Supporting Information: "Donor-extended tripodal pyrroles: encapsulation, metallation, and H-bonded tautomers," John S. Hart, Fraser J. White, and Jason B. Love

General Experimental details

The synthesis of tris(5,5',5''-formyl-2,2',2''-pyrryl)ethane was carried out as described in the literature.[1] The syntheses of $[Li_3(L)]$ and $[K_3(L)]$ were carried out using standard Schlenk procedures or in a Vacuum Atmospheres OmniLab glovebox and using solvent dried by a Vacuum Atmospheres solvent purification assembly. All other synthetic procedures were carried out using commercial-grade solvent in air. Pyrrole was distilled under reduced pressure prior to use. All other chemicals were used as purchased. ^{1}H NMR spectra were recorded at 298 K on a Bruker DPX360, AVA400 and AVA500 at 360.13, 399.90 and 500.12 MHz respectively; $^{13}C\{^1H\}$ NMR spectra were recorded at 298 K on a Bruker DPX360 and AVA500 at 90.55, and 125.76 respectively. All ^{1}H NMR were referenced internally to residual protio-solvent resonances. Electrospray mass spectra were recorded using a Thermo-Finnigay LCQ Classic ion trap mass spectrometer and IR spectra on a Nicolet Avatar 320 FTIR spectrometer as KBr disks or Nujol mulls. Elemental analyses were carried out by Mr. Stephen Boyer at the London Metropolitan University.

Synthesis of H_3L

To a mixture of tris(5,5',5''-formyl-2,2',2''-pyrryl)ethane (0.48 g, 1.76 mmol) in acetonitrile (20 mL) was added cyclohexylamine (0.61 g, 6.16 mmol). The mixture was stirred for 16 h during which a colourless precipitate formed which was filtered, washed with acetonitrile and dried under vacuum to yield 0.89 g, 92% of H_3L as a colourless solid. Single crystals were grown by cooling a saturated CH_3CN solution.
^{1}H NMR (500MHz, C_6D_6): δ_H 8.47 (br. s., 3H, NH), 7.62 (s, 3H, CH imine), 6.26 (d, 3H, $^3J_{HH}$ = 3.57 Hz, pyrrole), 6.02 (d, 3H, $^3J_{HH}$ = 3.57 Hz, pyrrole), 2.84 (tt, 3H, $^3J_{HH}$ = 10.28 Hz, $^3J_{HH}$ = 3.63 Hz, CH Cyh), 1.70 (s, 3H, CH_3), 1.68 (m, 6H, Cyh), 1.62–1.50 (m, 12H, Cyh), 1.26-1.08 (m, 12H, Cyh) ppm; $^{13}C\{^1H\}$ NMR (360 MHz, C_6D_6): δ_C 149,1, 141.3, 130.6, 128.0, 114.7, 107.9, 68.23, 40.8, 34.7, 25.8, 24.8 ppm; Analysis. Found: C, 75.99, H, 8.89, N, 15.16% $C_{35}H_{48}N_6$ requires C, 76.05, H, 8.75, N, 15.20%; ESMS (+ve ion): m/z 553.73 ($[M+H]^+$, 100%); IR (KBr): υ 3288 (pyrrole NH), 1639 (C=N) cm^{-1}.

Synthesis of [Li_3(L)]

To a solution of H_3L (0.11 g, 0.20 mmol) in THF (5 mL), was added a solution of $LiN(SiMe_3)_2$ (0.11 g, 0.7 mmol) in THF (5 mL).The mixture was boiled for 16 h under N_2 after which the solvents were removed under reduced pressure to afford 0.10 g, 88 % of [Li_3(L)] as a colourless powder. Single crystals were grown by diffusion of hexane into a THF solution at –25 ^oC.

^1H NMR (500 MHz, C_6D_6/THF): δ_H 7.55 (s, 3H, CH imine), 6.85 (d, 3H, $^3J_{HH}$ = 3.68 Hz, pyrrole), 6.66 (d, 3H, $^3J_{HH}$ = 3.68 Hz, pyrrole), 2.78 (s, 3H, CH cyclohexyl amine), 1.62 (s, 3H, Me) 1.60 (m, 6H, Cyh) 1.55-1.42 (m, 12H, Cyh), 1.15-0.86 (m, 12H, Cyh) ppm. $^{13}C\{^1H\}$ NMR (500 MHz, C_6D_6): 149.09, 131.0 (q), 127.6, 114.1 (q), 108.7, 69.5, 41.1, 35.7, 30.0(q), 26.1, 25.2 ppm.

IR (nujol): υ No NH observed, 1639 (C=N) cm^{-1}

Synthesis of [K_3(L)]

To a solution of H_3L (0.20 g, 0.36 mmol) in THF (10 mL), was added a slurry of KH (0.06 g, 1.45 mmol) in THF (5 mL). The mixture was boiled for 16 h under N_2 after which the solvent was evaporated under reduced pressure to afford 0.22 g, 90 % of K_3L as a colourless solid.

^1H NMR (500MHz, C_6D_6/THF): δ_H 8.13 (s, 3H, CH imine), 6.53 (d, 3H, $^3J_{HH}$ = 2.78 Hz, pyrrole), 6.15 (d, 3H, $^3J_{HH}$ = 2.78 Hz, pyrrole), 3.08 (m, 3H, CH cyclohexyl), 2.10 (m, 9H, CH_3 and cyclohexyl), 1.76-1.48 (m, 24H, Cyh) ppm. $^{13}C\{^1H\}$ NMR (500 MHz, d5-pyridine): 161.9 (q), 156.4, 135.0, 116.0 (q), 105.7, 69.1, 48.7, 35.9, 31.1 (q), 26.0, 25.6 ppm

IR (nujol): υ No NH observed, 1605 (C=N) cm^{-1}

Synthesis of [$Co(H_3L)_2$][Cl]$_3$

To a solution of H_3L (0.10 g, 0.181 mmol) in EtOH (5 mL), was added a solution of $CoCl_2$ (0.024 g, 0.185 mmol) in EtOH (10 mL) and a mixture of NaCl (0.011 g, 1.81 mmol) in EtOH (2 mL). The resulting mixture was stirred at room temperature for 16 h after which the mixture was filtered. The filtrate was dried under reduced pressure and the residues were washed with EtOAc to afford 0.10 g, 88% of the cobalt complex as a green powder. Single crystals were grown by slow diffusion of Et_2O into a saturated MeOH solution. ^1H NMR (500MHz, MeOD): δ_H 7.45 (d, 6H, $^3J_{HH}$ = 4.57 Hz, pyrrole), 6.89 (d, 6H, $^3J_{HH}$ = 4.57 Hz, pyrrole), 5.60 (s, 6H, CH imine), 2.62

(m, 12H, CH_3 and CH cyclohexyl), 1.87 - 0.67 (m, 60H, cyclohexyl) ppm; $^{13}C\{^1H\}$ NMR (500 MHz, MeOD): δ_C 160.4 (q), 152.8, 129.6 (q), 125.0, 111.5, 59.6, 47.0, 32.3, 24.5, 24.2, 17.2 (q) ppm; ESMS (+ve ion): m/z 1161 ($[M+H]^+$, 100%); ESMS (-ve ion): m/z 1159 ($[M]^-$, 15.90%), 1195 ($[M+Cl]^-$, 76.88%), 1231($[M+2Cl]^-$, 100%); IR (KBr): υ 3419 (NH), 1636 (C=N) cm^{-1}.

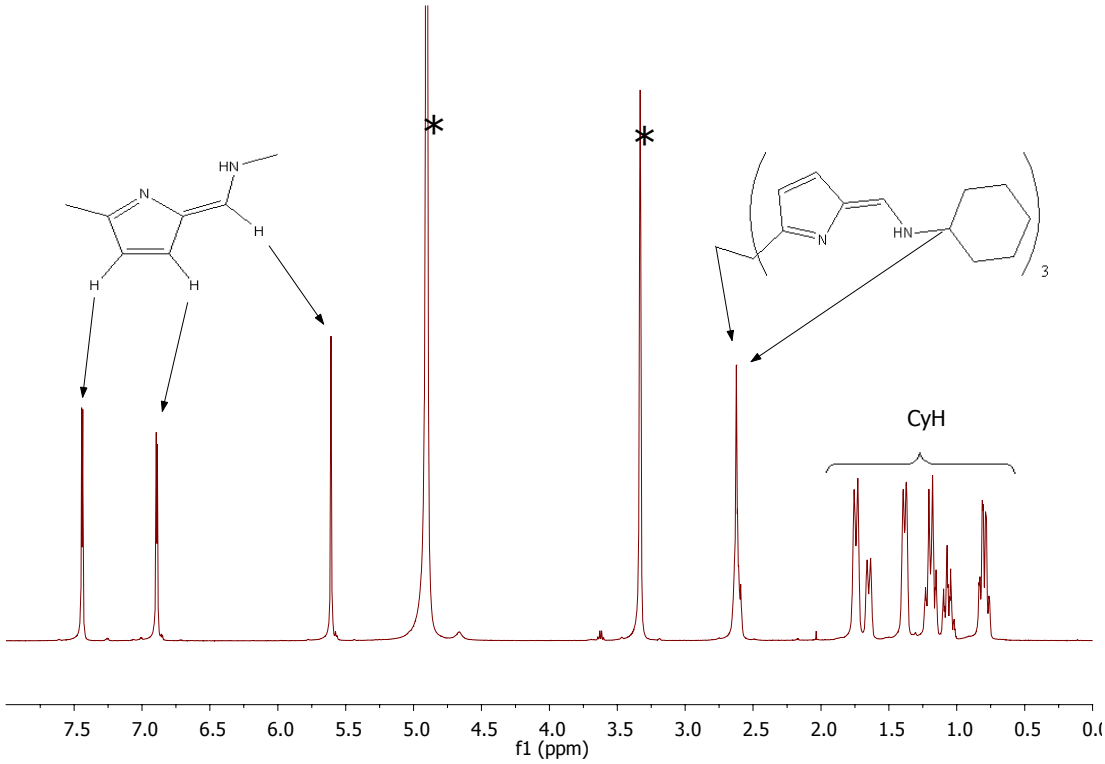

Figure S1. ^1H NMR spectrum of $[Co(H_3L)_2][Cl]_3$ in methanol-d_4

Synthesis of $[Zn_2(H_2L)_2][Cl]_2$

To a solution of H_3L (1.044 g, 1.89 mmol) in EtOH (50 mL), was added NEt_3 (0.38 g, 3.78 mmol) and a solution of $ZnCl_2$ (0.26 g, 1.89 mmol) in EtOH (10 mL). The resulting solution was stirred at room temperature for 16 h after which the solvents were evaporated under reduced pressure. The residual solids were extracted into $CHCl_3$ (50 mL), filtered, and the filtrate dried under reduced pressure to afford 0.32 g, 26 % of the binuclear zinc complex as a colourless solid.

^1H NMR (400 MHz, MeOD): δ_H 10.2 (dd, 4H, $^3J_{HH}$ = 15.1 Hz, $^3J_{HH}$ = 3.8 Hz, NH), 8.1 (s, 2H, imine), 7.65 (d, 4H, $^3J_{HH}$ = 4.4 Hz, pyrrole), 6.80 (d, 2H, $^3J_{HH}$ = 3.7, pyrrole), 6.67 (d, 2H, $^3J_{HH}$ = 3.7 Hz, pyrrole), 6.50 (d, 4H, $^3J_{HH}$ = 15.1 Hz, alkene), 5.98 (d, 4H, $^3J_{HH}$ = 3.9 Hz, pyrrole), 3.20 (m, 6H, CH Cy), 2.1 – 0.66 (m, 60H, Cy), 1.94 (s, 6H, Me) ppm; $^{13}C\{^1H\}$ NMR (400 MHz, MeOD): δ_C 160.5, 155.9, 155.0,

149.0, 136.0, 128.1, 124.8, 117.3, 117.1, 109.0, 65.7, 57.3, 45.1, 34.9, 32.6, 31.6, 25.3, 25.1, 24.7, 24.6 ppm; Analysis. Found: C, 64.49, H, 7.24, N, 12.72% $C_{70}H_{94}Cl_2N_{12}Zn_2$ requires C, 64.41, H, 7.26, N, 12.88%; ESMS (+ve ion): m/z 617.70 ([M-Zn-ligand]$^+$, 100%), 1233.7 ([M]$^+$, 59.92%); IR (KBr): υ 3419 (NH), 1652 (N=H), 1586 (C=N), 1281 (C-N) cm^{-1}

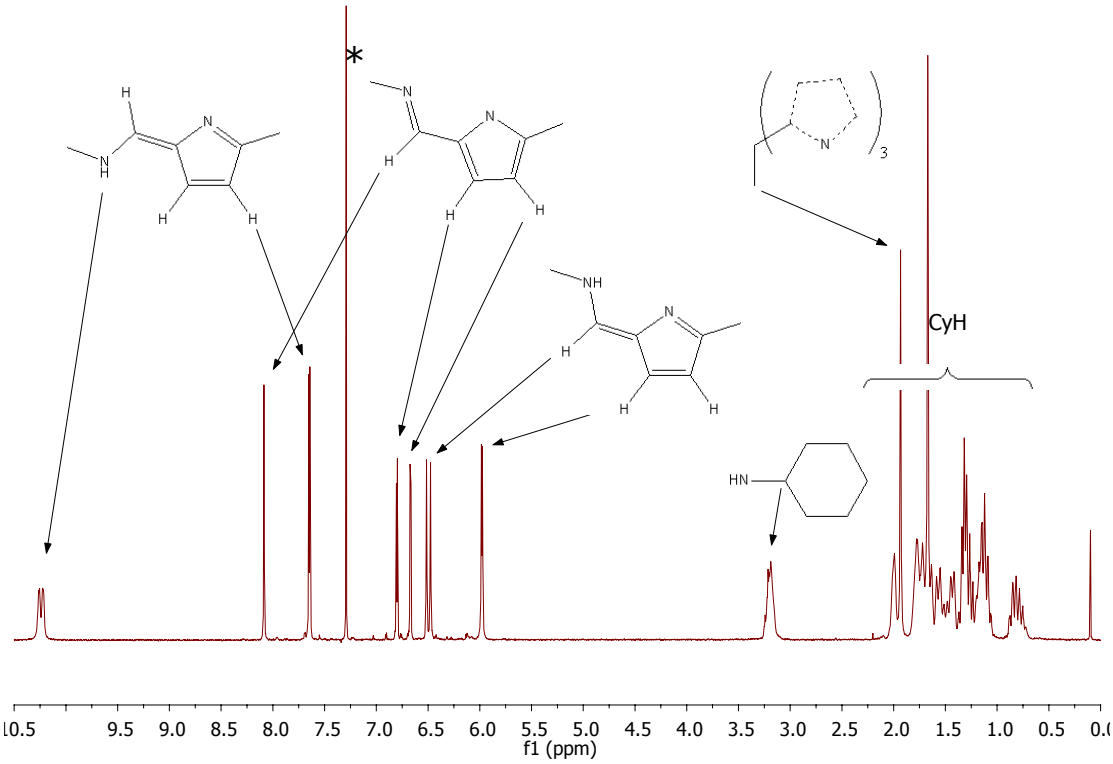

Figure S2. ^{1}H NMR spectrum of $[Zn_2(H_2L)_2][Cl]_2$ in $CDCl_3$

Crystallography

Single-crystal X-ray diffraction data were collected at 150 K using either a Bruker Apex II CCD diffractometer or an Oxford Diffraction Xcalibur Eos diffractometer equipped with an Eos detector, with graphite monochromated Mo*K*α radiation (λ = 0.71073Å) or using an Oxford Diffraction SuperNova Dual Atlas diffractometer with graphite-monochromated Cu*K*α radiation (λ = Å) (see Table S1 for details). The structures were solved by direct methods using the WinGX suite of programs[2] and refined using full-matrix least square refinement on $|F^2|$ using SHELXTL-97.[3] Unless otherwise stated, all non-hydrogen atoms were refined with anisotropic displacement parameters while hydrogen atoms were placed at calculated position and included as part of a riding model. The symmetry-generated structure of $H_3L.H_2O$ exhibited three-fold rotational disorder of the pyrrole-imine arms from the apical carbon atom C2 and was best refined with anisotropic atomic displacement parameters using a two site

50:50 occupancy protocol. The cyclohexyl carbon atoms were disordered and were refined using a restrained anisotropic model. The hydrogen atoms on the molecule of water were neither located nor placed geometrically, but were added to the formula; this has resulted in an A-alert in the CIF check. In $[Li_3(THF)_3(LiOH)_3(L)]_2$, the hydrogen atoms H100, H101, H102, located on O4, O5, and O6 respectively, were located from the difference Fourier map and refined with bond length restraints and riding thermal parameters. In this structure, one cyclohexyl group and THF ligand were disorder and were refined with variable two-site occupancies and with isotropic atomic displacement parameters. Also, the THF solvent of crystallization was disordered and was refined with restrained bond distances and isotropic atomic displacement parameters. In $[Co(H_3L)_2][Cl]_2$, all three cyclohexyl groups were disordered and were modelled with variable two-site occupancy and anisotropic atomic displacement parameters. The SQUEEZE routine of PLATON[4] was used to evaluate the void space, and it was found that 1070.4 $Å^3$ of void space was present in the unit cell, yet this contained only 20 e^-. The primary electron density was found to be within hydrogen-bonding distance to the Cl atoms, so it is likely that it is due to poorly-described water of crystallization within the void structure. Due to the poor modelling of this electron density, no atoms have been added to the formula. In $[Zn_2(H_2L)_2][Cl]_2$, one cyclohexyl group was disordered and was modelled over two sites with 0.52:0.48 occupancy, bond length restraints, and anisotropic atomic displacement parameters. Solvent of crystallization could not be modelled satisfactorily and the SQUEEZE routine of PLATON was used which found 646.3 $Å^3$ of void space with 148.5 e^- in the unit cell, which equates to the presence of approximately two molecules of THF per asymmetric unit; the appropriate number of C, H, and O atoms were added to the UNIT instruction; this has resulted in an A-alert in the CIF check. The relatively high residual electron density was located 0.916 Å from Zn1 and is attributed to absorption problems

References

1. P. D. Beer, A. G. Cheetham, M. G. B. Drew, O. D. Fox, E. J. Hayes and T. D. Rolls, *Dalton Trans.*, 2003, 603.
2. L. J. Farrugia, *J. Appl. Cryst.*, 1999, **32**, 837-838.
3. G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112-122.
4. A. L. Speck, PLATON, a multipurpose crystallographic tool, Utrecht University, Utrecht, The Netherlands, 2001.

Table S1. Crystal data for $H_3L.H_2O$, $[Li_3(THF)_3(LiOH)_3(L)]_2$, $[Co(H_3L)_2][Cl]_3$ and $[Zn_2(H_2L)_2][Cl]_2$

	$H_3L.H_2O$	**$[Li_3(THF)_3(LiOH)_3(L)]_2$**	**$[Co(H_3L)_2][Cl]_3$**	**$[Zn_2(H_2L)_2][Cl]_2(C_4H_8O)_2$**
Chemical formula	$C_{35}H_{50}N_6O$	$C_{100}H_{156}Li_{12}N_{12}O_{13.50}$	$C_{70}H_{88}CoN_{12}Cl_3$	$C_{78}H_{110}N_{12}O_2Zn_2Cl_2$
M_r	570.81	1825.65	1262.80	1449.42
Crystal system, space group	Trigonal, *R*3	Monoclinic, $P2_1/c$	Monoclinic, *C*2/*c*	Monoclinic, $P2_1/c$
a, *b*, *c* (Å)	14.6784 (2), 14.6784 (2), 12.8656 (2)	14.2257 (5), 20.6980 (6), 20.3016 (6)	31.439 (5), 14.0249 (7), 22.558 (4)	13.6569 (4), 25.0290 (8), 10.9583 (4)
α, β, γ (°)	90, 90, 120	90, 109.511 (4), 90	90, 130.79 (3), 90	90, 96.887 (3), 90
V (Å^3)	2400.59 (6)	5634.4 (3)	7531 (4)	3718.7 (2)
Z	3	2	4	2
Temperature	150(2)	150(2)	150(2)	150(2)
Radiation type	Mo *K*α	Mo *K*α	Mo *K*α	Cu *K*α
μ (mm^{-1})	0.07	0.07	0.38	1.87
Crystal size (mm)	0.30 × 0.21 × 0.19	0.50 × 0.32 × 0.17	0.20 × 0.17 × 0.10	0.21 × 0.11 × 0.05
Diffractometer	Bruker Apex II CCD on D8 diffractometer	Xcalibur, Eos diffractometer	Xcalibur, Eos diffractometer	SuperNova, Dual, Cu at zero, Atlas diffractometer
Absorption correction	Multi-scans *SADABS* 2007/2	Multi-scans CrysAlisPro, Oxford Diffraction Ltd.	Multi-scans CrysAlisPro, Oxford Diffraction Ltd.	Multi-scans CrysAlisPro, Oxford Diffraction Ltd.
T_{min}, T_{max}	0.661, 0.745	0.931, 1.000	0.168, 1.000	0.289, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5228, 940, 734	37811, 13199, 5744	36514, 6406, 4147	34512, 7361, 5203
R_{int}	0.026	0.033	0.051	0.101
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.065, 0.210, 1.06	0.076, 0.254, 1.01	0.075, 0.266, 1.06	0.097, 0.277, 1.06
No. of reflections	940	13199	6406	7361
No. of parameters	236	631	508	407
No. of restraints	93	61	548	151
H-atom treatment	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.14, -0.14	0.93, -0.37	1.21, -0.42	1.88, -0.73
CCDC number	816434	816435	816436	816437

CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.33.55 (release 05-01-2010 CrysAlis171 .NET) (compiled Jan 5 2010,16:28:46) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
Computer programs: *SMART* (Siemens, 1993), CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.33.55 (release 05-01-2010 CrysAlis171 .NET) (compiled Jan 5 2010,16:28:46), *SAINT* (Siemens ,1995), *SHELXS97* (Sheldrick, 1990), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 1997), *SHELXL97* (Sheldrick, 2008), *ORTEP* (Farrugia, 1997), *enCIFer* (Allen *et al.*, 2004).