.4, 144.7, 144.6, 140.8, 139.7, 131.5, 131.1, 122.7, 21.0; ESI-MS: m/z: ({[Zn(NCS)₄]²⁻ \subset Zn-1 + 3NTf₂⁻}³⁺) = 1247.0, ({[Zn(NCS)₄]²⁻ \subset Zn-1 + 2NTf₂⁻}³⁺) = 865.8, ({[Zn(NCS)₄]²⁻ \subset Zn-1 + NTf₂⁻}³⁺) = 636.6.



Figure S14: ESI-MS of $[Zn(NCS)_4]^2 \subset Zn-1$.

1.2.6 Complex SbF₆⁻ \subset **Zn-1:** Zn(NTf₂)₂·xH₂O (7.87 mg, 0.01 mmol), 6,6'-diformyl-3,3'-bipyridine (4.0 mg, 18.9 µmol) and *p*-toluidine (4.0 mg, 0.04 mmol) were loaded into a J-Young NMR tube and dissolved in CD₃CN (0.6 mL). The Zn-**DL** solution was heated overnight, then allowed to cool before addition of KSbF₆ (3.0 mg, 0.01 mmol). The reaction was then heated at 343 K overnight. Addition of diethyl ether to the reaction mixture yielded the final product as a pale yellow powder. ¹H NMR spectra indicated the same species were present before and after precipitation with ether. ¹H NMR (500 MHz, 298 K, CD₃CN): δ = 8.72 (s, 12H, imine), 8.25 (dd, *J* = 1.9, 8.0 Hz, 12H, 4,4'-bipyridine), 8.19 (d, *J* = 8.1 Hz, 12H, 5,5'-bipyridine), 7.71 (s, 12H, 2,2'-bipyridine), 7.15 (d, *J* = 8.8 Hz, 24H, 3-aniline), 6.49 (d, *J* = 8.8 Hz, 24H, 2-aniline), 2.35 (s, 36H, methyl), and additional minor peaks consistent with the Zn₁₀L₁₅ complex also observed as a minor species by ESI-MS (Figure S15); ¹³C NMR (126 MHz, 298 K, CD₃CN): δ = 163.3, 148.4, 147.8, 144.7, 143.7, 141.0, 139.5, 131.2, 130.6, 122.8, 21.1; ¹⁹F NMR (376 MHz, 298 K, CD₃CN): δ = -80.1 (s, NTf₂⁻), -120.0 (br. m, free and encapsulated SbF₆⁻ multiplets overlapping); ESI-MS: *m*/*z*: ({[Zn-1](NTf₂⁻)(SbF₆⁻)₂}⁵⁺) = 671.3, ({[Zn-1](NTf₂⁻)(SbF₆⁻)₃}⁵⁺) = 680.2, ({[Zn-1](SbF₆⁻)₄⁴⁺) = 886.7, ({[Zn-1](NTf₂⁻)(SbF₆⁻)₃⁴⁺) = 680.2, ({[Zn-1](SbF₆⁻)₄⁴⁺) = 886.7, ({[Zn-1](NTf₂⁻)(SbF₆⁻)₄⁴⁺) = 680.2, ({[Zn-1](SbF₆⁻)₄⁴⁺) = 886.7, ({[Zn-1](NTf₂⁻)

898.0, $(\{[Zn-1](NTf_2^{-})_2(SbF_6^{-})_2\}^{4+}) = 908.7$, $(\{[Zn-1](NTf_2^{-})_3(SbF_6^{-})\}^{4+}) = 920.0$, $(\{[Zn-1](NTf_2^{-})_3(SbF_6^{-})_3\}^{3+}) = 1275.5$, $(\{[Zn-1](NTf_2^{-})_2(SbF_6^{-})_3\}^{3+}) = 1290.5$, $(\{[Zn-1](NTf_2^{-})_3(SbF_6^{-})_2\}^{3+}) = 1304.8$, $(\{[Zn-1](NTf_2^{-})_4(SbF_6^{-})\}^{3+}) = 1320.3$.



Figure S15: ESI-MS of $SbF_6^- \subset Zn-1$. Each charge state is represented by a series of peaks corresponding to the Zn-1 complex with different numbers of NTf_2^- and SbF_6^- counteranions. At least one SbF_6^- anion is associated with each m/z peak. In addition, peaks labelled in blue correspond to a minor $Zn_{10}L_{15}$ complex, Zn-2, with SbF_6^- peripheral template anions and a centrally bound F⁻ anion.^{S3} Corresponding peaks are observed in the ¹H NMR spectrum of the mixture. Formation of Zn-2 under these reaction conditions highlights the limited templation ability of the singly charged anions for the Zn₄L₆ structural type.

1.2.7 Complex Br⁻ \subset **Zn-2(ClO₄)**₅: 6,6'-Diformyl-3,3'-bipyridine (4.0 mg, 18.9 µmol), *p*-toluidine (4.04 mg, 0.04 mmol), and zinc(II) perchlorate hexahydrate (4.8 mg, 0.01 mmol) were added to a J-Young NMR tube with CD₃CN (0.6 mL). The NMR tube was subjected to three evacuation/nitrogen fill cycles. The reaction heated at 363 K for 24 hours then allowed to cool. KBr (0.58 mg, 0.01 mmol) was added and the reaction mixture was then heated at 363 K for a further 24 hours before the sample was precipitated with diethyl ether. The yellow microcrystalline powder displayed the same ¹H resonances before and after precipitation. ¹H NMR (700 MHz, 298 K, CD₃CN): $\delta = 10.75$ (dd, J = 1.9, 8.6 Hz, 10H, 4,4'-bipyridine), 9.45 (s, 10H, imine), 9.22 (d, J = 9.05 Hz, 10H, 5,5'-bipyridine), 8.57 (s, 10H, 2,2'-bipyridine), 8.46 (s, 10H, imine), 8.09 (dd, J = 2.13, 7.78 Hz, 10H, 4,4'-bipyridine), 8.06 (d, J = 1.4 Hz, 10H, 2,2'-bipyridine), 7.48 (d, J = 7.4 Hz, 10H, 5,5'-bipyridine), 7.33 (d, J = 1.9 Hz, 10H, 2,2'-bipyridine), 7.17 (d, J = 8.7 Hz, 20H, 2-aniline), 7.04 (d, J = 9.15 Hz, 20H, 3-aniline), 6.84 (d, J = 7.8 Hz, 20H, 3-aniline), 6.71 (d, J = 7.8 Hz, 20H, 3-aniline), 2.54 (s, 30H, methyl), 2.25 (s, 30H, methyl),

2.23 (s, 30H, methyl); ¹³C NMR (126 MHz, 298 K, CD₃CN): $\delta = 162.5$, 160.9, 160.5, 148.1, 148.1, 148.0, 147.0, 147.0, 146.6, 145.2, 144.9, 142.6, 142.5, 142.3, 142.2, 141.6, 141.0, 140.5, 139.1, 139.0, 138.4, 131.4, 131.2, 130.9, 130.7, 130.5, 129.7, 123.3, 123.2, 122.5, 21.7, 21.0, 21.0; ESI-MS: *m/z*: ({[Br⁻ \subset Zn-2] + 9ClO₄-}¹⁰⁺) = 748.4, ({[Br⁻ \subset Zn-2] + 10ClO₄-}⁹⁺) = 842.8, ({[Br⁻ \subset Zn-2] + 11ClO₄-}⁸⁺) = 960.5, ({[Br⁻ \subset Zn-2] + 12ClO₄-}⁷⁺) = 1111.9, ({[Br⁻ \subset Zn-2] + 13ClO₄-}⁶⁺) = 1313.8, ({[Br⁻ \subset Zn-2] + 14ClO₄-}⁵⁺) = 1596.2.



Figure S16: Aromatic region of the ¹H NMR spectrum (700 MHz, 298 K, CD₃CN) of Br⁻ \subset Zn-2. Peaks highlighted with red squares correspond to excess *p*-toluidine. If chloride was not rigorously excluded from the reaction mixture the analogous Cl⁻ bound Zn-2 complex was observed alongside Br⁻ \subset Zn-2.



Figure S17: Portion of the high resolution ESI-mass spectrum confirming formation of a mixture of the desired host-guest complex [$Br^- \subset Zn-2$] and the corresponding chloride-bound adduct.

1.2.8 Complex Cl⁻ \subset **Zn-2(ClO₄)₅:** Synthesised as previously reported.^{S4} Suitable X-ray quality single crystals were grown through slow diffusion of diethyl ether into an acetonitrile solution.

Overall the ¹H NMR spectra of the chloride and bromide bound adducts of the $Zn_{10}L_{15}$ complex are very similar. Differences in the chemical shifts of resonances correspond to differences in the electronegativity of the centrally bound halide anion as previously reported.^{S1}



Figure S18: ¹H NMR spectra (400 MHz, 298 K, CD₃CN); a) Cl⁻ \subset Zn-2(ClO₄)₅ and b) Br⁻ \subset Zn-2(ClO₄)₅. Overall the solution and solid state data, reported below, for the two complexes are very similar. Differences in the chemical shifts of the complex resonances correspond to the electronegativity of the centrally bound anion.

2. Single Crystal X-ray Diffraction

Data were collected with an Oxford Gemini Ultra employing confocal mirror monochromated Cu-K_{α} radiation generated from a sealed tube (1.5418 Å) with ω and ψ scans at 120(2) K^{S5} or at Beamline I19 of Diamond Light Source employing silicon double crystal monochromated synchrotron radiation (0.6889 Å) with ω scans at 100(2) K^{S6}. Data integration and reduction were undertaken with CrysAlisPro^{S5} or with SAINT and XPREP^{S7} following treatment with ECLIPSE.^{S8} Gaussian absorption corrections were applied using CryAlisPro^{S5} and multi-scan empirical absorption corrections were applied using SADABS^{S9}. Subsequent computations were carried out using the WinGX-32 graphical user interface^{S10}. The structures were solved using SUPERFLIP^{S11} then refined and extended with SHELXL-2013^{S12}. Carbon-bound hydrogen atoms were included in idealised positions and refined using a riding model. Disorder was modelled using standard crystallographic methods including constraints, restraints and rigid bodies where necessary. Crystallographic data along with specific details pertaining to the refinement follow (CCDC 1047195-1047198).

2.1. Crystal Data for $[CoBr_4]^{2-} \subset Co-1$

 $[CoBr_4]^{2-} \subset Co-1.6BF_4$: Formula $C_{156}H_{132}B_6Br_4Co_5F_{24}N_{24}$, *M* 3478.01, cubic, space group $F4_132(\#210)$, *a* 34.5284(4), *b* 34.5284(4), *c* 34.5284(4) Å, *V* 41165.1(8) Å³, D_c 1.122 g cm⁻³, *Z* 8, crystal size 0.15 by 0.15 by 0.15 mm, colour orange, habit cube, temperature 120(2) Kelvin,

 $\lambda(\text{CuK}\alpha) \ 1.54180 \ \text{\AA}, \ \mu(\text{CuK}\alpha) \ 4.560 \ \text{mm}^{-1}, \ T(\text{CRYSALISPRO})_{\text{min,max}} \ 0.71520, \ 1.00000, \ 2\theta_{\text{max}} \ 100.86, \ hkl \ \text{range} \ -34 \ 34, \ -26 \ 33, \ -34 \ 23, \ N \ 13531, \ N_{\text{ind}} \ 1804(R_{\text{merge}} \ 0.0326), \ N_{\text{obs}} \ 1413(\text{I} > 2\sigma(\text{I})), \ N_{\text{var}} \ 117, \ \text{residuals}^* \ R1(F) \ 0.0693, \ wR2(F^2) \ 0.1940, \ \text{GoF}(\text{all}) \ 1.022, \ \Delta\rho_{\text{min,max}} \ -0.324, \ 0.522 \ \text{e}^{-} \ \text{\AA}^{-3}. \ ^*R1 = \Sigma ||F_0| \ - |F_c||/\Sigma|F_0| \ \text{for} \ F_0 > 2\sigma(F_0); \ wR2 = (\Sigma w(F_0^2 - F_c^2)^2/\Sigma(wF_c^2)^2)^{1/2} \ \text{all reflections}, \ w=1/[\sigma^2(F_0^2)+(0.1474P)^2+0.0000P] \ \text{where} \ P=(F_0^2+2F_c^2)/3$

Specific refinement details:

The crystals were very susceptible to solvent loss and rapid (<10 seconds) handling prior to flashcooling in the cryostream was required to collect data. Despite these measures and the use of a highintensity laboratory source the crystals were weakly diffracting and no reflections were observed at better than 1 Å resolution. The tetrahedral cage shows a high degree of crystallographic symmetry with 1/12 of the tetrahedron in the asymmetric unit. There is a significant amount of thermal motion/dynamic disorder in the extremities of the molecule and the thermal parameters of the toluidine groups are larger than ideal resulting in a high non-solvent carbon U_{iso} min/max ratio. The anions and solvent within the lattice were significantly disordered and despite numerous attempts at modelling, including with rigid bodies no satisfactory model for the electron-density associated with them could be found and the SQUEEZE^{S13} function of PLATON^{S14} was employed. The structure was refined as a racemic twin with BASF of 0.53102; the Flack parameter refined to 0.53(2).

2.2. Crystal Data for $SbF_6^- \subset Co-1$

SbF₆⁻ ⊂ **Co-1**·**2SbF**₆·**5PF**₆ Formula C₁₅₆H₁₃₂Co₄F₄₈N₂₄P₅Sb₃, *M* 4014.47, monoclinic, space group C2/c(#15), *a* 43.7451(7), *b* 25.1150(4), *c* 39.7763(10) Å, β100.245(2), *V* 43003.8(15) Å³, *D*_c 1.240 g cm⁻³, *Z* 8, crystal size 0.52 by 0.47 by 0.29 mm, colour orange, habit prism, temperature 120(2) Kelvin, λ(CuKα) 1.54180 Å, μ(CuKα) 6.412 mm⁻¹, *T*(SADABS)_{min,max} 0.5025, 0.7488, 2θ_{max} 89.44, *hkl* range -38 39, -22 22, -34 36, *N* 53033, *N*_{ind} 16916(*R*_{merge} 0.0520), *N*_{obs} 13176(I > 2σ(I)), *N*_{var} 1592, residuals^{*} *R*1(*F*) 0.1016, *wR*2(*F*²) 0.3025, GoF(all) 1.103, Δρ_{min,max} -0.680, 0.826 e⁻ Å⁻³.

*
$$R1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$$
 for $F_0 > 2\sigma(F_0)$; $wR2 = (\Sigma w(F_0^2 - F_c^2)^2 / \Sigma (wF_c^2)^2)^{1/2}$ all reflections,
w=1/[$\sigma^2(F_0^2)$ +(0.1958P)²+214.7197P] where P=(F_0^2 +2 F_c^2)/3

Specific refinement details:

The crystals were very susceptible to solvent loss and rapid (<10 seconds) handling prior to flashcooling in the cryostream was required to collect data. Despite these measures and the use of a highintensity laboratory source the crystals were weakly diffracting and no reflections were observed at better than 0.9 Å resolution. The asymmetric unit contains one complete tetrahedron and associated counterions. The crystal analysed was found to contain three SbF₆⁻ and five PF₆⁻ counterions per tetrahedron (including one SbF_6^- encapsulated inside the cavity of the tetrahedron). There is a significant amount of thermal motion in the extremities of the tetrahedron and a number of restraints were required for the realistic modelling of the toluidine groups. Even with these restraints the thermal parameters of these groups are larger than ideal and combined with the poor diffraction resulted in a high non-solvent carbon U_{iso} min/max ratio. Five of the toluidine groups were modelled as disordered over two locations and several more show evidence of thermal motion resulting from the presence of dynamic disorder in these groups. Consequently there are a number of close contacts between symmetry-generated and/or disordered methyl groups. The central bipyridyl unit of one ligand was also disordered and modelled over two locations with refined occupancies of 0.545 and 0.455. The anions also show substantial disorder. The encapsulated SbF_6^- anion shows significant rotational disorder and its fluorine atoms were modelled over four locations with a total occupancy of one. Four PF6- anions were modelled as disordered over two locations while the three nonencapsulated SbF₆⁻ sites were modelled as a disordered mixture of SbF₆⁻ and PF₆⁻ with occupancies of 0.62:0.38, 0.64:0.36 and 0.77:0.27; the fluorine atoms of the minor occupancy PF_6^- were not modelled. The SQUEEZE^{S13} function of PLATON^{S14} was employed to remove the contribution of electron density associated with disordered solvent molecules that could not be successfully modelled.

2.3. Crystal Data for $Br^- \subset Zn-2$

Br⁻ ⊂ **Zn-2**·19ClO₄: Formula C₃₉₀H₃₃₀BrCl₁₉N₆₀O₇₆Zn₁₀, *M* 8480.28, Monoclinic, space group *P*2/n(#13), *a* 21.4814(19), *b* 30.514(2), *c* 34.022(3) Å, β97.399(4), *V* 22115(3) Å³, *D*_c 1.274 g cm⁻³, *Z* 2, crystal size 0.010 by 0.010 by 0.010 mm, colour colourless, habit cube, temperature 100(2) Kelvin, λ(synchrotron) 0.6889 Å, μ(synchrotron) 0.812 mm⁻¹, *T*(SADABS)_{min,max} 0.3258, 0.7440, 2θ_{max} 33.27, *hkl* range -13 16, -25 25, -28 26, *N* 47225, *N*_{ind} 12009(*R*_{merge} 0.0597), *N*_{obs} 7352(I > 2σ(I)), *N*_{var} 1061, residuals^{*} *R*1(*F*) 0.1249, *wR*2(*F*²) 0.3585, GoF(all) 1.074, Δρ_{min,max} -0.617, 1.019 e⁻ Å⁻³.

*
$$R1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$$
 for $F_0 > 2\sigma(F_0)$; $wR2 = (\Sigma w (F_0^2 - F_c^2)^2 / \Sigma (wF_c^2)^2)^{1/2}$ all reflections

Specific refinement details:

The crystals were extremely small and very susceptible to solvent loss and rapid (<10 seconds) handling prior to flash-cooling in the cryostream was required to collect data. Despite these measures and the use of synchrotron radiation the crystals were weakly diffracting and no reflections were observed at better than 1.2 Å resolution. Nevertheless, the quality of the data is more than sufficient to establish the connectivity of the structure. The $Zn_{10}L_{15}$ complex lies astride a centre of symmetry such that one half of it is crystallographically unique. The structure of Zn-2·Br·19ClO₄ is approximately isomorphous with that of Zn-2·Cl·19ClO₄·2MeCN, with just minor differences in disorder between the two structures. The central bromide ion in $Zn-2 \cdot Br \cdot 19ClO_4$ is disordered around the inversion centre at the centre of the complex and was modelled over two locations. The considerably higher central electron density observed in Zn-2 Br 19ClO₄ compared to Zn-2 Cl 19ClO₄ 2MeCN is consistent with the presence of bromide rather than chloride. There is a significant amount of thermal motion in the extremities of the molecule and a number of restraints were required for the realistic modelling of the toluidine groups. Even with these restraints the thermal parameters of these groups are larger than ideal and combined with the poor diffraction resulted in a high non-solvent carbon and hydrogen U_{iso} min/max ratios. Three of the toluidine groups were modelled as disordered over two locations and several more show evidence of thermal motion resulting from the presence of dynamic disorder in these groups. Consequently there are a number of close contacts between symmetrygenerated and/or disordered methyl groups. The perchlorate anions also show substantial disorder and 6 were modelled as disordered over two locations. Further reflecting the solvent loss and poor diffraction properties there is a significant amount of void volume in the lattice containing smeared electron density from disordered solvent and 5 perchlorate anions per $Zn_{10}L_{15}$ complex. This area of diffuse electron density could not be successfully modelled and the SQUEEZES13 function of PLATON^{S14} was employed.

2.4. Crystal Data for Cl⁻ ⊂ Zn-2

X-ray quality crystals of $[Cl^- \subset Zn-2](ClO_4)_{19}$ were obtained upon slow diffusion of diethyl ether into an acetonitrile mixture of the sample prepared following the published procedure.^{S4} Suitable crystals were not available at the time of publication and are included here for completeness. The complex is isostructural with other published M₁₀L₁₅ complexes,^{S1-2,4} as expected from solution state data.

CI[−] ⊂ Zn-2·19ClO₄·2MeCN: Formula C₃₉₄H₃₃₆Cl₂₀N₆₂O₇₆Zn₁₀, *M* 8517.95, monoclinic, space group *P*2/n(#13), *a* 21.4479(14), *b* 30.381(2), *c* 34.189(2) Å, β 97.460(3), *V* 22089(2) Å³, *D*_c 1.281 g cm⁻³, *Z* 2, crystal size 0.03 by 0.01 by 0.01 mm, colour orange, habit block, temperature 100(2) Kelvin, λ (synchrotron) 0.68890 Å, μ (synchrotron) 0.730 mm⁻¹, *T*(SADABS)_{min,max} 0.4041, 0.7442, $2\theta_{max}$ 33.94, *hkl* range -18 18, -25 25, -28 28, *N* 82363, *N*_{ind} 14048(*R*_{merge} 0.1177), *N*_{obs} 8438(I > 2σ(I)), N_{var} 1681, residuals^{*} R1(F) 0.0998, $wR2(F^2)$ 0.2950, GoF(all) 1.050, $\Delta \rho_{\min,\max}$ - 0.582, 0.871 e⁻ Å⁻³.

*
$$R1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$$
 for $F_0 > 2\sigma(F_0)$; $wR2 = (\Sigma w(F_0^2 - F_c^2)^2 / \Sigma (wF_c^2)^2)^{1/2}$ all reflections,
w=1/[$\sigma^2(F_0^2)$ +(0.2000P)²+0.0000P] where P=(F_0^2 +2 F_c^2)/3

Specific refinement details:

The crystals were extremely small and very susceptible to solvent loss and rapid (<10 seconds) handling prior to flash-cooling in the cryostream was required to collect data. Despite these measures and the use of synchrotron radiation the crystals were weakly diffracting and no reflections were observed at better than 1.18 Å resolution. Nevertheless, the quality of the data is more than sufficient to establish the connectivity of the structure. The $Zn_{10}L_{15}$ complex lies astride a centre of symmetry such that one half of it is crystallographically unique; the central chloride ion is located on the centre of inversion. There is a significant amount of thermal motion in the extremities of the molecule and a number of restraints were required for the realistic modelling of the toluidine groups. Even with these restraints the thermal parameters of these groups are larger than ideal and combined with the poor diffraction resulted in a high non-solvent carbon U_{iso} min/max ratio. Three of the toluidine groups were modelled as disordered over two locations and several more show evidence of thermal motion resulting from the presence of dynamic disorder in these groups. Consequently there are a number of close contacts between symmetry-generated and/or disordered methyl groups. The perchlorate anions also show substantial disorder and five were modelled as disordered over two locations. Further reflecting the solvent loss and poor diffraction properties there is a significant amount of void volume in the lattice containing smeared electron density from disordered solvent and four perchlorate anions per $Zn_{10}L_{15}$ complex. This area of diffuse electron density could not be successfully modelled and the SQUEEZE^{S13} function of PLATON^{S14} was employed.



Figure S19: Single-crystal X-ray structures of $[Cl^- \subset Zn-2(ClO_4^-)_5]$ formed from *p*-toluidine. Disorder, solvent molecules and additional anions omitted for clarity.

2.5. Volume Calculations

In order to determine the available void space within $[Cl^- \subset Zn-2]$ and $[Br^- \subset Zn-2]$, VOIDOO calculations^{S15} based on the crystal structures were performed. A virtual probe with a radius of 1.4 Å (default, water-sized) was employed, and the standard parameters tabulated below were used, following the previously published procedures.^{S16}

Maximum number of volume-refinement cycles:		
Minimum size of secondary grid:	3	
Grid for plot files:	0.1	
Primary grid spacing:	0.1	
Plot grid spacing:	0.1	

As $[Cl^- \subset Zn-2]$ and $[Br^- \subset Zn-2]$ differed only in central anion we were interested to see if the increased size of bromide (28 Å³) relative to chloride (24 Å³) resulted in any measurable change in the average volume of the peripheral binding pockets of the two complexes.

Table S1: Table showing key volumes of central anion and peripheral binding pockets for Zn-2 complexes. Anion volumes calculated using Spartan'10 (MP2//6-311+G**).^{S17}

Complex	Central Anion (volume/ Å ³)	Average volume of peripheral binding pocket / Å ³
[Cl ⁻ ⊂ Zn-2]	Cl ⁻ (24)	83
[Br - Czn-2]	Br (28)	82

No significant change in the volume of the peripheral binding pockets was measured.

3. Reaction Dynamics

3.1 Determination of Thermodynamic Species

A series of reactions A-F (Scheme S1) were performed to determine whether the Zn_4L_6 tetrahedron, Zn-1, or the bromide bound $Zn_{10}L_{15}$ pentagonal prism, Zn-2, was the thermodynamic product.

Scheme S1: Reactions A-F were performed to determine whether Zn-1 or Zn-2 is the thermodynamically favoured product in the presence of ClO_4^- (red oval) and Br anions (blue sphere) with *p*-toluidine, 6,6'-diformyl-3,3'-bipyridine and zinc triflimide. The tetrahedral dianion, $[ZnBr_4]^{2-}$, represented by the green sphere, is generated *in situ* through the reaction of zinc triflimide and bromide.

3.1.1 Experiment A

Formation of Zn-**DL** following previously published procedure.^{S4} Zn(NTf₂)₂·xH₂O (9.8 mg, 9.5 μ mol), 6,6'-diformyl-3,3'-bipyridine (4.0 mg, 18.9 μ mol) and *p*-toluidine (4.0 mg, 0.04 mmol) were loaded into a J-Young NMR tube and dissolved in CD₃CN (0.6 mL). The NMR tube was then heated for 24 hours at 363 K. The resultant ¹H NMR of the reaction mixture was characteristically broad, consistent with formation of a mixture of species in a dynamic library.

3.1.2 Experiment B

Formation of $[ZnBr_4]^{2-} \subset Zn-1$ following the procedure described in section 1.2.2.

3.1.3 Experiment C

Formation of Br \subset Zn-2(ClO₄)₅ from Zn-**DL** upon addition of LiClO₄ (1.56 mg, 14.6 µmol) and KBr (1.43 mg, 12.0 µmol), followed by equilibration of the sample at 343 K for 24 hours.

3.1.4 Experiment D

Formation of Br⁻ \subset Zn-2(ClO₄)₅ from *p*-toluidine (4.04 mg, 0.04 mmol), 6,6'-diformyl-3,3'-bipyridine (4.0 mg, 18.9 µmol), Zn(ClO₄)₂·6H₂O (4.7 mg, 12.6 µmol) and KBr (1.43 mg, 12.0 µmol).

This experiment was performed to determine if the overall salt concentration of the reaction mixture affected the outcome. Both pathways C and D gave ¹H NMR profiles consistent with clean formation

of the desired Zn-2 species. Addition of excess KBr to Zn-2 generated through each route resulted in significant precipitation of the sample as discussed below in experiment F.

3.1.5 Experiment E

Formation of $Br \subset Zn-2(ClO_4)_5$ from Zn-1 through addition of excess LiClO₄. LiClO₄ was added in three separate additions (1.48mg, 13.9 µmol; 0.88 mg, 8.3 µmol; 0.76 mg, 7.1 µmol) to a solution of $[ZnBr_4]^{2-} \subset Zn-1$. After each addition the reaction was heated at 373 K for 48 hours at which point no further changes in the ¹H NMR spectra were observed and the reaction mixture was determined to be fully equilibrated. After the final addition of LiClO₄ no evidence of remaining $[ZnBr_4]^{2-} \subset Zn-1$ was observed. A small amount of precipitate was observed during this reaction, however, it was considerably less than that observed in experiment F.

3.1.6 Experiment F

Attempted formation of $[ZnBr_4]^{2-} \subset Zn-1$ from $Br^- \subset Zn-2(ClO_4)_5$ from through addition of KBr. KBr was added in three separate additions (0.73 mg, 6.1 µmol; 0.71 mg, 6.0 µmol; 0.96 mg, 8.0 µmol) to a solution of $Br^- \subset Zn-2(ClO_4)_5$. After each addition the reaction was heated at 373 K for 48 hours at which point no further changes in the ¹H NMR spectra were observed and the reaction mixture was determined to be fully equilibrated. A significant amount of precipitate was observed during these reactions. Precipitation could not be avoided by lowering the overall salt concentration of the reaction mixture through use of $Zn(ClO_4)_2$ as the metal salt (Experiment D) and use of low equivalents of KBr. No evidence for formation of any $[ZnBr_4]^{2-} \subset Zn-1$ was observed under any conditions.



Figure S20: ¹H NMR stack plot (400 MHz, 298 K, CD₃CN); a) $Br \subset Zn-2(ClO_4)_5$ reference spectrum; b) $[ZnBr_4]^{2-} \subset Zn-1$ reference spectrum. Spectra c, d and e correspond to experiment E: c) $[ZnBr_4]^{2-} \subset Zn-1$ after addition of 1.4 mg LiClO₄ (11.1 eq. per Zn-2); d) a further 0.88 mg LiClO₄ (6.6 eq. per Zn-2); e) a further 0.76 mg LiClO₄ (5.7 eq. per Zn-2). Spectra f,g and h correspond to experiment F: f) $Br \subset Zn-2(ClO_4)_5$ after addition of 0.73 mg KBr (1.9 eq. per Zn-1); g) a further 0.71 mg of KBr (1.9 eq. per Zn-1) and; h) a further 0.96 mg of KBr (2.5 eq. per Zn-1). No evidence for formation of $[ZnBr_4]^{2-} \subset Zn-1$ from $Br \subset Zn-2(ClO_4)_5$ was observed, instead the ¹H NMR profile of the reaction was observed to broaden and significant precipitation of the sample was observed. In contrast, addition of LiClO₄ to $[ZnBr_4]^{2-} \subset Zn-1$ resulted in conversion of the tetrahedron into the pentagonal prism $Br \subset Zn-2(ClO_4)_5$.

3.2 Direct Dianion Addition to Co and Zn-DL

3.2.1 Addition of Preformed [CoBr₄]²⁻ to Co-DL

Formation of Co-**DL** following previously published procedure.^{S2} Co(NTf₂)₂.5H₂O (4.2 mg, 6.6 μ mol), 6,6'-diformyl-3,3'-bipyridine (2.0 mg, 9.4 μ mol) and *p*-toluidine (2.0 mg, 0.02 mmol) were loaded into a J-Young NMR tube and dissolved in CD₃CN (0.6 mL). The NMR tube was subjected to three evacuation/nitrogen fill cycles to remove oxygen, sealed and then heated for 24 hours at 363 K.

The ¹H NMR of the reaction mixture was characteristically broad, consistent with formation of a mixture of species in a dynamic library. Following this $[EtN_4]_2[CoBr_4]$ (1.06 mg, 1.66 µmol) was added to the reaction mixture, the sample was subject to three evacuation/nitrogen fill cycles to remove oxygen, sealed and then heated for 48 hours at 363 K, after which time the ¹H NMR profile was consistent with formation of the desired tetrahedral complex. ¹H NMR (400 MHz, 298 K, CD₃CN): $\delta = 233.5$ (s, 12H, imine), 82.2 (br. s, 12H, 2,2'-bipyridine), 69.5 (s, 12H, 5,5'-bipyridine), 16.2 (s, 12H, 4,4'-bipyridine), 10.4 (s, 36H, methyl), 10.0 (s, 24H, 3-aniline), -24.7 (s, 24H, 2-aniline); ESI-MS: m/z: ({[CoBr₄]²⁻ \subset Co-1 + NTf₂⁻}⁵⁺) = 647.6, ({[CoBr₄]²⁻ \subset Co-1 + 2NTf₂⁻}⁴⁺) = 879.5, ({[CoBr₄]²⁻ \subset Co-1 + 3NTf₂⁻}³⁺) = 1266.0.

3.2.2 Addition of Preformed [CoCl₄]²⁻ to Co-DL

Formation of Co-**DL** following previously published procedure. Co(NTf₂)₂.H₂O (4.2 mg, 6.6 µmol), 6,6'-diformyl-3,3'-bipyridine (2.0 mg, 9.4 µmol) and *p*-toluidine (2.0 mg, 0.02 mmol) were loaded into a J-Young NMR tube and dissolved in CD₃CN (0.6 mL). The NMR tube was subjected to three evacuation/nitrogen fill cycles to remove oxygen, sealed and then heated for 24 hours at 363 K. The ¹H NMR of the reaction mixture was characteristically broad, consistent with formation of a mixture of species in a dynamic library. Following this [Et₄N]₂[CoCl₄] (0.64 mg, 1.38 µmol) was added to the reaction mixture, the sample was subject to three evacuation/nitrogen fill cycles to remove oxygen, sealed and then heated for 48 hours at 363 K, after which time the ¹H NMR profile was consistent with formation of the desired tetrahedral complex alongside a range of minor species (Figure S6). ESI-MS: m/z: ({[CoCl₄]²⁻ \subset Co-1 + NTf₂⁻}⁵⁺) = 611.0, ({[CoCl₄]²⁻ \subset Co-1 + 2NTf₂⁻}⁴⁺) = 834.8, ({[CoCl₄]²⁻ \subset Co-1 + 3NTf₂⁻}³⁺) = 1206.3.

3.2.3 Addition of Preformed [CoBr₄]²⁻ to Zn-DL

Formation of Zn-**DL** following previously published procedure.^{S4} Zn(NTf₂)₂.xH₂O (7.9 mg, 12.6 μ mol), 6,6'-diformyl-3,3'-bipyridine (4.0 mg, 18.9 μ mol) and *p*-toluidine (4.0 mg, 0.04 mmol) were loaded into a J-Young NMR tube and dissolved in CD₃CN (0.6 mL). The NMR tube was then heated for 24 hours at 363 K. The resultant ¹H NMR of the reaction mixture was characteristically broad, consistent with formation of a mixture of species in a dynamic library. Following this [Et₄N]₂[CoBr₄] (2.14 mg, 3.34 μ mol) was added to the reaction mixture, which was then purified of oxygen through three evacuation/ nitrogen fill cycles, sealed and heated at 363 K for 24 hours. The ¹H NMR showed groups of resonances at characteristic chemical shifts for paramagnetic M₄L₆ tetrahedra (Figure S21).



Figure S21: ¹H NMR spectrum (400 MHz, 298 K, CD₃CN) generated upon addition of $[EtN_4]_2[CoBr_4]$ to Zn-**DL**. Each ligand proton is observed to correspond to a series of resonances, indicating that a library of mixed metal M_4L_6 tetrahedra have been formed.



Figure S22: ESI-MS generated upon addition of [EtN₄]₂[CoBr₄] to Zn-DL.



Figure S23: Experimental (upper black trace) and simulated ESI-MS generated upon addition of $[EtN_4]_2[CoBr_4]$ to Zn-**DL**. Simulated spectra correspond to mixed metal species containing mixtures of five cobalt metal centres through to five zinc centres.

3.2.4 Addition of Preformed [CoCl₄]²⁻ to Zn-DL

Formation of Zn-**DL** following previously published procedure.^{S4} Zn(NTf₂)₂.xH₂O (7.9 mg, 12.6 μ mol), 6,6'-diformyl-3,3'-bipyridine (4.0 mg, 18.9 μ mol) and *p*-toluidine (4.0 mg, 0.04 mmol) were loaded into a J-Young NMR tube and dissolved in CD₃CN (0.6 mL). The NMR tube was then heated for 24 hours at 363 K. The resultant ¹H NMR of the reaction mixture was characteristically broad, consistent with formation of a mixture of species in a dynamic library. Following this [EtN₄]₂[CoCl₄] (1.47 mg, 3.18 μ mol) was added to the reaction mixture, which was then purified of oxygen through three evacuation/ nitrogen fill cycles, sealed and heated at 363 K for 24 hours. The ¹H NMR showed groups of resonances at characteristic chemical shifts for paramagnetic M₄L₆ tetrahedra (Figure S24).



Figure S24: ¹H NMR spectrum (400 MHz, 298 K, CD₃CN) generated upon addition of $[EtN_4]_2[CoCl_4]$ to Zn-**DL**. Each ligand proton is observed to correspond to a series of resonances, indicating that a library of mixed metal M_4L_6 tetrahedra have been formed.



Figure S25: ESI-MS generated upon addition of [EtN₄]₂[CoCl₄] to Zn-DL.





Figure S26: Experimental (upper black trace) and simulated ESI-MS generated upon addition of $[EtN_4]_2[CoCl_4]$ to Zn-**DL**. Simulated spectra correspond to mixed metal species containing mixtures of five cobalt metal centres through to five zinc centres.

3.2.5 Discussion of Mixed Metal Complexes

The ¹H NMR profiles of the mixed metal systems generated upon addition of $[CoBr_4]^{2-}$ and $[CoCl_4]^{2-}$ to Zn-**DL** are remarkably similar. In each spectrum the chemical shift range for each ligand proton is found within the range previously observed for M_4L_6 tetrahedra containing Co^{2+} metal ions^{S2} and importantly do not extend into the wider chemical shift ranges which have been observed for other architectures generated with this ligand.^{S4} The observation of multiple resonances per ligand proton is in good agreement with the ESI-MS data.

4. References

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