Electronic Supplementary Material for CrystEngComm

Experimental

General

Infrared spectra were recorded on an ATI Mattson FTIR spectrometer using potassium bromide or sodium chloride discs. Ultraviolet spectra were recorded using a Perkin-Elmer Lambda 15 UV-VIS spectrometer with $CHCl_3$, MeOH or THF as the solvent. ^1H and ^{13}C NMR spectra were recorded at 250 MHz and 62.9 MHz respectively using a Brucker AC 250 spectrometer. In some cases ^1H and ^{13}C NMR spectra were recorded at 400 MHz and 100.5 MHz respectively using a Varian 400 spectrometer. Solvents used for NMR spectral analyses include $CDCl_3$, CD_3OD, $(CD_3)_2SO$ and D_2O. Chemical shifts, δ are given in ppm relative to the residual solvent and coupling constants, *J* are given in Hz. Elemental analysis was carried out at Butterworth Laboratories using a PE 2400 CHN analyser. A number of low resolution mass spectra were obtained using electrospray ionisation on a Finnigan Navigator Mass Spectrometer. Additionally, a number of low resolution mass spectra were obtained at the University of Wales, Swansea using electron impact ionisation, chemical ionisation and electrospray ionisation methods. Accurate mass spectra were determined at the University of Wales, Swansea using fast atom bombardment methods. Melting points were determined on a Kofler hot-stage microscope.

All starting materials were obtained from either Aldrich and Lancaster Synthesis. Solvents were used as supplied unless otherwise stated. DCM was dried under argon over sodium wire. THF was dried under argon over sodium wire with benzophenone as an indicator. EtOH was distilled from CaH_2 under nitrogen.

Dibromo-*p*-xylenes **1** and **3** were commercially available from Aldrich.

1,4-Bis(methyltributylphosphonium)benzene dibromide 2

α,α-Dibromo-*p*-xylene **1** (10.0 g, 38 mmol) and tributylphosphine (15.3 g, 76 mmol) were slowly added to DMF (100 ml) and refluxed for 1 h. During this time a white precipitate formed. The mixture was cooled to room temperature and the precipitate was filtered and washed with petrol (40-60 ^oC) (3 × 100 ml) then dried for 24 h to give the *title compound* (21.1 g, 83 %) as a white crystalline solid, mp > 250 °C (Found: C, 57.0; H, 9.0. $C_{32}H_{62}Br_2P_2$ requires C, 57.5; H, 9.4 %); λ_{max} ($CHCl_3$)/nm 284 (log ε 4.3); ν_{max} (KBr)/cm^{-1} 3444w, 2959s, 2924s, 2893s, 2795w, 1512w, 1456m, 1409w, 1097w, 907w and 716w; δ_H (250 MHz; $CDCl_3$) 0.86 (18H, t, *J* 5.5), 1.42 (24H, m), 2.30 (12H, m), 4.32 (4H, d, *J* 14.8) and 7.54 (4H, s); δ_C (62.9 MHz; $CDCl_3$) 13.5, 18.4, 19.2, 23.7, 26.7, 129.2 and 131.3; *m/z* 254.3 ($[M - 2Br]^{2+}$, 100 %).

1,3-Bis(methyltributylphosphonium)benzene dibromide 4

α,α-Dibromo-*m*-xylene **3** (5 g, 19 mmol) and tributylphosphine (7.8 g, 38 mmol) were slowly added to DMF (75 ml) and refluxed for 1 h. The mixture was cooled to room temperature and EtOAc (40 ml) was added to induce precipitation of a white solid. The material was filtered and washed with petrol (40 - 60 °C), (3 × 100 ml) then dried for 24 h to yield the *title compound* (11.8 g, 94 %) as a white crystalline solid, mp 182 -184 °C; λ_{max} ($CHCl_3$)/nm 239 (log ε 3.8); ν_{max} (KBr)/cm^{-1} 2960vs, 2924s, 2873s, 2791w, 1601w, 1484m, 1466m, 1409m, 1384w, 1229w, 1098m, 940w, 912m, 819w and 713m; δ_H (250 MHz; $CDCl_3$) 0.87 (18H, t, *J* 5.5, CH_3), 1.41 (24H, m, CH_2CH_2), 2.36 (12H, m, PCH_2), 4.24 (4H, d, *J* 15.3, P*CH₂*Ph), 7.30 (1H, m), 7.41 (2H, d, *J* 7) and 8.23 (1H, s); δ_C (62.9 MHz; $CDCl_3$) 13.5, 18.5, 19.3, 23.7, 26.4, 130.3 and 132.4 (2 resonance's missing); *m/z* 254.2158 ($[M - 2Br]^{2+}$. $C_{32}H_{62}P_2$ requires 254.2158), 254.1 ($[M - 2Br]^{2+}$, 100 %) and 507.4 ($[M - Br - HBr]^+$, 12 %).

2-Pyridylstilbenes

2-Acetylpyridine (2.42 g, 20 mmol) was added to a solution of 1,4-*bis*(methyltributylphosphonium)benzene dibromide **2** (6.69 g, 10 mmol) in dry EtOH (100 ml). A fresh solution of NaOEt was slowly added to the stirred mixture over 30 min. After a further 72 h the EtOH was removed and H_2O (100 ml) was added to the residue and this mixture was stirred vigorously for 2 h yielding a grey precipitate that was filtered off. The solid was dried for 72 h furnishing a mixture of *compounds* (1.87 g, 61 %) as an off white solid. The mixture was purified by column chromatography (silica gel, 200 g; eluent 80 % DCM : 20 % EtOAc) The fraction with an R_f of 0.67 was collected to yield *1,4-bis[2-(2-pyridyl)-2-methyl-trans-ethenyl]benzene* **5** (1.16 g, 38 %) as a white solid, mp 114 - 116 °C (from ethylacetate); λ_{max} ($CHCl_3$)/nm 326 (log ε 4.7); ν_{max} (KBr)/cm^{-1} 3391w, 3046w, 3001m, 2861m, 1581vs, 1561m, 1468s, 1427vs, 1382m, 1152m, 1032w, 909m, 889w, 822m, 775vs and 742s; δ_H (250 MHz; $CDCl_3$) 2.40 (6H, s, trans CH_3), 7.16 (2H, t, *J* 5.0), 7.46 – 7.56 (8H, m), 7.68 (2H, t, *J* 7.3) and 8.62 (2H, d, *J* 3.8); δ_C (62.9 MHz; $CDCl_3$) 16.1, 120.2, 121.9, 129.3, 129.9, 136.5, 136.6, 148.9 and 159.9 (one resonance is overlapping); *m/z* 313.1703 ($[M + H]^+$ $C_{22}H_{21}N_2$ requires 313.1699), 313.5 ($[M + H]^+$, 100 %); The fraction with an R_f of 0.45 was collected to yield *1,4-bis[2-(2-pyridyl)-2-methyl-cis-ethenyl]benzene* **6** (0.22 g, 7 %) a white solid, mp 108 - 110 °C (from hexane); λ_{max} ($CHCl_3$)/nm 312 (log ε 4.6); ν_{max} (KBr)/cm^{-1} 3074m, 3054w, 3011m, 2966s, 2912m, 2847w, 1585vs, 1561s, 1508m, 1469vs, 1429s, 1409m, 1371m, 1279w, 1237w, 1149m, 1096m, 1044w, 1000w, 879vs, 823w, 791vs, 752s and 628; δ_H (250 MHz; $CDCl_3$) 2.22 (6H, s, cis-CH_3), 6.52 (2H, s, cis vinyllic CH), 6.65 (4H, s, cis Ph), 6.97 (2H, d, *J* 7.8) 7.08 (2H, t, *J* 5) 7.41 (2H, t, *J* 7.8) and 8.58 (2H, d, *J* 3.8); δ_C (62.9 MHz; $CDCl_3$) 24.9, 121.8, 124.1, 128.4, 128.6, 135.5, 135.9, 138.3, 149.6 and 160.4; *m/z* 313.1703 ($[M + H]^+$ $C_{22}H_{21}N_2$ requires 313.1699), 313.3 ($[M + H]^+$, 100 %)

(*R,R*)-, (*S,S*)- and (*R,S*)-1,4-*Bis*[2-(2-pyridyl)-2-methyl)ethyl]benzene 7

1,4-*Bis*[(2-(2-pyridyl)-2-methyl-*trans*-ethenyl)]benzene (1.0 g, 3.2 mmol) was dissolved in MeOH (10 ml) and 10 % palladium on carbon (100 mg) was added. This mixture was stirred vigorously and hydrogenated at 1 atmosphere pressure at 24 °C until no more hydrogen was absorbed. The solution was filtered through a celite pad then through a plug of silica to yield the *title products* **7** (0.71 g, 70 %) as a viscous oil, bp 164 - 166 °C; λ_{max} ($CHCl_3$)/nm 260 (log ε 4.7); $[\alpha]_D$ ($CHCl_3$)/° – 3.4 °; ν_{max} (NaCl)/cm^{-1} 3049w, 3006m, 2963s, 2929s, 2867m, 1590vs, 1569s, 1513m, 1474s, 1433s, 1369w, 1148m, 1098w, 1048w, 1019w, 991w, 786m and 748s; δ_H (250 MHz; $CDCl_3$) 1.21 (6H, d, *J* 7.5, CH_3), 2.78 (2H, dd, *J* 7.5, 5.3, Ph$CH_{\beta'}$), 2.97 – 3.15 (4H, m, Ph$CH_{\beta}CH$), 6.90 (4H, s, Ph), 6.97 (2H, d, *J* 8.0), 7.06 (2H, t, *J* 5.3), 7.50 (2H, dt, *J*, 7.5, 1.8) and 8.54 (2H, d, *J* 4.3); δ_C (62.9 MHz; $CDCl_3$) 19.9, 42.9, 63.9, 121.2, 121.9, 128.9, 136.2, 138.1, 149.2 and 165.7; *m/z* 317.2016 ($[M + H]^+$ $C_{22}H_{25}N_2$ requires 317.2012), 317.3 ($[M + H]^+$, 100 %).

3-Pyridylstilbenes

3-Acetylpyridine (2.42 g, 20 mmol) was added to a solution of 1,4-*bis*(methyltributylphosphonium)benzene dibromide **2** (6.69 g, 10 mmol) in dry EtOH (100 ml). A fresh solution of NaOEt was slowly added to the stirred mixture over 30 min. After a further 72 h the EtOH was removed and H_2O (100 ml) was added to the residue and this mixture was stirred rigorously for 2 h to yield a grey precipitate and a dark oil. The grey precipitate which is the crude mixture of isomers was filtered off and dried and then purified by column chromatography (silica gel 200 g; eluent 90 % $CHCl_3$: 10 % EtOAc gradiented to 90 % EtOAc : 10 % $CHCl_3$) to yield a mixture of compounds (0.75 g, 34 %) as a white solid, mp 146 - 150 °C. The isomer mixture (0.75 g, 2.4 mmol) was added to EtOAc (10 ml) and heated until the sample had totally dissolved. The solution was allowed to cool down to room temperature during which crystals formed which were filtered and dried for 24 h yielding *1,4-bis[2-(3-pyridyl)-2-methyl-cis-ethenyl)]benzene* **8** (0.14 g, 19 %) as transparent blocks, mp 158 - 160 °C; λ_{max} ($CHCl_3$)/nm

306 (log ε 4.5); ν_{max} (KBr)/cm^{-1} 3021m, 2968s, 2906m, 1584w, 1562s, 1508m, 1476m, 1405vs, 1372s, 1080w, 1024s, 885vs, 808s and 716vs; δ_H (250 MHz; $CDCl_3$) 2.16 (6H, s, cis CH_3), 6.45 (2H, s, cis vinyllic CH), 6.66 (4H, s, cis Ph), 7.15 (2H, t, *J* 6.3), 7.42 (2H, d, *J* 7.5), 8.36 (2H, s) and 8.42 (2H, d, *J* 4.5); δ_C (62.9 MHz; $CDCl_3$) 26.5, 123.3, 128.2, 128.8, 134.8, 135.2, 135.8, 137.6, 148.1 and 149.4; *m/z* 313.1700 ([M + H]$^+$ $C_{22}H_{21}N_2$ requires 313.1699), 313.2 ([M + H]$^+$, 100 %).

(*R,R*)-, (*S,S*)- and (*R,S*)-1,4-*Bis*[2-(3-pyridyl)-2-methyl)ethyl]benzene 9

Compound mixture of 3-pyridyl stilbenes (1.0 g, 3.2 mmol) was dissolved in MeOH (10 ml) and 10 % palladium on carbon (100 mg) was added. This rigorously stirred mixture was hydrogenated at 1 atmosphere pressure and at 24 °C until no more hydrogen was absorbed. The solution was filtered through a celite pad then through a plug of silica to yield the *title products* **9** (0.64 g, 63 %) as a white solid, mp 52 - 54 °C; λ_{max} ($CHCl_3$)/nm 263 (log ε 4.4); $[\alpha]_D$ ($CHCl_3$)/° 34.4 °; ν_{max} (KBr)/cm^{-1} 3019m, 2967s, 2929s, 2869w, 1573m, 1514m, 1452w, 1421vs, 1010m, 809s and 718vs; δ_H (250 MHz; $CDCl_3$) 1.24 (6H, d, *J* 7.0, CH_3), 2.74 – 3.01 (6H, m, $CHCH_2$), 6.87 (4H, d, *J* 2.8, Ph), 7.16 (2H, dd, *J* 8.0, 5.0), 7.39 (2H, dd, *J* 8.0, 1.5), 8.35 (2H, t, *J* 2.0) and 8.00 (2H, dt, *J*, 4.8, 1.5); δ_C (62.9 MHz; $CDCl_3$) 20.9, 39.5, 44.3, 123.3, 128.9, 134.4, 137.6, 141.7, 147.6 and 149.2; *m/z* 317.2014 ([M + H]$^+$. $C_{22}H_{25}N_2$ requires 317.2012), 317.3 ([M + H]$^+$, 100 %).

4-Pyridylstilbenes

4-Acetylpyridine (2.42 g, 20 mmol) was added to a solution of 1,4-*bis*(methyltributylphosphonium)benzene dibromide **2** (6.69 g, 10 mmol) in dry EtOH (100 ml). A fresh solution of sodium ethoxide was slowly added to the stirred mixture over 30 min. After a further 72 h the EtOH was removed and H_2O (100 ml) was added to the residue and the mixture was stirred vigorously for 2 h. A grey precipitate was filtered off and dried. The crude isomer mixture was purified by column chromatography (silica, 200 g; eluent 90 % $CHCl_3$: 10 % EtOAc, gradiented to 90 % EtOAc : 10 % $CHCl_3$) to yield a mixture of compounds (1.89 g, 60 %) as a white solid, mp 130 - 134 °C. The isomer mixture (1.89 g, 6 mmol) was added to MeOH (25 ml) and heated until the sample had totally dissolved. The solution was cooled to room temperature to give crystals which were filtered and dried for 24 h yielding *1,4-bis[2-(4-pyridyl)-2-methyl-cis-ethenyl]benzene* **10** (0.39 g, 21 %) as transparent blocks, mp 187 - 188 °C (Found: C, 84.2; H, 6.4; N, 8.9. $C_{22}H_{20}N_2$ requires C, 84.6; H, 6.5; N, 8.9 %); λ_{max} ($CHCl_3$)/nm 307 (log ε 4.7); ν_{max} (KBr)/cm^{-1} 3899m, 3590w, 3487w, 3445m, 3324w, 1589s, 1538w, 1409m, 1373w, 1213w, 895m, 821s and 737w; δ_H (250 MHz; $CDCl_3$) 2.12 (6H, s), 6.44 (2H), 6.68 (4H, s), 7.02 (4H, d, *J* 4.5) and 8.45 (4H, d, *J* 4.5); δ_C (62.9 MHz; $CDCl_3$) 26.1, 123.3, 128.3, 128.7, 135.1, 135.8, 150.0 (one resonance is overlapping); *m/z* 313.1703 ($[M + H]^+$ $C_{22}H_{21}N_2$ requires 313.1699), 313.1 ($[M + H]^+$, 100 %).

(*R,R*)-, (*S,S*)- and (*R,S*)-1,4-Bis[2-(4-pyridyl)-2-methylethyl]benzene 11

The isomer mixture of 4-pyridylstilbenes (1.2 g, 3.8 mmol) was dissolved in MeOH (10 ml) and 10 % palladium on carbon (100 mg) was added. The mixture was stirred vigorously and hydrogenated at 1 atmosphere pressure and at 24 ^oC until no more hydrogen was absorbed. The solution was filtered through a celite pad then through a plug of silica to yield a mixture of the *title products* **11** (0.72 g, 60 %) as a white solid, mp 71 - 73 ^oC; λ_{max} ($CHCl_3$)/nm 284 (log ε 4.1); $[\alpha]_D$ ($CHCl_3$)/^{o} – 4.7 ^{o}; ν_{max} (KBr)/cm^{-1} 3495w, 3454m, 3418w, 3377s, 3345m, 3291m, 2987m, 2924m, 2901w, 2843m, 1598vs, 1556m, 1493m, 1453m, 1412s, 1377w, 1228w, 1116w, 1067w, 991w, 785vs and 763w; δ_H (250 MHz; $CDCl_3$) 1.21 (6H, d, *J* 6.8), 2.71 – 2.90 (6H, m), 6.85 (4H, s,), 6.99 (4H, d, *J* 5.0) and 8.42 (4H, d, *J* 5.0); δ_C (62.9 MHz; $CDCl_3$) 20.5, 41.3, 43.7, 122.6, 128.9, 137.5, 149.6 and 155.6; *m/z* 317.2015 ($[M + H]^+$ $C_{22}H_{25}N_2$ requires 317.2012), 317.0 ($[M + H]^+$, 100 %).

(*R,R*)-, (*R,S*)- and (*S,S*)-1,3-Bis[2-(4-pyridyl)-2-methyl)ethyl]benzene 13

4-Acetylpyridine (1.30 g, 11 mmol) was added to a solution of 1,3-*bis*(methyltributylphosphonium)benzene dibromide **4** (3.60 g, 11 mmol) in dry EtOH (60 ml). A fresh solution of sodium ethoxide was slowly added to the stirred mixture over 30 min. After a further 72 h the EtOH was removed and H_2O (100 ml) was added to the residue and this mixture was shaken rigorously for 10 min. This solution was centrifuged for a further 10 min then the H_2O layer was decanted off leaving the oil residue. This process was repeated twice before the sample, as a mixture of isomers **12**, was dried under vacuum for 4 h. The material was passed through a column, (silica, 200 g; eluent 100 % EtOAc gradiented to 80 % EtOAc : 20% EtOH, R_f 0.52) before being dissolved in MeOH (10 ml) and 10 % palladium on carbon (80 mg) was added. This rigorously stirred mixture was hydrogenated at 1 atmosphere pressure and at 24 ^oC until no more hydrogen was absorbed. The solution was filtered through a celite pad then passed through a column, (silica; eluent 80 % EtOAc : 20 % EtOH, R_f 0.52) where the first 50 % of tubes containing product were collected to yield the *title products* **13** (0.38 g, 26 %) as a viscous clear oil, bp 187 - 189 ^oC; λ_{max} ($CHCl_3$)/nm 256 (log ε 4.7); $[\alpha]_D$ ($CHCl_3$)/^{o} 4.3 ^{o}; ν_{max} (NaCl)/cm^{-1} 3024m, 2961s, 2923s, 2871w, 1597vs, 1557m, 1489w, 1456m, 1414s, 1376w, 1220w, 1069w, 993m, 819s, 760m and 704m; δ_H (250 MHz; $CDCl_3$) 1.17 (6H, d, *J* 6.5, CH_3), 2.68 – 3.89 (6H, m, $CH_{\beta}H_{\beta'}CH$), 6.63 (1H, s,), 6.83 (1H, d, *J* 7.8), 6.99 – 7.09 (6H, m) and 8.43 (4H, d, *J* 4.3); δ_C (62.9 MHz; $CDCl_3$) 20.5, 41.4, 44.0, 122.6, 126.9, 128.2, 129.8, 139.6, 149.7 and 155.5; *m/z* 317.2014 ($[M + H]^+$. $C_{22}H_{25}N_2$ requires 317.2012), 317.3 ($[M + H]^+$, 100 %).

Single crystal structures of 6, 8 and 10

The X-ray structure determinations were carried out using the same general procedure as described in the main section for the metal complexes. Crystallographic details for **6**, **8** and **10** are listed in Table 1. Each of the three title compounds crystallises in a monoclinic ($P2_1/c$) structure. Each of the molecules (shown in Fig. 1) possesses a centre of inversion. The asymmetric units of **6** and **8** contain half a molecule (Z = 2), whereas the asymmetric unit of **10** contains the halves of two different molecules (Z = 4). It is convenient to use the three torsion angles T_1, T_2, and T_3, defined in Scheme 4, in order to characterise the conformation of these ligands. These angles are also useful to describe the ligand **11** in structures **14–17** and **19**, respectively. The crystallographic inversion symmetry found in the solid state structures of molecules 6, 8 and 10 means that $T_1 = -T_3$ and $T_2 = 180°$. The values of T_1 are 3.1(2)° (in 6), 3.9(5)° and 4.0(5)° (in 8) and 4.7(2)° (in 10). The conformation of the molecules of these three structures is therfore, with reference to T_1, T_2 and T_3, *cis-trans-cis*.

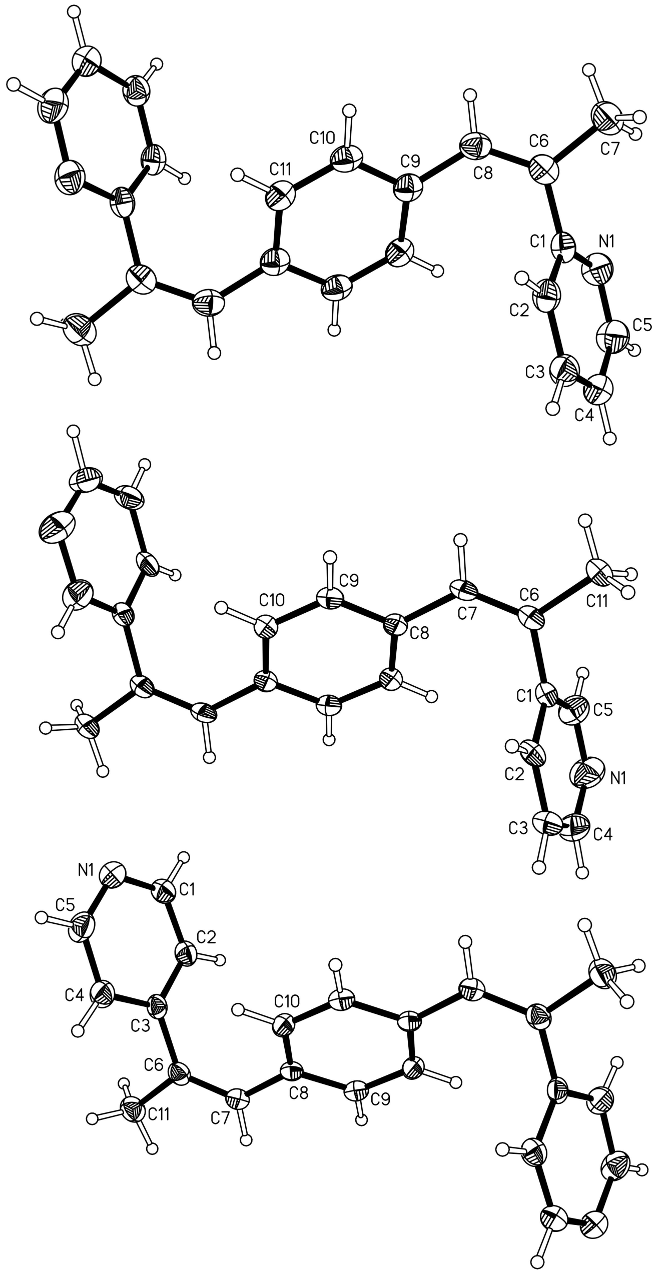

Fig. S1 Molecular structures of **6** (top), **8** (middle; one of two independent molecules) and **10** (bottom). Displacement ellipsoids are drawn at the 50% level.

Tables

Table S1. Crystallographic data for structures **6**, **8**, **10**

	6	**8**	**10**
Formula	$C_{22}H_{20}N_2$	$C_{22}H_{20}N_2$	$C_{22}H_{20}N_2$
Formual weight	312.40	312.40	312.40
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
Z	2	4	2
a (Å)	5.1824(2)	24.7921(9)	6.6661(2)

b (Å)	15.3047(8),	5.9555(2)	12.8086(4)
c (Å)	11.2209(5)	11.8649(3)	10.5343(4)
α (°)			
β (°)	100.618(3)	101.992(2)	105.883(1)
γ (°)			
V (Å^3)	874.75(7)	1713.61(10)	865.12(5)
D_{calc} (g/cm^{-})	1.186	1.211	1.199
μ(Mo-K$_a$) (mm^{-1})	0.070	0.071	0.070
Reflections collected	7759	14219	4712
Independent reflections (R_{nt})	1694 (0.0553)	3055 (0.1214)	1591 (0.0461)
Parameters	120	238	118
R_1 [I> 2σ(I)]^e	0.0410	0.0787	0.0385
wR_2 (all data)^e	0.1129	0.1558	0.1062
Crystal	colourless block	colourless plate	colourless block
Crystal size (mm)	0.20 × 0.20 × 0.10	0.50 × 0.20 × 0.07	0.50 × 0.50 × 0.30

Cd1–N3	2.324(8)	N3–Cd1–O1	82.9(4)
Cd1–O1	2.350(12)	N3–Cd1–N4^i	169.5(4)
Cd1–N4^i	2.359(7)	O1–Cd1–N4^i	105.7(3)
Cd1–N2	2.379(7)	N3–Cd1–N2	94.3(3)
Cd1–N1	2.390(8)	O1–Cd1–N2	87.9(4)
Cd1–O4	2.464(12)	N4^i–Cd1–N2	91.9(3)
		N3–Cd1–N1	86.2(3)
		O1–Cd1–N1	79.7(4)
		N4^i–Cd1–N1	89.6(3)
		N2–Cd1–N1	167.5(4)
		N3–Cd1–O4	85.2(4)
		O1–Cd1–O4	158.4(3)
		N4^i–Cd1–O4	88.2(3)
		N2–Cd1–O4	75.0(4)
		N1–Cd1–O4	117.4(4)

Table S2. Selected bond lengths and angles for **14** (Å, °).

Symmetry operation: (i): x, $y + 1$, z

Cd1–N1	2.324(3)	N1–Cd1–N2	89.40(13)
Cd1–N2	2.329(4)	N1–Cd1–N2^i	90.60(13)
Cd1–O10	2.376(3)	N1–Cd1–O10	87.58(12)
		N2–Cd1–O10	90.59(13)

Symmetry operation: (i): $-x$, $-y$, $-z$

Table S3. Selected bond lengths and angles for **15** (Å, °).

Co1–O1	2.073(6)	O1–Co1–O2	174.8(3)

Co1–O2	2.077(6)	O1–Co1–N11	89.8(2)
Co1–N11	2.147(5)	O2–Co1–N11	90.5(2)
Co1–N12^{i}	2.150(5)	O1–Co1–N12^{i}	90.7(2)
Co1–N22^{ii}	2.155(7)	O2–Co1–N12^{i}	89.5(2)
Co1–N21	2.165(6)	N11–Co1–N12^{i}	174.6(3)
		O1–Co1–N22^{ii}	88.1(3)
		O2–Co1–N22^{ii}	86.7(2)
		N11–Co1–N22^{ii}	92.6(3)
		N12^{i}–Co1–N22^{ii}	92.9(2)
		O1–Co1–N21	92.7(3)
		O2–Co1–N21	92.6(2)
		N11–Co1–N21	87.5(3)
		N12^{i}–Co1–N21	87.0(2)
		N22^{ii}–Co1–N21	179.2(3)

Table S4. Selected bond lengths and angles for **16** (Å, °).

Symmetry operations: (i) –x+3/2,y+1/2,z–1/2 (ii) –x+3/2,y+1/2,z+1/2

Ni1–O2	2.080(5)	O2–Ni1–O1	174.5(2)
Ni1–O1	2.082(5)	O2–Ni1–N22^{i}	86.4(2)
Ni1–N22^{i}	2.097(6)	O1–Ni1–N22^{i}	88.2(3)
Ni1–N12^{ii}	2.098(5)	O2–Ni1–N12^{ii}	89.1(2)
Ni1–N11	2.102(5)	O1–Ni1–N12^{ii}	91.8(2)
Ni1–N21	2.120(6)	N22^{i}–Ni1–N12^{ii}	91.4(2)
		O2–Ni1–N11	90.8(2)
		O1–Ni1–N11	88.6(2)
		N22^{i}–Ni1–N11	92.9(2)
		N12^{ii}–Ni1–N11	175.7(2)
		O2–Ni1–N21	93.2(2)
		O1–Ni1–N21	92.2(2)
		N22^{i}–Ni1–N21	178.8(3)
		N12^{ii}–Ni1–N21	87.5(2)
		N11–Ni1–N21	88.2(2)

Table S5. Selected bond lengths and angles for **17** (Å, °).

Symmetry operations: (i) –x+3/2,y+1/2,z+1/2 (ii) –x+3/2,y+1/2,z–1/2

Cd1–N1	2.324(3)	N1^{i}–Cd1–N1	165.73(13)
Cd1–N2^{ii}	2.385(3)	N1^{i}–Cd1–N2^{ii}	89.14(9)
Cd1–O22	2.499(17)	N1–Cd1–N2^{ii}	93.09(9)
Cd1–O12	2.5864(14)	N1–Cd1–N2^{iii}	89.14(9)
Cd1–O21	2.5732(14)	N2^{ii}–Cd1–N2^{iii}	161.97(13)
		N20···Cd1···N10	173.29(9)
		N1–Cd1···N20	89.32(12)
		N1–Cd1···N10	97.14(6)
		N2^{ii}–Cd1···N10	80.98(7)
		N2^{ii}–Cd1···N20	96.91(18)
		N2^{i}–Cd1···N20	101.01(18)
		N1^{i}–Cd1···N20	76.41(12)
		N1–Cd1···N20	89.32(12)

Table S6. Selected interactomic distances and angles for **18** (Å, °).

Symmetry operations: (i) –x+1,y,–z+5/2 (ii) x,y,z+1 (iii) –x+1,y,–z+3/2

Cu1–N11	2.001(6)	N11–Cu1–N12	92.5(2)
Cu1–N12	2.057(6)	N11–Cu1–O3	89.9(2)
Cu1–O3	2.563(6)	N12–Cu1–O3	93.2(2)
Cu2–N21	2.011(7)	N21–Cu2–N22	93.0(3)
Cu2–N22	2.015(6	N21–Cu2–O5	89.6(2)
Cu2–O5	2.609(5)	N22–Cu2–O5	87.0(2)

Table S7. Selected bond lengths and angles for **19** (Å, °).