Electronic Supplementary Material (ESI) for Chemical Communications

Steric Control of the Formation of Dinuclear Double Helicate and Dinuclear Meso-helicate Assemblies.

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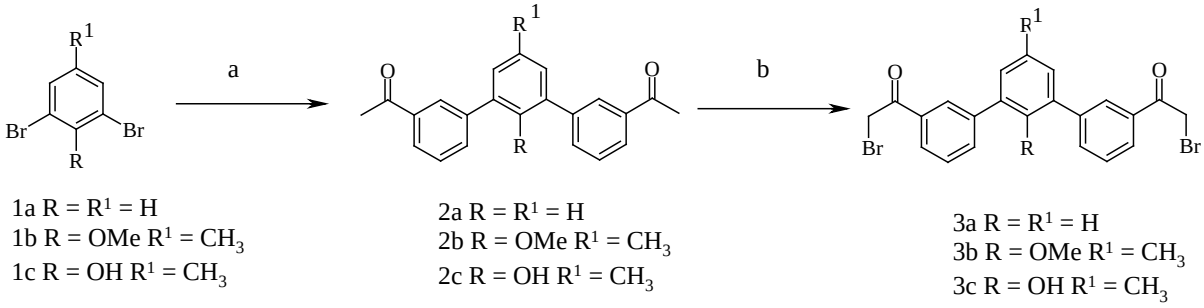
Electronic Supplementary Information.

Chemicals were purchased and used without further purification. ^{1}H NMR spectra were recorded on a 400MHz Bruker Avance DP X400. Mass spectra were obtained on a Bruker MicroTOF LC. *Great care should be taken with perchlorate salts as they are potentially explosive, in all cases they are used in small quantities (> 5 mgs).*



1a R = R^1 = H
1b R = OMe R^1 = CH_3
1c R = OH R^1 = CH_3

2a R = R^1 = H
2b R = OMe R^1 = CH_3
2c R = OH R^1 = CH_3

3a R = R^1 = H
3b R = OMe R^1 = CH_3
3c R = OH R^1 = CH_3

L^3 R = OCH_2Ph R^1 = CH_3

L^1 3a R = R^1 = H
L^2 3b R = OMe R^1 = CH_3
4c R = OH R^1 = CH_3

Scheme 1. Reagents and conditions: a) 3-Acetylphenylboronic acid, $(Ph_3P)_2PdCl_2$, Bu^n_4NBr, $NaHCO_3$, H_2O, EtOH; b) Br_2, CH_3CO_2H; c) 2,2'-bipyridine-6-thioamide, EtOH; d) BnBr, NaH, DMF.

Synthesis of 1,3-di(3-acetylphenyl)benzene 2a. To a 50 ml round bottom flask containing 1,3-dibromobenzene (**1a**) (0.17 g, 0.7 mmol), 3-acetyl phenylboronic acid (0.3 g, 2.0 mmol), sodium carbonate (0.08 g, 0.76 mmol), Bu^n_4NBr (0.03 g, 0.09 mmol) and $(Ph_3P)_2PdCl_2$ (0.01 g, 2 mol %) was added deionised water (10 ml) and ethanol (10 ml). The reaction was left to stir at 70˚C for 20 h. The ethanol was removed by rotary evaporation and the crude product extracted into DCM (3 x 30ml), the combined organic layers dried over $MgSO_4$ and evaporation provided a crude product that was purified *via* column chromatography (SiO_2, 1% MeOH in DCM,). Producing the desired product (**2a**) as a cream solid (0.12 g, 54 % yield). ^{1}H NMR [400 MHz, $CDCl_2$]: δ_H = 8.24 (t, *J*= 1.7, 2H, Ph), 7.98 (dt, *J*=7.8, 1.2, 2H, Ph), 7.87 (dq, *J*=7.7, 1.2, 2H, Ph), 7.84 (t, *J*= 1.7 1H, Ph^{cent}), 7.65 (dt, *J*= 7.6, 2H, Ph^{cent}), 7.59 (t, *J*=7.7, 2H, Ph), 7.58 (t, *J*=7.5 Hz, H, Ph^{cent}), 2.69 (s, 6H, -C*H*$_3$). ESI-MS *m/z* 629 (M + Na^+), HR ESI-MS found 337.1199 $C_{22}H_{18}NaO_2$ requires 337.1199 (error 0.07ppm).

Synthesis of 1,3-di(3-α-bromoacetylphenyl)benzene 3a. 1,3-di(3-acetylphenyl)benzene (**2a**) (0.10 g, 0.32 mmol) was dissolved in acetic acid (25 ml) and set to stir at 80˚C under an atmosphere of dinitrogen. Bromine (0.10 g, 0.64 mmol) was diluted with acetic acid to give approximately 1 ml (approx. 0.9 ml acetic acid) to allow slow addition to the reaction. The reaction was monitored *via* TLC (SiO_2, 1% MeOH in DCM) and once the starting material was consumed the reaction was allowed to cool then poured onto deionised water (30 ml), $NaHCO_3$ (0.1 g) was added and the crude product extracted into DCM (3 x 30 ml) and the combined organic layers dried ($MgSO_4$). Removal of solvent left the crude product as a yellow-orange oil. Purification *via* column chromatography (SiO_2, DCM) gave **3a** as an off white solid (0.1 g, 63 % yield). ^{1}H NMR [400 MHz, $CDCl_2$]: δ_H = 8.27 (t, *J*= 1.7, 2H, Ph), 8.01 (dq, *J*= 7.8,1.6, 1.2, 2H, Ph), 7.91 (dq, *J*= 7.8, 1.8, 1.1, 2H, Ph), 7.83 (t, *J*= 1.1, 1H, Ph^{cent}), 7.66 (dt, *J*= 7.8, 1.2 Hz, 2H, Ph^{cent}), 7.63-7.59 (m, overlap, 3H, Ph, Ph^{cent}), 4.53 (s, 4H, -C*H*$_2$-Br). ESI-MS *m/z* 493 (M + Na^+), HR ESI-MS found 492.9419 $C_{22}H_{16}Br_2NaO_2$ requires 492.9409 (error 1.97 ppm).

Synthesis of L^1. To a solution of 2,2'-bipyridine-6-thioamide (0.075 g, 0.35 mmol) in ethanol (25 ml) was added the 1,3-di(3-α-bromoacetylphenyl)benzene (**3a**) (0.075 g, 0.16 mmol) and the reaction refluxed for 8 h, during which a precipitate was produced. This was isolated by filtration, whilst hot, followed by washing with EtOH and Et_2O (2 x 2 ml). The compound was isolated as the HBr salt, to obtain the free ligand the product was suspended in concentrated ammonia (0.88 S.G., 10 ml) for 24 h. Filtration and washing with H_2O, EtOH and Et_2O (2 x 2 ml) gave the desired ligand, **L^1**, as a light brown powder (0.08 g, 71 % yield). ^{1}H NMR [400 MHz, $CDCl_3$]: δ_H = 8.71 (dq, *J*= 4.8, 1.7, 0.9, 2H, Py^{term}), 8.61 (d, *J*= 8.0, 2H, Py^{term}), 8.49 (dd, *J*= 7.8. 0.9, 2H, Py), 8.37 (dd, *J*= 7.8. 0.9, 2H, Py), 8.35 (t, *J*= 1.6, 2H, Ph), 8.05 (dt, *J*= 7.8. 1.4, 2H, Ph), 8.01 (t, *J*= 1.6, 1H, Ph^{cent}), 7.96 (t, *J*= 7.8, 2H, Py), 7.90 (dt, *J*= 7.7, 1.8, 2H, Py^{term}), 7.74 (s, 2H, Tz), 7.73 (dd, *J*= 7.3, 1.7, 2H, Ph^{cent}), 7.70 (dt, *J*= 8.0, 1.2, 2H, Ph), 7.64-7.58 (m, overlap, 3H, Ph^{cent}, Ph), 7.37 (ddd, *J*= 7.5. 4.8, 1.2 Hz, 2H, Py^{term}). ^{13}C NMR [500 MHz, $CDCl_3$]: δ_C = 169.3 (quaternary, Q), 156.6 (Q), 155.6 (Q), 155.3 (Q), 150.7 (Q), 149.0 (CH), 141.9 (Q), 141.8 (Q), 138.0 (CH), 137.1 (CH), 135.2 (Q), 129.2 (CH), 127.2 (CH), 126.5 (CH), 126.4 (CH), 125.4 (CH), 124.0 (CH), 121.8 (CH), 121.3 (CH), 119.8 (CH), 115.6 (CH). ESI-MS *m/z* 705 (M + H^+), HR ESI-MS found 705.1894 $C_{44}H_{29}N_6S_2$ requires 705.1890 (error 0.55 ppm).

Synthesis of 2,6-di(3-acetylphenyl)-4-methylanisole 2b. This compound was produced in an identical manner to compound **2a**, except 2,6-dibromo-4-methylanisole (**1b**), was used in place of **1a**.

The reaction was monitored *via* TLC (SiO_2, 1 % MeOH in DCM). Purification *via* column chromatography (SiO_2, 1 % MeOH in DCM) gave the desired compound as a white powder (60 % yield). ^{1}H NMR [500 MHz, $CDCl_3$]: δ_H = 8.20 (t, *J*= 1.6, 2H, Ph), 7.97 (dt, *J*= 7.8, 1.5, 2H, Ph), 7.85 (dt, *J*= 7.6, 1.5, 2H, Ph), 7.56 (t, *J*= 7.6 Hz, 2H, Ph), 7.21 (s, 2H, Ph^{cent}), 3.12 (s, 3H, -O-C*H*$_3$), 2.67 (s, 6H, -C*H*$_3$), 2.43 (s, 3H, -ArC*H*$_3$). ESI-MS *m/z* 381 (M + Na^+), HR ESI-MS found 381.1464 $C_{24}H_{22}NaO_3$ requires 381.1461 (error 0.73 ppm).

Synthesis of 2,6-di(3-α-bromoacetylphenyl)-4-methylanisole 3b. This compound was produced in an identical manner to compound **3a**, except derivative **2b** instead of **2a** was used. The reaction was monitored *via* TLC (SiO_2, 0.5 % MeOH in DCM). Purification *via* column chromatography (SiO_2, 0.5 % MeOH in DCM) gave the desired compound as a white powder (44 % yield). ^{1}H NMR [500 MHz, $CDCl_3$]: δ_H = 8.23 (t, *J*= 1.6, 2H, Ph), 8.00 (dt, *J*= 7.8, 1.3, 2H, Ph), 7.89 (dt, *J*= 7.8, 1.3, 2H, Ph), 7.58 (t, *J*= 7.8 Hz, 2H, Ph), 7.22 (s, 2H, Ph^{cent}), 4.53 (s, 4H, -C*H*$_2$-Br), 3.13 (s, 3H, -O-C*H*$_3$), 2.44 (s,3H, -ArC*H*$_3$). ESI-MS *m/z* 536 (M + Na^+), HR ESI-MS found 536.9671 $C_{24}H_{20}Br_2NaO_3$ requires 536.9671 (error 0.10 ppm).

Synthesis of L^2. This ligand was produced in an identical manner as L^1, except **3b** was used in place of **3a**. After filtration $NaHCO_{3\ (aq)}$ (30 ml) was added to the resulting yellow powder, extracted into DCM (3 x 30 ml). The combined organic layers dried ($MgSO_4$) and concentrated followed by purification *via* column chromatography (Al_2O_3, DCM). This gave the desired ligand, L^2, as a light yellow powder (65 % yield). ^{1}H NMR [500 MHz, DMSO]: δ_H = 8.75 (dq, *J*= 4.7, 0.9, 2H, Py^{term}), 8.50 (dt, *J*= 7.9, 1.0, 2H, Py^{term}), 8.49 (dd, *J*= 7.8, 0.9, 2H, Py), 8.43 (s, 2H, Tz), 8.33 (dd, *J*= 7.8, 0.9, 2H, Py), 8.28 (br s, 2H, Ph), 8.15 (t, *J*= 7.8, 2H, Py), 8.12 (dt, *J*= 6.7, 2, 2H, Ph), 8.06 (dt, *J*= 7.7, 1.8, 2H, Py^{term}), 7.61-7.60 (m, overlap, 4H, Ph), 7.53 (ddd, *J*= 7.5, 4.8, 1.2 Hz, 2H, Py^{term}), 7.32 (s, 2H, Ph^{cent}), 3.21 (s, 3H, --OC*H*$_3$), 2.44 (s, 3H, ArC*H*$_3$). ^{13}C NMR [500 MHz, $CDCl_3$/CD_3OD]: δ_C = 169.1 (quaternary, Q), 156.8 (Q), 155.2 (2 x Q), 152.9 (Q), 150.9 (Q), 148.7 (CH), 139.4 (Q), 138.1 (CH), 137.5 (CH), 135.3 (Q), 134.5 (Q), 133.7 (Q), 131.1 (CH), 129.3 (CH), 128.6 (CH), 127.3 (CH), 125.2 (CH), 124.1 (CH), 121.9 (CH), 121.6 (CH), 119.9 (CH), 115.5 (CH), 60.8 (OCH_3), 20.8 (CH_3). ESI-MS *m/z* 749 (M + H^+), HR ESI-MS found 749.2145 $C_{46}H_{33}N_6OS_2$ requires 749.2152 (error 0.89 ppm).

Synthesis of 2,6-di(3-acetylphenyl)cresol 2c. This compound was produced in an identical manner to compound **2a**, except 2,6-dibromocresol (**1c**), was used in place of 1,3-dibromobenzene (**1a**). The reaction was monitored *via* TLC (SiO_2, 1:3 ethyl acetate: petroleum ether 40-60). Purification *via* column chromatography (SiO_2, 1:3 ethyl acetate: petroleum ether 40-60) gave the desired compound as a yellow oil (65 % yield). ^{1}H NMR [400 MHz, $CDCl_3$]: δ_H = 8.13 (t, *J*= 7.7, 2H, Ph), 7.98 (dt, , *J*= 7.7, 1.5, 2H, Ph), 7.78 (dt, , *J*= 7.7, 1.5, 2H, Ph), 7.58 (t, *J*= 7.8 Hz, 2H, Ph), 7.14 (s, 2H, Ph^{cent}), 5.15 (s, 1H, -O*H*), 2.65 (s, 6H, -C*H*$_3$), 2.05 (s, 3H, -ArC*H*$_3$). ESI-MS *m/z* 367 (M + Na^+), HR ESI-MS found 367.1302 $C_{23}H_{20}NaO_3$ requires 367.1304 (error 0.60 ppm).

Synthesis of 2,6-di(3-α-bromoacetylphenyl)cresol 3c. This compound was produced in an identical manner to compound **3a**, except derivative **2c** was used instead of **2a**. The reaction was monitored *via* TLC (SiO_2, 1 % MeOH in DCM). Purification *via* column chromatography (SiO_2, 1 % MeOH in DCM) gave the desired compound as an off white powder (89 % yield). ^{1}H NMR [400 MHz, $CDCl_3$]: δ_H = 8.17 (t, *J*= 1.6, 2H, Ph), 8.02 (dd, *J*= 7.8, 1.2, 2H, Ph), 7.82 (dd, , *J*= 7.7, 1.1, 2H, Ph), 7.62 (t, *J*= 7.8 Hz, 2H, Ph), 7.15 (s, 2H, Ph^{cent}), 5.08 (s, 1H, -O*H*), 4.50 (s, 4H, -C*H*$_2$*Br*), 2.40 (s, 3H, -ArC*H*$_3$). ESI-MS *m/z* 523 (M + Na^+), HR ESI-MS found 522.9520 $C_{23}H_{18}Br_2NaO_3$ requires 522.9515 (error 0.90 ppm).

Synthesis of derivative 4c. This ligand was produced in an identical manner as $\mathbf{L^1}$, except **3c** was used in place of **3a**. Giving the desired compound as a light brown powder (79 % yield). ^{1}H NMR [500 MHz, $CDCl_3$]: δ_H = 8.71 (dq, *J*= 4.8, 0.9, 2H, Py^{term}), 8.60 (dt, *J*= 7.9, 0.9, 2H, Py^{term}), 8.48 (dd, *J*= 7.9, 1.0, 2H, Py), 8.35 (dd, *J*= 7.8, 1.0, 2H, Py), 8.24 (Br s, 2H, Ph), 8.06-8.04 (m, 2H, Ph), 7.96 (t, *J*= 7.8, 2H, Py), 7.89 (dt, *J*= 7.7, 1.7, 2H, Py^{term}), 7.69 (s, 2H, Tz), 7.60-7.59 (m, overlap, 4H, Ph), 7.36 (ddd, *J*= 7.5, 4.8, 1.2 Hz, 2H, Py^{term}), 7.24 (s, 2H, Ph^{cent}), 5.45 (Br s, 1H, -*OH*), *2*.42 (s, 3H, -ArC*H*$_3$). ESI-MS *m/z* 735 (M + H^+), HR ESI-MS found 735.1994 $C_{45}H_{31}N_6OS_2$ requires 735.1995 (error 0.19 ppm).

Synthesis of $\mathbf{L^3}$. A two necked round bottom flask charged with **4c** (0.14 g, 0.19 mmol) and sodium hydride (0.04 g, 0.95 mmol), was placed under an atmosphere of dinitrogen and to this anhydrous DMF (~5 ml) was added. This was left to stir at 80˚C for 1h. After this time benzyl bromide (0.07 g, 0.38 mmol) was added to the reaction and set to stir at 80˚C. The reaction was monitored *via* TLC (Al_2O_3, 1% hexane in DCM), once all the starting material had been consumed methanol was added to the reaction whilst under nitrogen, to remove any unreacted sodium hydride. The reaction was concentrated and aqueous $NaHCO_3$ (30 ml) added, extracted into DCM (3 x 30 ml) and the combined organic layers dried ($MgSO_4$) and solvent removed by rotary evaporator. Purification *via* column chromatography (Al_2O_3, 1% hexane in DCM) gave $\mathbf{L^3}$ as a fine cream powder once dry (0.052 g, 56 % yield). ^{1}H NMR [400 MHz, $CDCl_3$]: δ_H = 8.72 (dq, *J*= 4.8, 0.8 2H, Py^{term}), 8.62 (d, *J*= 7.9, 2H, Py^{term}), 8.50 (dd, *J*= 7.9, 0.8, 2H, Py), 8.36 (dd, *J*= 7.7, 0.9, 2H, Py), 8.31 (t, *J*= 1.6, 2H, Ph), 8.09 (d, *J*= 7.8, 2H, Ph), 7.98 (t, *J*= 7.8, 2H, Py), 7.91 (dt, *J*= 7.7, 1.8, 2H, Py^{term}), 7.71 (d, *J*= 7.8, 2H, Ph), 7.62 (s, 2H, Tz), 7.56 (t, *J*= 7.7, 2H, Ph), 7.37 (ddd, *J*= 7.5, 4.8,1.1, 2H, Py^{term}), 7.36 (s, 2H, Ph^{cent}), 7.08 (t, *J*= 7.2, 1H, Bn), 7.03 (t, *J*= 7.2, 2H, Bn), 6.79 (d, *J*= 6.9 Hz, 2H, Bn), 4.29 (s, 2H, O-C*H*$_2$-), 2.50 (s, 3H, -ArC*H*$_3$). ^{13}C NMR [500 MHz, $CDCl_3$]: δ_C= 169.2 (quaternary, Q), 156.7 (Q), 155.7 (Q), 155.4 (Q), 151.4 (Q), 150.8 (Q), 149.2 (CH), 139.2 (Q), 138.0 (CH), 137.0 (CH), 136.7 (Q), 135.8 (Q), 134.5 (Q), 134.1 (Q), 131.0 (CH), 129.7 (CH), 128.7 (CH), 128.6 (CH), 128.0 (CH), 127.7 (CH), 127.5 (CH), 125.3 (CH), 124.1 (CH), 121.7 (CH), 121.3 (CH), 119.8 (CH), 115.6 (CH), 75.0 (CH_2, Bn), 21.0 (CH_3). ESI-MS *m/z* 825 (M + H^+), HR ESI-MS found 825.2455 $C_{52}H_{37}N_6OS_2$ requires 825.2465 (error 1.24 ppm).

Synthesis of Complexes

In all cases the complexes were synthesized in a similar manner and the ligand (5 mg) was reacted with 1.1 equivalents of the relevant metal ion (either as the perchlorate or tetrafluoroborate salt) in $MeNO_2$ (for the Fe(II) Co(II) Zn(II) complexes) or MeCN (for both Cd(II) complexes) and the reaction heated and sonicated until complete dissolution. Slow diffusion of ethyl acetate ($[Fe_2(\mathbf{L^1})_2]^{4+}$, and $[Zn_2(\mathbf{L^2})_2]^{4+}$), dichloromethane ($[Cd_2(\mathbf{L^2})_2]^{4+}$) and chloroform ($[Co_2(\mathbf{L^2})_2]^{4+}$ and $[Cd_2(\mathbf{L^3})_2]^{4+}$) gave crystalline materials which were isolated by filtration, washed with the diffusion solvent and dried under vacuum.

$Fe_2(\mathbf{L^1})_2][ClO_4]_4{\cdot}CH_3NO_2$ (as dark purple crystals 75 % yield). Found: C, 54.3; H, 2.6; N, 9.6%. Calculated for $C_{89}H_{59}Cl_4Fe_2N_{13}O_{18}S_4$: C, 54.0; H, 3.0; N, 9.2%.

$[Cd_2(\mathbf{L^2})_2][ClO_4]_4{\cdot}CH_3CN$ (as colourless crystals 63 % yield). Found: C, 51.8; H, 3.0; N, 8.1%. Calculated for $C_{94}H_{67}Cd_2Cl_4N_{13}O_{18}S_4$: C, 52.2; H, 3.1; N, 8.4%.

$[Co_2(\mathbf{L^2})_2][BF_4]_4$ (as orange crystals 45 % yield). Found: C, 56.4; H, 2.9; N, 9.0 %. Calculated for $C_{92}H_{64}B_4Co_2F_{16}N_{12}O_2S_4$: C, 56.3; H, 3.3; N, 8.6 %.

$[Zn_2(\mathbf{L}^2)_2][CF_3SO_3]_4$ (as colourless crystals 69 % yield). Found: C, 52.0; H, 2.6; N, 7.4%. Calculated for $C_{96}H_{64}F_{12}N_{12}O_{14}S_8Zn_2$: C, 51.8; H, 2.9; N, 7.6%.

$[Cd_2(\mathbf{L}^3)_2][ClO_4]_4$ (as colourless crystals 55 % yield). Found: C, 55.2; H, 3.4; N, 7.1%. Calculated for $C_{104}H_{72}Cd_2Cl_4N_{12}O_{18}S_4$: C, 54.9; H, 3.2; N, 7.4%.

Crystallography

Single crystal X-ray diffraction data was collected at 150(2) K on a Bruker Apex Duo diffractometer equipped with a graphite monochromated Mo(Kα) 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] Structures $[Fe_2(\mathbf{L}^1)_2][ClO_4]_4$, $[Cd_2(\mathbf{L}^2)_2][ClO_4]_4$ and $[Cd_2(\mathbf{L}^3)_2][ClO_4]_4$ contained disorder; specifically, for $[Fe_2(\mathbf{L}^1)_2][ClO_4]_4$ the terminal phenyl spacer showed slight positional disorder resulting in large anisotropic displacement parameters. For simplicity five carbon atoms were constrained using DELU and SIMU constrains and one was further constrained using ISOR. $[[Cd_2(\mathbf{L}^1)_2][ClO_4]_4]$ contained substitution disorder comprising of a molecule of acetonitrile and a water molecule and these were modelled in two positions using the part instruction and were both constrained using DELU and SIMU and ISOR for the water oxygen atom (figure 1). Also a perchlorate anion was situated on a special position and the chlorine oxygen bonds were restrained using SADI as well as ISOR for the two oxygen atoms. $[Cd_2(\mathbf{L}^2)_2][ClO_4]_4$ contained a substitution disorder comprising of a molecule of acetonitrile and a water molecule and these were modelled in two positions using the part instruction and were both constrained using DELU and SIMU and the bond lengths of the acetonitrile molecule constrained using DFIX. $[Cd_2(\mathbf{L}^3)_2][ClO_4]_4$ contained position disorder of a perchlorate anion (along with a molecule of acetonitrile) which was modelled in two positions using the part instruction. However, the disordered molecules were poorly behaved and constrained using SADI for the chlorine-oxygen and oxygen-oxygen distances as well as DELU and SIMU and ISOR for one of the oxygen atoms. Crystals of $[Zn_2(\mathbf{L}^2)_2][CF_3SO_3]_2$ decomposed rapidly and despite exhaustive attempts to collect data and growing the crystals under different conditions (changing solvents, counter ions and temperature) only very poorly diffracting crystals were formed. However, despite this data was collected and a gross molecular structure was obtained but contained sever disorder of a triflate counter ion and solvent molecules and to obtain data of reasonable quality the diffuse electron density was removed using the solvent mask facility in Olex2, resulting in very large voids in the crystal structure.[3] The solvent mask removed a total of 611.4 electrons in the unit cell which corresponds to triflate anion and one ethyl acetate and nitromethane solvent molecules per helicate complex (which corresponds to a total of 612 electrons in the unit cell). Given the obvious problems associated with extensive anion disorder in this crystal structure we have omitted any

structural discussion in the manuscript apart from we are confident that the gross solution is correct and that the complex is isostructural with $[Co_2(\mathbf{L}^2)_2][BF_4]_4$ (i.e. a *meso*-helicate Fig. 2).

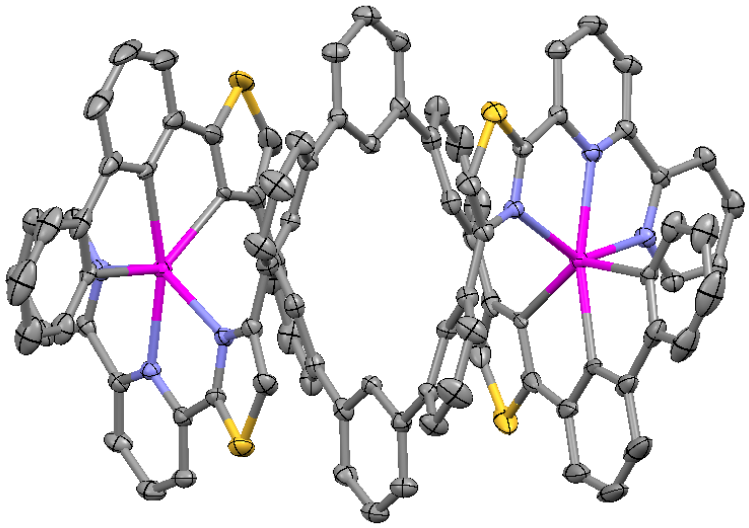


Fig 1 Solid-state structure of $[Cd_2(\mathbf{L}^1)_2]^{4+}$ complex cation (thermal ellipsoids shown at 40% probability level). The complex has crystallographically-imposed inversion symmetry.

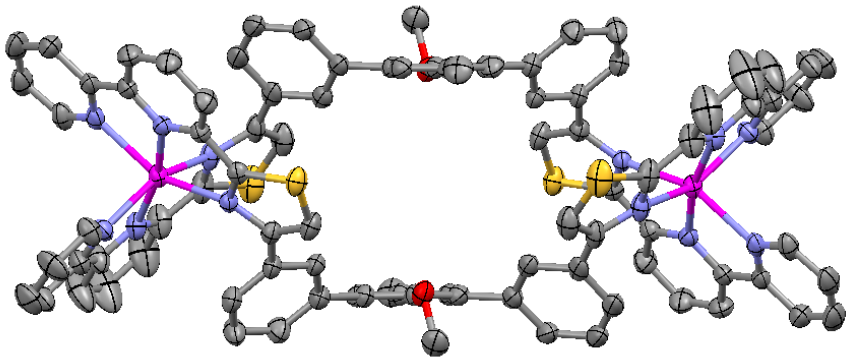


Fig 2 Solid-state structure of $[Zn_2(\mathbf{L}^2)_2]^{4+}$ complex cation (thermal ellipsoids shown at 40% probability level). The complex has crystallographically-imposed inversion symmetry.

Compound	$[Fe_2(\mathbf{L^1})_2][ClO_4]_4 \cdot 2MeNO_2$	$[Cd_2(\mathbf{L^1})_2][ClO_4]_4 \cdot 2MeNO_2 \cdot CHCl_3$ 0.47(CH_3NO_2) 1.05 (H_2O)	$[Cd_2(\mathbf{L^2})_2][ClO_4]_4 \cdot 4.7(CH_3CN)$ 0.3(H_2O)
Formula	$C_{45}H_{31}Cl_2FeN_7O_{10}S_2$	$C_{95.95}H_{60.51}Cd_2Cl_7N_{6.95}O_{18.95}S_4$	$C_{101.53}H_{78}Cd_2Cl_4N_{16.76}O_{18.24}S_4$
M	2041.28	2215.01	2319.48
Crystal system	Orthorhombic	Orthorhombic	Triclinic
Space group	Cmca	Cmca	P-1
a (Å)	45.5093(11)	47.3227(17)	12.6829(8)
b (Å)	22.2219(5)	21.8469(8)	16.4451(10)
c (Å)	17.1211(4)	17.0480(6)	25.0185(14)
α (˚)	90.00	90.00	94.6030(10)
β (˚)	90.00	90.00	101.5490(10)
γ (˚)	90.00	90.00	97.467(2)
V (Å^3)	17314.6(7)	17625.2(11)	5038.7(5)
Z	8	8	2
ρ_{calc} (Mg cm^{-1})	1.566	1.669	1.529
F(000)	8352	8923	2357
Crystal dimensions (mm)	0.5, 0.4, 0.2	0.25, 0.22, 0.21	0.2, 0.15, 0.1
Reflections measured	46105	56917	112792
Range	$1.79 \leq \theta \geq 28.42^{\circ}$	$1.58 \leq \theta \geq 30.51^{\circ}$	$1.43 \leq \theta \geq 30.03^{\circ}$
hkl range indices	$-60 \leq h \geq 60$, $-29 \leq k \geq 25$, $-22 \leq l \geq 15$	$-56 \leq h \geq 67$, $-31 \leq k \geq 28$, $-24 \leq l \geq 19$	$-17 \leq h \geq 17$, $-23 \leq k \geq 23$, $-35 \leq l \geq 33$
N^o independent reflections	10977	13590	29420
Reflections with $I > 2\sigma(I)$	6702	9178	16062
R_{int}	0.0544	0.0484	0.0807
Final R_1 values	0.0549	0.0546	0.0582
Final $wR(F^2)$ values	0.1354	0.1451	0.1237

Final R_1 values (all data)	0.1053	0.0901	0.1328
Final $wR(F^2)$ values (all data)	0.1586	0.1674	0.1518
GOF	1.019	1.046	1.014
Refined parameters	620	628	1361
Restraints	37	29	24
Largest peak and hole (e Å^{-3})	1.129, -0.792	1.656, -1.489	1.073, -0.958
CCDC Number	945477	949899	945476

Compound	$[Zn_2(\mathbf{L}^2)_2][CF_3SO_3]_4\cdot(CH_3CO_2CH_3CH_3)$ (CH_3NO_2)	$[Co_2(\mathbf{L}^2)_2][BF_4]_4\cdot 4(CHCl_3)$	$[Cd_2(\mathbf{L}^3)_2][ClO_4]_4\cdot 3.48(CH_3CN)$
Formula	$C_{101}H_{75}F_{12}N_{13}O1_8S_8Zn_2$	$C_{96}H_{68}B_4Cl_{12}Co_2F_{16}N_{12}\ O_2\ S_4$	$C_{110.95}H_{82.43}Cd_2Cl_4N_{15.47}O_{18}S_4$
M	1926.81	2440.36	2415.24
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	C 2/c	P-1	$P2_1/c$
a (Å)	40.525(4)	11.2403(4)	21.7000(11)
b (Å)	24.073(2)	14.2668(6)	12.4488(6)
c (Å)	12.188(1)	15.9890(6)	22.2200(11)
α (˚)	90	97.9160(10)	90
β (˚)	105.746(2)	102.7040(10)	117.0500(10)
γ (˚)	90	91.6320(10)	90
V (Å^3)	11443.7(18)	2472.85(16)	5345.9(5)
Z	4	1	2
ρ_{calc} (Mg cm^{-1})	1.1183	1.639	1.500
F(000)	3951.1988	1230	2457
Crystal dimensions (mm)	0.3, 0.15, 0.15	0.30, 0.30, 0.15	0.4, 0.15, 0.12

Reflections measured	53010	56159	53131
Range	$1.74 \leq \theta \geq 28.46^{\circ}$	$1.32 \leq \theta \geq 30.51^{\circ}$	$1.84 \leq \theta \geq 28.33^{\circ}$
hkl range indices	$-54 \leq h \geq 52$, $0 \leq k \geq 32$, $0 \leq l \geq 16$	$-16 \leq h \geq 16$, $-20 \leq k \geq 20$, $-22 \leq l \geq 22$	$-28 \leq h \geq 28$, $-8 \leq k \geq 16$, $-29 \leq l \geq 29$
N° independent reflections	14217	14975	13301
Reflections with $I > 2\sigma(I)$	6799	9866	8746
R_{int}	0.0675	0.0518	0.0618
Final R_1 values	0.0635	0.0611	0.0546
Final $wR(F^2)$ values	0.2050	0.1684	0.1503
Final R_1 values (all data)	0.1291	0.1036	0.0963
Final $wR(F^2)$ values (all data)	0.2419	0.1935	0.1743
GOF	0.9833	1.041	1.023
Refined parameters	578	669	734
Restraints	0	0	60
Largest peak and hole (e $Å^{-3}$)	0.7376, -0.9178	1.469, -1.185	2.560, -0.920
CCDC Number	945475	945478	945479

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