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### Self-assembly of chelating, bridging N, N, N donor ligands and Cu(I), Cu(II), Cd(II), Hg(II): molecular box versus coordination polymer

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#### Abstract

Three flexible chelating and bridging ligands, (E)-N-(pyridin-2-ylmethylene)-1-(pyridin-3yl)methanamine  $(L_1)$ , 1-(pyridine-2-yl)-N-(pyridin-3-ylmethyl)methanamine  $(L_1')$ , (E)-N-(pyridin-2-ylmethylene)-1-(pyridin-4-yl)methanamine (L<sub>2</sub>), have been synthesized. The reaction of these ligands with various metal salts yielded a series of compounds, namely  $[Cu_2(L_1)(PPh_3)_2I_2]_2$  (1),  $[Cu_2(L_2)(PPh_3)_2I_2]_n$  (2),  $[CuL_1(NO_3)_2]_2$  (3),  $[ZnL_1(NO_3)_2]_2$  (4),  $[CdL_1(NO_3)_2]_2$  [(5),  $[CdL_1'(NO_3)_2]_2$  (6) and  $[HgL_1Cl_2]_n$  (7). The compounds were characterized by elemental analysis, spectroscopic methods (IR, UV/Vis) and X-ray crystallography. X-ray structural analysis of compound 1 reveals the formation of a centrosymmetric tetranuclear compound. The repeat unit of coordination polymer 2 comprises a Cu<sub>2</sub>I<sub>2</sub> unit with a triphenyl phosphane substituent on Cu1 linked to an adjacent  $Cu_2I_2$  unit by the ligand  $L_2$  that acts as a bridge. Compounds 3, 4, 5 and 6 exhibit a common metallo-cyclophane  $[M_2(L)_2(NO_3)_4]$  skeleton. Two M<sup>2+</sup> cations are linked by two L<sub>1</sub> ligands and these ligands chelate to each metal atom through the imine nitrogen (or amine nitrogen) atoms and the nitrogen atom of the 2-pyridyl ring, and bind to the other metal atom of the pair via the nitrogen atoms of the 3-pyridyl rings. Structural studies of 7 revealed the formation of a coordination polymer in which the polymer chain propagates in helical spirals along a two-fold screw axis parallel to b. The metal coordination geometries and coordination of the nitrato anions to the metals are noted and discussed.

**Keywords**: Diimine ligands, flexible chelating and bridging ligands, molecular box, coordination polymer, X-ray structure analyses, spectroscopy.

#### 1. Introduction

Recently, the use of multifunctional N-donor bridging ligands for the construction of metallosupramolecular arrays has been investigated. Extensive studies have been carried out using rigid and flexible bridging ligands and a variety of one-, two- and three-dimensional structures, discrete macrocycles, such as grids, boxes, cylinders, molecular polyhedra and helices have been obtained [1-6]. Several factors, such as the nature of the coordination sites, geometrical disposition of donor sites, template molecules, the effect of counterions and the presence of non-covalent interactions, play important roles in the development of the final structures. Extensive studies have been carried out using rigid bridging ligands such as 4,4'bipyridines, Schiff-bases, 2,4,6-tri(4-pyridyl)-1,3,5-triazine, etc. and a variety of polymeric networks with beautiful topologies have been obtained. A metallo-cyclophane or "molecularbox" has been formed upon coordination of such ligands to the Cu(II) ion [7]. Helical and triple-helical conformations have also been observed for Re(I), Cu(I) and Zn(II) ions, often showing unusual structural and chemical properties [8-10]. Sun and co-workers reported some coordination polymers constructed from reduced bis-Schiff base ligands, namely 1,2bis(4-pyridylmethylamino)-ethane, 1,2-bis(3-pyridylmethylamino)ethane and N,N'-bis(3pyridylmethyl)-1,4-benzenedimethylamine [11-14]. Lee and co-workers have prepared coordination polymers from 4-(4-aminophenoxy)-N-(pyridin-3-ylmethylene)aniline, 4-(4aminophenoxy)-N-(pyridin-4-ylmethylene)aniline, N,N'-4,4'-oxybis(N-(pyridin-3ylmethylene)aniline) and N,N'-4,4'-oxybis(N-(pyridin-4-ylmethylene)aniline) [15-20]. However, the use of unsymmetrical chelating and bridging ligands for the construction of discrete macrocycles and/or coordination polymers is less common [21-23]. Recently, we have prepared 3-(2'-pyridylmethyleneamino)pyridine and explored its coordination behaviour

and the formation of novel homo and heterometallic coordination polymers [21]. Herein, we

report the design and preparation of (E)-N-(pyridin-2-ylmethylene)-1-(pyridin-3yl)methanamine ( $L_1$ ), 1-(pyridine-2-yl)-N-(pyridin-3-ylmethyl)methanamine ( $L_1$ ), and (E)-N- $(pyridin-2-ylmethylene)-1-(pyridin-4-yl)methanamine (L_2)$  (Scheme 1), with the aim to construct discrete macrocycles and coordination polymers with Cu(I), Cu(II), Zn(II), Cd(II) and Hg(II). The compounds have been characterized by IR spectroscopy, elemental analysis, single crystal X-ray diffraction and thermogravimetric analysis. Jusci

#### 2. Experimental Section

#### 2.1. General

All reagents were analytical grade commercial products and were purchased from Sigma Aldrich and used without further purification. Infrared (IR) samples were prepared as KBr pellets and their spectra obtained in the range 400-4000 cm<sup>-1</sup> on a Bruker Tensor 27 spectrophotometer. Electronic absorption spectra were recorded on a Perkin Elmer Lambda 35 double beam spectrophotometer. Emission spectra of the solid samples were obtained using a Varian Cary Eclipse fluorescence spectrophotometer at room temperature. Elemental analyses were performed using a Heraeus CHN-O-RAPID elemental analyzer. NMR spectra were obtained on a BRUKER AVANCE DRX500 (500 MHz) spectrometer. Emission spectra were obtained using a Varian Cary Eclipse fluorescence spectrophotometer at room temperature.

#### 2.2. Syntheses

### 2.2.1. (E)-N-(pyridin-2-ylmethylene)-1-(pyridine-3-yl)methanamine $(L_1)$

(E)-N-(pyridin-2-ylmethylene)-1-(pyridine-3-yl)methanamine ( $L_1$ ) was prepared by slightly modifying a known literature procedure [24,25]. To a solution of pyridine-2-carbaldehyde

(1.07 g, 10 mmol) in 25 mL CH<sub>2</sub>Cl<sub>2</sub> was added a solution of 3-aminomethylpyridine (1.08 g, 10 mmol) in 25 mL ethanol and then anhydrous MgSO<sub>4</sub> (2.5 g) was added to the mixture. The resulting mixture was heated at reflux for 2 h, then stirred for another 3 h, and filtered. The solvent was removed in *vacuo* and the ligand, (E)-N-(pyridin-2-ylmethylene)-1-(pyridine-3-yl)methanamine (L<sub>1</sub>), was obtained as a pale yellow oil. Yield: 81%. Anal, Calc. for C<sub>12</sub>H<sub>11</sub>N<sub>3</sub>: C 73.07, H 5.62, N 21.30. Found C 73.17, H 5.58, N 21.25%. <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>): 8.65 (d, 1H, J<sub>HH</sub> = 7.9 Hz), 8.54 (s, 1H, HC=N), 8.53 (b, 2H), 8.04 (d, 1H, J<sub>HH</sub> = 8.4 Hz), 7.75 (m, 2H), 7.31 (m, 2H), 4.86 (s, 2H, =NCH<sub>2</sub>-3Py). IR (KBr/v, cm<sup>-1</sup>): 3055, 1709, 1646 (C=N<sub>im</sub>), 1585, 1471, 1428, 1368, 1317, 1294, 1225, 1186, 1149, 1125, 1102, 1044, 1027, 994, 865, 827, 777, 743, 713, 666, 640, 617, 504. UV-Vis,  $\lambda$ , nm (log  $\varepsilon$ ) (DMSO): 270 (4.48).

### 2.2.2. 1-(pyridine-2-yl)-N-(pyridin-3-ylmethyl)methanamine ( $L_1$ )

To a solution of (E)-N-(pyridin-2-ylmethylene)-1-(pyridine-3-yl)methanamine (L<sub>1</sub>) (197 mg, 1 mmol) in methanol (10 ml) was added sodium borohydride (189 mg, 5 mmol) in small portions with stirring at room temperature. The resulting mixture was stirred at room temperature for 24 h. Then 50 mL of saturated NaCl solution was added and refluxed for 5 hours. The suspension was filtered and the product extracted with dichloromethane. The solvents were removed *in vacuo* and the product obtained as a pale yellow oil. Yield: 73%. Anal. Calc. for  $C_{12}H_{13}N_3$ : C 72.33, H 6.58, N 21.09. Found C 72.29, H 6.61, N 21.10%. <sup>1</sup>H NMR ( $\delta$ , DMSO): 8.56 (s, 1H), 8.5 (m, 2H), 7.77 (m, 2H, H<sub>4</sub>), 7.23-7.49 (m, 3H), 4.85 (b, 1H, NH), 3.82 (s, 2H, 2pyCH<sub>2</sub>N) 3.73 (s, 2H, 3pyCH<sub>2</sub>N). IR (KBr/v, cm<sup>-1</sup>): 3285 (N–H), 3053, 2992, 1590 (C=N<sub>py</sub>), 1474, 1429, 1362, 1222, 1188, 1120, 1047, 1028, 994, 841, 789, 760, 714, 628. UV-Vis,  $\lambda$ , nm (log  $\varepsilon$ ) (DMSO): 265 (4.46).

#### 2.2.3. (E)-1-(pyridin-3-yl)-N-(pyridine-4-ylmethylene)methanamine $(L_2)$

(E)-1-(pyridin-3-yl)-N-(pyridine-4-ylmethylene)methanamine (L<sub>2</sub>), was synthesized by a procedure similar to that used for L<sub>1</sub>, but using pyridine-4-carbaldehyde (1.07 g, 10 mmol) and 3-aminomethylpyridine (1.08 g, 10 mmol). Yield: 83%. Anal. Calc. for C<sub>12</sub>H<sub>11</sub>N<sub>3</sub>: C 73.07, H 5.62, N 21.30. Found C 73.14, H 5.60, N 21.26%. <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>): 8.68 (d, 2H, J<sub>HH</sub> = 8.6 Hz), 8.53 (s, 1H, HC=N), 8.41 (m, 2H), 7.85 (m, 2H), 7.31 (m, 2H), 4.85 (s, 2H, =NCH<sub>2</sub>-3Py). IR (KBr/v, cm<sup>-1</sup>): 3031, 2998, 1708, 1645 (C=N<sub>im</sub>), 1597, 1558, 1478, 1422, 1382, 1349, 1322, 1234, 1187, 1125, 1103, 1059, 1025, 994, 872, 814, 713, 642, 614, 519. UV-Vis,  $\lambda$ , nm (log  $\varepsilon$ ) (DMSO): 265 (4.77).

#### 2.2.4. $[Cu_2(L_1)(PPh_3)_2I_2]_2(1)$

To a solution of CuI (19 mg, 0.1 mmol) in 5 mL acetonitrile was added dropwise triphenylphosphine (26 mg, 0.1 mmol) in 4 ml acetonitrile under a nitrogen atmosphere. The mixture was stirred for 30 min and then L<sub>1</sub> (19.7 mg, 0.1 mmol) in 5 ml acetonitrile was added and stirred for an additional 10 min. The volume of the solvent was reduced under vacuum to about 1 mL. Diffusion of diethyl ether vapor into the concentrated solution gave red crystals. The crystals were filtered off and washed with a mixture of diethyl ether-acetonitrile (9:1 v/v), and dried in *vacuo*. Yield: 76%. Anal. Calc. for C<sub>96</sub>H<sub>82</sub>Cu<sub>4</sub>I<sub>4</sub>N<sub>6</sub>P<sub>4</sub>: C 52.28, H 3.75, N 3.81. Found C 52.19, H 3.84, N 3.87%. <sup>1</sup>H-NMR ( $\delta$ , DMSO): 8.85 (s, 1H, HC=N), 8.38 (m, 1H), 8.15 (m, 1H), 8.08 (m, 1H), 7.64 (m, 5H), 7.37 (m, 30H, phenyl ring), 4.98 (s, 2H, =NCH<sub>2</sub>-3Py). IR (KBr/v, cm<sup>-1</sup>): 3047, 1621 (C=N<sub>im</sub>), 1584, 1476, 1432, 1383, 1351, 1297, 1261, 1221, 1183, 1154, 1125, 1093, 1069, 1027, 995, 969, 921, 848, 793, 774, 744, 696, 666, 519, 498. UV-Vis,  $\lambda$ , nm (log  $\varepsilon$ ) (DMSO): 264 (4.43), 281 (3.95), 384 (1.45), 485 (1.21).

### 2.2.5. $[Cu_2(L_2)(PPh_3)_2I_2]_n(2)$

This compound was synthesized by a procedure similar to that for **1**, but using L<sub>2</sub> (19.7 mg, 0.1 mmol). Yellow single crystals suitable for X-ray diffraction were obtained by slow evaporation from the filtrate over several days. Yield: 69%. Anal. Calc. for C<sub>48</sub>H<sub>41</sub>Cu<sub>2</sub>I<sub>2</sub>N<sub>3</sub>P<sub>2</sub>: C 52.28, H 3.75, N 3.81. Found C 52.35, H 3.81, N 3.76%. <sup>1</sup>H-NMR ( $\delta$ , DMSO): 8.65 (s, 1H, HC=N), 7.93 (m, 3H), 7.45 (m, 5H), 7.39 (m, 30H, phenyl ring), 4.98 (s, 2H, =NCH<sub>2</sub>-3Py). IR (KBr/v, cm<sup>-1</sup>): 3047, 1602 (C=N<sub>im</sub>), 1477, 1430, 1382, 1307, 1234, 1185, 1156, 1125, 1093, 1064, 1026, 998, 876, 820, 791, 745, 696, 618, 517, 432. UV-Vis,  $\lambda$ , nm (log  $\epsilon$ ) (DMSO): 267 (4.56), 288 (3.91), 303 (2.12).

#### 2.2.6. $[CuL_1(NO_3)_2]_2$ (3)

At room temperature, a solution of Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O (24.1 mg, 0.1 mmol) in 2 mL methanol was carefully layered onto the top of a solution of L<sub>1</sub> (19.7 mg, 0.1 mmol) in 2 mL dichloromethane. After two weeks, the resulting blue needle-like crystals were filtered, and air-dried to give [CuL<sub>1</sub>(NO<sub>3</sub>)<sub>2</sub>]<sub>2</sub>. Yield: 58%. Anal. Calc. for C<sub>24</sub>H<sub>22</sub>Cu<sub>2</sub>N<sub>10</sub>O<sub>12</sub>: C 37.46, H 2.88, N 18.20. Found C 37.39, H 2.90, N, 18.26%. IR (KBr/v, cm<sup>-1</sup>): 3047, 2924, 1642 (C=N<sub>im</sub>), 1598, 1438 (NO<sub>3</sub>), 1382, 1282 (NO<sub>3</sub>), 1229, 1193, 1106, 1024, 818, 791, 730, 701, 655, 505, 421. UV-Vis,  $\lambda$ , nm (log  $\varepsilon$ ) (DMSO): 268 (4.21), 280 (4.53), 483 (1.51).

### 2.2.7. $[ZnL_1(NO_3)_2]_2(4)$

At room temperature, a solution of  $Zn(NO_3)_2.6H_2O$  (29.7 mg, 0.1 mmol) in 4 mL methanol was carefully layered onto the top of a solution of L<sub>1</sub> (19.7 mg, 0.1 mmol) in 2 mL dichloromethane. After two weeks, the resulting colorless crystals were filtered, and air-dried to give [ZnL<sub>1</sub>(NO<sub>3</sub>)<sub>2</sub>]<sub>2</sub>. Yield: 45%. Anal. Calc. for C<sub>24</sub>H<sub>22</sub>N<sub>10</sub>O<sub>12</sub>Zn<sub>2</sub>: C 37.28, H 2.87, N 18.11. Found C 37.34, H 2.84, N 18.16%. <sup>1</sup>H NMR ( $\delta$ , DMSO): 8.80 (s, 1H, HC=N), 8.54

(m, 1H), 8.34 (m, 2H), 8.11 (m, 1H), 7.92 (m, 2H), 7.37 (m, 2H), 4.85 (s, 2H, =NCH<sub>2</sub>-3Py). IR (KBr/v, cm<sup>-1</sup>): 3098, 2950, 1648 (C=N<sub>im</sub>), 1595, 1462 (NO<sub>3</sub>), 1380, 1293 (NO<sub>3</sub>), 1225, 1192, 1124, 1102, 1056, 1026, 886, 816, 788, 738, 700, 648, 501. UV-Vis, λ, nm (log ε) (DMSO): 265 (4.11), 271 (2.17).

### 2.2.8. $[CdL_1(NO_3)_2]_2$ (5)

At room temperature, a solution of Cd(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O (30.8 mg, 0.1 mmol) in 4 mL methanol was layered onto the top of a solution of L<sub>1</sub> (19.7 mg, 0.1 mmol) in 2 mL dichloromethane. After three weeks, the resulting yellow crystals were filtered and air-dried to give  $[CdL_1(NO_3)_2]_2$ . Yield: 42%. Anal. Calc. for C<sub>24</sub>H<sub>22</sub>Cd<sub>2</sub>N<sub>10</sub>O<sub>12</sub>: C 33.24, H 2.56, N 16.15. Found C 33.29, H 2.59, N 16.09%. <sup>1</sup>H NMR ( $\delta$ , DMSO): 8.75 (s, 1H, HC=N), 8.57 (m, 1H), 8.46 (m, 2H), 8.17 (m, 1H), 8.02 (m, 1H), 7.68 (m, 2H), 7.30 (m, 1H), 4.87 (s, 2H, =NCH<sub>2</sub>-3Py). IR (KBr/v, cm<sup>-1</sup>): 3047, 2921, 1648 (C=N<sub>im</sub>), 1583, 1458 (NO<sub>3</sub>), 1384, 1291 (NO<sub>3</sub>), 1221, 1192, 1125, 1100, 1053, 1025, 877, 818, 791, 735, 702, 647, 500. UV-Vis,  $\lambda$ , nm (log  $\epsilon$ ) (DMSO): 264 (4.23), 281 (3.95).

### 2.2.9. $[Cd(L_1')(NO_3)_2]_2(6)$

A mixture of Cd(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O (30.8 mg, 0.1 mmol), ligand L<sub>1</sub>' (19.7 mg, 0.1 mmol), methanol (10 ml) and benzene (3 ml) was heated in a vial at 70 °C for 3 days and then cooled to room temperature. The crystalline product that formed was collected by filtration, washed with methanol and air-dried to give colorless crystals of  $[Cd(L_1')(NO_3)_2]_2$ . Yield: 41%. Anal. Calc. for C<sub>24</sub>H<sub>26</sub>Cd<sub>2</sub>N<sub>10</sub>O<sub>12</sub>: C 33.08, H 3.01, N 16.07. Found C 32.99, H 3.06, N 16.12%. <sup>1</sup>H NMR ( $\delta$ , DMSO): 8.53 (m, 3H), 7.97 (m, 1H), 7.81 (d, 1H, J = 9 Hz), 7.38-7.55 (m, 3H), 4.53 (b, 1H, NH), 3.82 (s, 2H, 2pyCH<sub>2</sub>N), 3.80 (s, 2H, 3pyCH<sub>2</sub>N). IR (KBr/v, cm<sup>-1</sup>): 3256 (N–H), 2922, 1605 (C=N<sub>py</sub>), 1457 (NO<sub>3</sub>), 1389, 1287 (NO<sub>3</sub>), 1216, 1182, 1119, 1058, 1023, 930,

807, 771, 735 (m), 705, 651, 510. UV-Vis, λ, nm (log ε) (DMSO): 262 (4.19), 271 (3.98).

#### 2.2.10. $HgL_1Cl_2]_n(7)$

To a solution of anhydrous HgCl<sub>2</sub> (27.1 mg, 0.1 mmol) in 10 ml acetonitrile was added a solution of L<sub>1</sub> (19.7 mg, 0.1 mmol) in 4 ml N,N-dimethylformamide (DMF). On slow evaporation of the solution, yellow crystals were obtained, which were collected by filtration, and air-dried to give [HgL<sub>1</sub>Cl<sub>2</sub>]<sub>n</sub>. Yield: 41%. Anal. Calc. for C<sub>12</sub>H<sub>11</sub>Cl<sub>2</sub>HgN<sub>3</sub>: C 30.75, H 2.37, N 8.96. Found C 30.69, H 2.41, N, 8.91%. <sup>1</sup>H NMR ( $\delta$ , DMSO): 8.86 (s, 1H, HC=N), 8.73 (s, 1H), 8.53 (m, 2H), 8.1 (m, 1H), 7.77 (m, 2H), 7.39 (m, 2H), 4.97 (s, 2H, =NCH<sub>2</sub>-3Py). IR, (KBr/v, cm<sup>-1</sup>): 3055, 2909, 1653 (C=N<sub>im</sub>), 1586, 1475 (NO<sub>3</sub>), 1435, 1388, 1297 (NO<sub>3</sub>), 1257, 1219, 1188, 1122, 1101, 1047, 1006, 984, 961, 871, 832, 795, 774, 705, 672, 643, 625, 493. UV-Vis,  $\lambda$ , nm (log  $\varepsilon$ ) (DMSO): 261 (4.21), 282 (3.91).

#### 2.3. X-ray analyses

The X-ray measurements of single crystals of **1** and **3** were carried out on a Bruker-Nonius Kappa-CCD diffractometer equipped with a graphite monochromator and a low temperature device (Oxford Cryosystems) at the Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland. Data for **2**, **4**, **5**, **6** and **7** were collected on a similar system at the University of Otago, New Zealand. MoK<sub> $\alpha$ </sub> radiation ( $\lambda = 0.71073$  Å) was used for all of the collections, which were controlled by APEX2 [26], with data for **1** and **3** collected at 100(2) K, while those for **2** and **4**-**7** were collected at 90(2) K. The collected data were corrected for Lorentz and polarization effects using SAINT [27] and numerical absorption corrections were applied using SADABS [24]. The structures were solved by direct methods (SHELXS-97 [27] for **1**-**6**, and SIR92 [28] for **7**) and refined using full-matrix least-squares procedures (SHELXL-97 [27]). With the exception of **1**, all non-hydrogen atoms were refined

anisotropically. In **1** there is a solvating acetonitrile molecule which is orientationally disordered over two positions, with the terminal carbon (methyl group) placed in one position and the C-N part adopting two orientations. The non-hydrogen atoms of this solvent were refined isotropically. With the exception of **1** and **6**, all hydrogen atoms were placed in calculated positions, and their thermal parameters were refined isotropically. In **1**, hydrogen atoms of the acetonitrile molecule were not included in the refinement as they are bonded to a carbon atom having two different orientations (this leads to a small disagreement between the chemical formula and the content of the unit cell, as seen in the CIF file). The N—H hydrogen atom for **6** was located in a difference Fourier map and its coordinates were refined with  $U_{eq} = 1.2 U_{eq}(N)$ . Compound **2** is disordered such that the pyridyl rings have two distinct orientations and pivot on the well-defined imino group. The asymmetric unit thus comprises one complete ligand at half occupancy, the Cu(I) cation, an iodide anion and a PPh<sub>3</sub> ligand. For compound **5**, three low angle reflections with  $F_o << F_c$  were omitted from the final stages of the refinement. Details of the X-ray measurements, crystal data and bond lengths and angles for all of the complexes are given in Tables 1-3.

### 3. Results and discussion

#### 3.1. Synthesis and spectral properties

Two potential linking ligands  $L_1$  and  $L_2$  (Scheme 1) were prepared by a simple and straightforward Schiff-base condensation of pyridine-2-carbaldehyde and pyridine-3carbaldehyde with 3-aminomethylpyridine.  $L_1$  was reduced with sodium borohydride to give  $[(3-py)-CH_2-NH-CH_2-(2-py)]$  ( $L_1'$ ). Because of the possible rotations about the NH-CH<sub>2</sub> single bond, the ligand  $L_1'$  is expected to be considerably more flexible than  $L_1$  or  $L_2$ .  $[Cu_2(L_1)(PPh_3)_2I_2]_2$ , (1) and  $[Cu_2(L_2)(PPh_3)_2I_2]_n$ , (2) were prepared by the reaction of the

ligands ( $L_1$  and  $L_2$ ) with PPh<sub>3</sub> and copper(I) iodide. [CuL<sub>1</sub>(NO<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, (**3**) was prepared by the reaction of L<sub>1</sub> with Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O. [ZnL<sub>1</sub>(NO<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, (**4**) and [CdL<sub>1</sub>(NO<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, (**5**) were prepared by layering a methanol solution containing M(NO<sub>3</sub>)<sub>2</sub> on top of a dichloromethane solution containing the corresponding ligand L<sub>1</sub>. [HgL<sub>1</sub>Cl<sub>2</sub>]<sub>n</sub>, (**7**) was obtained upon slow evaporation of a solution containing of HgCl<sub>2</sub> and L<sub>1</sub> at room temperature. Solvothermal treatment of cadmium(II) nitrate with the ligand L<sub>1</sub>' in methanol–benzene at 70 °C produced [Cd(L<sub>1</sub>')(NO<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, (**6**). These complexes are insoluble in chloroform, methanol, ethanol and acetone, and are stable under ambient conditions.

The IR spectra of the free ligands (L<sub>1</sub> and L<sub>2</sub>) exhibit v(C=N) at 1646 and 1645 cm<sup>-1</sup>, respectively. In complexes 1-5 and 7, v(C=N) appears at 1602-1653 cm<sup>-1</sup>. The IR spectra of complexes 3-7 show strong absorption bands for the coordinated stretching vibrations of the nitrate group at about 1290 and 1490 cm<sup>-1</sup> [6]. The band at 3298 cm<sup>-1</sup> for L<sub>1</sub>' can be assigned to the N—H stretching vibration. The corresponding N—H deformation vibrations in L<sub>1</sub>' appear at 1362 cm<sup>-1</sup> [29,30].

The <sup>1</sup>H NMR spectra and peak assignments are presented in the experimental section. These peaks are assigned based on the splitting of the resonance signals, spin coupling constants and literature data, [21,31] and are clearly in accordance with the molecular structures determined by X-ray crystal structure analysis. The spectra of the ligands are clearly divided into two parts; the downfield part is due to the pyridine and imine protons while the upfield signals represent the -NCH<sub>2</sub>- proton resonances. The <sup>1</sup>H NMR spectra of L<sub>1</sub> and L<sub>2</sub> show a singlet at ca. 4.8 ppm due to the -NCH<sub>2</sub>- protons, whilst the aromatic H-atoms and imine protons appear at 7.75-8.63 ppm. The imine protons appear as a singlet at 8.54 and 8.53 ppm for L<sub>1</sub> and L<sub>2</sub>, respectively. In L<sub>1</sub>', however, the methylene protons are not equivalent and appear as two singlets while the aromatic H-atoms and imine protons appear at 7.23-8.56 ppm. The <sup>1</sup>H NMR spectra of complexes **1** and **2** show typical patterns for the ligands L<sub>1</sub> (in

1) and  $L_2$  (in 2) together with the PPh<sub>3</sub> protons. Inevitably, the aromatic protons of the coordinated PPh<sub>3</sub> ligands overlap to some extent with those of the pyridyl protons of the ligands. Aside from the aromatic protons, which appear at 7.37–8.38 ppm, the imine protons appear as singlets at about 8.80 ppm. A singlet at 4.98 ppm is assigned to the =NCH<sub>2</sub>-protons. The <sup>1</sup>H resonances of the coordinated ligands are commonly observed in 4, 5 and 7. The imine protons appear as a singlet at about 8.74 ppm. The down-field shift of the iminic protons in the complexes relative to those of the free ligands can be attributed to the deshielding effect resulting from the metal coordination [32,33].

The electronic absorption spectra of the ligands  $L_1$ ,  $L_1'$  and  $L_2$  and the corresponding complexes 1-7 are presented in experimental section. Since no d-d transitions are expected for a d<sup>10</sup> complex (1 and 2), the UV/VIS bands are assigned to MLCT or intraligand transitions [34,35]. The absorption spectrum of 1 features a band with a true maximum at 485 nm, whereas 2 shows a clear shoulder at 303 nm. The visible range of the spectra is dominated by metal-ligand charge transfer (MLCT) transitions, which are characteristic features of copper(I) complexes when bonded to a conjugated organic chromophore [36]. Additional absorption bands are also observed in the spectra of 1 and 2 in the UV region. The intensities of these bands are consistent with their assignment to ligand-centered  $\pi \rightarrow \pi^*$ or/and charge-transfer transitions. The UV-Vis spectrum of the copper(II) compound 3 exhibits d-d transitions. In complex 3, a higher energy transition was observed at 483 nm due to d-d transitions [37-40]. Strong bands at about 268 and 280 nm are assigned to a ligand centered  $\pi \rightarrow \pi^*$  transition and/or charge transfer transitions. The absorption spectra of the zinc, cadmium and mercury compounds show intense absorptions in the UV region. These broad bands are attributed to intraligand ( $\pi \rightarrow \pi^*$ ) and/or charge transfer transitions (MLCT). The free ligands show a fluorescent feature with an emission around 455 nm (458 nm for  $L_1$ , 449 nm for  $L_1'$  and 460 nm for  $L_2$ ) upon excitation at 270 nm in DMSO at room temperature.

Complex 1 displays a strong emission with a maximum intensity at 538 nm, while a weak band is observed at 541 nm for complex 2. These fluorescent emissions can be assigned to a metal-to-ligand charge transfer (MLCT) or halide-to-ligand charge transfer (XLCT) [41,42]. The zinc and cadmium compounds (4, 5 and 6) display a strong emission with maximum intensities at about 460 nm (459 nm for 4, 463 nm for 5 and 455 nm for 6). This fluorescent emission can be assigned to the intraligand transition of the ligand, modified by metal coordination, because a similar emission is observed at 458 and 449 nm for the free ligands  $L_1$  and  $L_1$ ', respectively. Compared to the free ligand, the coordination compounds show a significant enhancement of the fluorescence intensity, probably because the chelating and bridging coordination effectively increase the rigidity of the ligands and reduce the loss of energy by radiationless decay. Compounds **3** and **7** are non-emissive at room temperature.

### 3.2. Crystal structures

Selected bond lengths and angles for compounds 1–7 are given in Tables 2 and 3.

### 3.2.1. Structure of $[Cu_2(L_1)(PPh_3)_2I_2]_2(1)$

X-ray structural analysis of compound **1** reveals the formation of a centrosymmetric tetranuclear compound (Fig. 1). This compound contains four copper atoms, four iodide anions (two terminal and two bridging), four triphenylphosphine ligands and two L<sub>1</sub> ligands. The coordination environment around Cu1 in **1** is pseudotetrahedral,  $\tau_4 = 0.92$  for Cu1 [43] with a large angular distortion arising from the low N19—Cu1—I1 angle (100.28(7)°). The other five angles around the Cu1 center all lie within ±5° of those of a regular tetrahedron; however, the N19—Cu1—P1 angle (116.92(7)°) has opened up due to the steric influence of the bulky di-imine and PPh<sub>3</sub> ligands. The Cu1—N19 bond distance (2.063(2) Å) is similar to

those found in other Cu(I) pseudotetrahedral complexes [44-46]. Although a tetrahedral geometry is to be expected for a four-coordinated Cu(I) center, the geometry about Cu2 in 1 is distorted by the restricted bite of the chelating ligand. The N1—Cu—N41 angle is 80.67(9) °. The N41—Cu2—P2 and N1—Cu2—I2 angles are 121.30(7) and 119.94(6) °, respectively, being somewhat larger than the ideal tetrahedral angle such that for Cu2  $\tau_4 = 0.84$  and its coordination geometry tends towards a see-saw description [43]. The Cu-P distances are 2.230(8) and 2.196(7) Å, being in the same range as those in other tetrahedral copper complexes [44-48]. The Cu—I bond lengths (with the I anions fulfilling both terminal and bridging ligand roles) of 2.587(4), 2.674(4) and 2.639(4) Å agree well with the same distances in other tetrahedral copper complexes with iodido ligands [44-48]. In 1, L adopts the chelating mode to one Cu(I) ion and also it adopts a bridging mode and connects two Cu(I) ions. The dihedral angle between the pyridyl rings of each L ligand is  $46.76(9)^{\circ}$ . The value for the N1-C43-C42-N41 torsion angle is -8.873(4)°, and a comparison with the dihedral angle between the chelate ring and pyridine group (6.418(12) °) indicates that these are roughly coplanar. However, the terminal pyridine ring is tilted out-of-plane with respect to the metal chelate plane, with a calculated dihedral angle of 54.54(11) ° between the two planes.

### 3.2.2. Structure of $[Cu_2(L_2)(PPh_3)_2I_2]_n(2)$

The repeat unit of this coordination polymer comprises a  $Cu_2I_2$  unit with a triphenylphosphine substituent on Cu1, and it is linked to an adjacent  $Cu_2I_2$  unit by the ligand  $L_2$ , which acts as a bridge (Fig. 2). The almost square and strictly planar  $Cu_2I_2$  unit is generated by inversion symmetry, with Cu1—I1 bond distances of 2.6713(3) and 2.6586 (4) Å and a Cu1—Cu1<sup>ii</sup> (ii = -x+1, -y+1, -z+1) separation of 2.9549(6) Å. This motif is not unusual in Cu—I coordination chemistry, with 332 instances reported in the Cambridge

Structural Database[49]. A small number of representative complexes containing  $Cu_2I_2$  units with one or more pyridine based ligands on each Cu atom were found [48,50-52]. However refining the search to include a P and pyridine based ligand on each of the Cu atoms produced only three hits, [53-55] underlining the novelty of **1** and **2**.

The Cu—I (2.6712(3) and 2.6590(3) Å) and Cu—Cu (2.9554(5) Å) distances, Table 2, compare reasonably with those for **1**, and are also similar to the mean values [Cu—I, 2.66(9) Å and Cu—Cu, 2.9(3) Å] found for the 332 equivalent, planar Cu<sub>2</sub>I<sub>2</sub> units in the Cambridge database, despite the fact that this compound, with a bridging bidentate dipyridyl ligand, is totally novel. In addition to the two bridging iodide ligands, each Cu(I) atom is coordinated to a triphenylphosphine ligand and one N atom of the bidentate ((E)-1-(pyridin-3-yl)-N-(pyridine-4-ylmethylene)methanamine L<sub>2</sub> ligand, Fig. 2. Because of the positional disorder involving this ligand, each Cu atom binds a nitrogen atom of both the 3- and 4 pyridyl substituents of the ligand with equal occupancy. A Cu atom of an adjacent Cu<sub>2</sub>I<sub>2</sub> unit similarly binds to one or other of the pyridyl N atoms, again with equal occupancy, propagating a one dimensional polymer system, Fig. 3.

The coordination geometry about the Cu atoms is again slightly distorted tetrahedral, with  $\tau_4$  = 0.91, suggesting only a slight departure from T<sub>d</sub> symmetry [43]. The coordination sphere of each Cu atom comprises two iodide ligands, forming the centrosymmetric Cu<sub>2</sub>I<sub>2</sub> unit, one triphenylphosphine ligand and one or other of the N atoms of the asymmetrical (E)-pyridin-3-yl-N-(pyridin-4-ylmethylene)methanamine ligand. The L—Cu—L angles are in the range 100.56(6) to 112.662(10)°, Table 2. The bridging L<sub>2</sub> ligands link adjacent Cu<sub>2</sub>I<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> units into infinite one dimensional chains that run parallel to (110). In the crystal lattice, these chains are further joined by weak C—H...I contacts, generating parallel columns along the crystallographic *b* axis.

#### 3.2.3. Structures of $[ML_1(NO_3)_2]_2$ [M = Cu(3), Zn(4), Cd(5)] and $[Cd L_1(NO_3)_2]_2$ (6).

The structures of compounds 3-6, shown in Figs. 4 and 6, are sufficiently similar to be discussed together. Each molecule of **3-5** lies about an inversion center and comprises two  $M^{2+}$  cations linked by two L<sub>1</sub> ligands that chelate to each metal atom through the imine N4 atom and the N3 atom of the 2-pyridyl ring, forming 5-membered chelate rings. Each ligand binds to the other metal atom of the pair via the N5 atom of the 3-pyridyl ring. For  $\mathbf{6}$  the coordination environment is similar, except that N4 is now an amine N atom and the C=N bond of  $L_1$  is reduced. In the  $L_1$  complexes, this coordination generates a molecular box bounded by the Cu1—N4 bonds on one side and the two strictly parallel 3-pyridyl rings on the other. In the case of 3, the approximate dimensions of this cavity are 5.3 x 3.1 Å, Fig. 5(a). An alternate view shows a smaller cavity, approximately 3.1 x 2.9 Å, which is bounded by the two 3-pyridyl rings and the planes of the 2-pyridyl rings Fig. 5(b). These ring planes for **3** are almost orthogonal, with a dihedral angle of  $89.1(7)^{\circ}$  between them. Similar cavities are formed by the Zn and Cd analogues with the dimensions of the major cavities being 5.9 x 3.3 Å for 4, 5.8 x 3.4 Å for 5 and 4.9 x 2.9 Å for 6. The dihedral angles between the 2-pyridyl and 3-pyridyl ring planes are  $80.40(7)^{\circ}$  for 4 and  $75.21(6)^{\circ}$  for 5. In contrast, the greater flexibility engendered by the saturated C8-N4 linkage in L<sub>1</sub>' widens the larger cavity to approximately 7.4 x 2.87 Å and reduces the angle between the 2- and 3-pyridyl rings to 72.89(9)°

The coordination of the nitrato anions to the metals in **3-6** varies in an interesting fashion as the metal changes. According to the criteria for the assignment for nitrate binding modes introduced by Kleywegt *et al.* [56], there are three common types of nitrate binding in coordination complexes, monodentate, where only one O atom is clearly bound to the metal, bidentate where two oxygens bind and the M—O distances are reasonably similar and finally anisobidentate where, again, both oxygens bind but one M—O bond is significantly longer

than the other.

The criteria used to determine the mode of coordination are determined by differences in the M—O and M--N bond distances and M—N—O angles [54], detailed in Fig. 7 and Table 4. All three coordination modes are seen in these complexes, with the tendency for bidentate coordination increasing with the radius of the metal. The binding of one of the nitrate anions N2O4O5(O6) in 3 is anisobidentate, with the Cu1—O4 bond length being 2.1062(13) Å and Cu1—O5 being 2.6619(15), while the N1O1O2(O3) anion is clearly unidentate. This has an interesting impact on the coordination geometry of the Cu(II) cation. The primary coordination sphere, discounting the longer Cu1-O5 bond, involves the two pyridyl N3 and N5 atoms, the azomethine N4 atom and the O1 and O4 atoms of the two nitrate anions Fig. 8(a). This generates a five-coordinate, highly distorted trigonal bipyramidal geometry. The distortion lies towards a square pyramidal structure, with the trigonality index  $\tau_5 = 0.51$  ( $\tau_5$  is the parameter describing the degree of trigonal distortion and is defined as  $\tau = (\theta 1 - \theta 2)/60$ , where  $\theta 1$  and  $\theta 2$  are the two largest ligand–metal–ligand angles;  $\tau_5 = 0$  for an ideal squarepyramid (SP) and  $\tau_5 = 1$  for an ideal trigonal bipyramid (TBP) [57]). However, there is the additional Cu1—O5 contact at 2.6619(15) Å. The O5 atom essentially caps the trigonal bipyramid, bisecting the O4-Cu1-N4 angle in an asymmetric fashion and creating a hugely distorted octahedral coordination environment. The Cu1--O2 contact at 2.8844(18) Å is too long to be considered a sensible bonding distance. The coordination numbers for the remaining L<sub>1</sub> derivatives are somewhat more clear cut, with complex 4 having a sixcoordinate Zn atom in a severely distorted octahedral geometry, Fig. 8(b), with one monodentate and one bidentate nitrato ligand. The larger Cd atom in 5 binds both nitrato ligands in a bidentate fashion, leading to seven coordination and a highly distorted pentagonal bipyramidal geometry, Fig. 8(c). Seven coordination persists for **6**, but in this case the coordination geometry is best described as a distorted capped octahedron, Fig. 8(d). An

alternative treatment of the metal coordination geometry when bidentate nitrate ligands are involved has been proposed by Hanton et al. [58-60]. They argue that the small bite angle of the bidentate nitrato ligand suggests that it can be considered to occupy just a single coordination site. The bite angles observed here for all of the bidentate nitrato ligands are certainly low, ranging from 51.10(4) to  $56.23(5)^{\circ}$  across the four molecules. Hence if we use the N atoms of the bidentate chelate nitrato ligands as a proxy for the locus of the single nitrato coordination site, the coordination geometries for complexes 4 and 5 tend more towards trigonal bipyramidal, Fig. 9, with trigonality indices,  $\tau_5 = 0.71$  for 4 and  $\tau_5 = 0.65$  for 5 [57]. In contrast, complex 6, involving the more flexible  $L_1$  ligand, tends slightly towards square planar with  $\tau_5 = 0.46$  [57]. Furthermore, applying the same procedure to **3** reinforces the concept of distortion towards a trigonal bipyramidal geometry with a much increased trigonality index,  $\tau_5 = 0.72$  [57]. For 3, the Cu—N bond lengths range between 1.9742(14) and 2.0447(14) Å (Table 2) and the Cu-O bond lengths for the nitrate ions range from 2.1062(13) to 2.1743(12) Å, consistent with the corresponding bond lengths found in similar structures [21,30,61-65]. The most closely related complexes to the Zn and Cd derivatives 4 and 5 involve the (E)-pyridin-2-yl-N-(pyridin-2-ylmethylene)methanamine and (E)-N-(1-(pyridin-2-yl)ethylidene)pyridin-2-amine ligands, each with two 2-pyridyl rings and interestingly NO<sub>3</sub><sup>-</sup> anions as the other ligands [66]. In these complexes it was found that the M-N<sub>imine</sub> distance was distinctly shorter than the M-N<sub>py</sub> distances (M= Zn, Cd) a trend that is clearly absent in the structures of 4 and 5. It is likely, therefore, that the M-N distances are determined by steric rather than electronic effects.

Only a single copper coordination complex of  $L_1'$  appears in the CSD, in which the metal is chelated by one pyridyl N atom and the amine N atom, with the second pyridyl N atom being protonated [67]. In contrast, structures of more than 200 complexes of the corresponding symmetrical bis(pyridin-2-ylmethyl)amine appear in the database, with Cd(II) derivatives

well represented [68-70]. However, only one of these structures also featured nitrato ligands [68] and no inversion dimers similar to **6** have been reported. Nonetheless the Cd—N distances observed here are not unusual.

#### 3.2.4. Structure of $[HgL_1Cl_2]_n$ (7)

The structure of the mercury complex with  $L_1$ , 7, departs markedly from those displayed by its lighter congeners from Group 12. Certainly the metal is chelated by the 2-pyridyl N atom and the imine N atom, but there the similarity ends as the N5 atom of the 3-pyridyl ring binds to an adjacent Hg1 centre to propagate a coordination polymer. The Hg1 atom is in a distorted square pyramidal coordination environment, Fig. 10, composed of two monodentate chlorido anions, the 2-pyridyl N3 atom and the imine N4 atom, that chelates the Hg1 centre forming a 5-membered ring. The coordination sphere is completed by the 3-pyridyl N5 atom of an adjacent  $L_1$  ligand in the polymer chain and the proposed coordination environment is supported by a trigonality index  $\tau_5 = 0.27$  [57]. The Hg atom lies 0.776(7) Å above the best fit N<sub>3</sub>Cl mean plane and the 2- and 3-pyridyl rings are inclined to one another at 78.8(7)°. Chelation of an HgCl<sub>2</sub> unit by a N-(pyridin-2-ylmethylene)methanamine fragment is not uncommon, with 16 examples in the CSD, see for example [71-75]. The mean Hg1-N3 [2.37(8) Å] and Hg-N4 [2.45(7) Å] distances across these examples are the complete reverse of the order found in 7, Hg1-N3 2.514(15) Å, Hg1-N4 2.345(16) Å, although the Hg-Cl distances observed here are unremarkable. An explanation for this reversal is not immediately obvious, particularly as the bite angle N3-Hg1-N4 of the chelate, 68.7(5)°, is closely comparable to those found in the related structures. However, it is interesting that for the closely comparable coordination polymer catena-poly[[dichloridomercury(II)]- $\mu$ -{N-[(E)pyridin-2-ylmethylidene- $\kappa$ N]-pyridin-3-amine- $\kappa^2$ N<sup>1</sup>:N<sup>3</sup>] [75], the equivalent distances are Hg1—N2 2.406(5) Å and Hg1—N4 2.535(6) Å; clearly the greater flexibility imparted to the

ligand system by the additional  $CH_2$  group in 7 has a significant effect on the Hg—N distances in the chelate ring. The polymer chain propagates in helical spirals along a two-fold screw axis parallel to *b*, Fig. 11. In the crystal, intermolecular C—H...Cl hydrogen bonds link adjacent polymer chains, forming parallel rows along *b*.

### 4. Conclusions

We have presented the syntheses of some molecular boxes and coordination polymers by employing three flexible N-bridging ligands  $(L_1, L_1')$  and  $L_2$ . From the reaction of different metal nitrate salts, M(NO<sub>3</sub>)<sub>2</sub> (M=Cu(II), Zn(II) and Cd(II)), with L<sub>1</sub> and L<sub>1</sub>', similar structures (molecular boxes) were obtained in these cases, although the metal centers have different geometries in these structures. When HgCl<sub>2</sub> reacts with L<sub>1</sub>, a coordination polymer was obtained. The metal atoms in the compounds 3-7 are present in highly distorted trigonal bipyramidal, distorted octahedral, highly distorted pentagonal bipyramidal, distorted capped octahedral and distorted square pyramidal environments, respectively. Dihedral angles between the terminal pyridyl rings of L in the compounds 3-7 vary considerably from a maximum of 89.13° for 3, to 80.41 and 72.89° for 6, with the other compounds having intermediate values. Hence, these flexible ligands (L1 and L1') possibly modulate their conformations in order to meet the coordination needs of the metal polyhedra and no clear correlation is observed between the structures of the compounds (box or chain) and the coordination environment of the metal or the conformation of the ligands. A careful analysis of structures 3 (4, 5 and 6) and 7 (through overlaying the metal atoms and the chelate ring systems in both molecules) clearly shows that the positioning of the chlorido ligands in the Hg complex (7) forces the N5 atom bound to the Hg atom into an orientation such that an inversion dimer simply cannot form, (Fig. 12). A coordination polymer, however, is a viable

alternative. In contrast, the bulky nitrato ligands in **3**, **4**, **5** and **6** cannot adopt similar orientations, but are ideally situated to allow the formation of inversion dimers.

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#### Supplementary material

CCDC 1000162-1000168 contain the supplementary crystallographic data for compounds 1-7, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version.

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Scheme 1 Chemical formulae of the ligands: (E)-N-(pyridin-2-ylmethylene)-1-(pyridin-3-yl)methanamine (L<sub>1</sub>), 1-(pyridine-2-yl)-N-(pyridin-3-ylmethyl)methanamine (L<sub>1</sub>) and (E)-N-(pyridin-2-ylmethylene)-1-(pyridin-4-yl)methanamine (L<sub>2</sub>).

### Table 1

#### Crystal data and structure refinement of 1-7.

-		1	2	3	4	5	6	7
-	Empirical	$C_{100}H_{88}Cu_4I_4$	$C_{48}H_{39}Cu_2I_2N_3P$	$C_{24}H_{22}Cu_2N_{10}O_1$	$C_{24}H_{22}N_{10}O_{12}Zn$	$C_{24}H_{22}Cd_2N_{10}O_1$	C24H26Cd2N10O1	$C_{12}H_{11}C_{12}HgN$
	formula	$N_8P_4$	2	2	2	2	2	3
	Formula weight	2287.46	1100.64	769.62	773.26	867.32	871.35	468.73
	T (K)	100(2)	90(2)	100(2)	93(2)	93(2)	93(2)	94(2)
	Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
	Crystal system	triclinic	triclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
	Space group	P-1	P-1	C2/c	$P2_1/n$	$P2_1/n$	P-1	$P2_1/n$
	a (Å)	8.2060(2)	9.6457(7)	20,1660(3)	7.5968(14)	7.8884(4)	7,1808(16)	7.5999(8)
	b (Å)	17.0610(5)	10.5521(7)	13.1830(3)	13.996(3)	14.0615(7)	7.589(2)	13.0542(12)
	c (Å)	18.8760(5)	12.0381(8)	14.8650(4)	13.796(2)	13.9354(7)	14.824(3)	13.5600(13)
	αÔ	115.0740(7)	103.642(3)	90.0000(12)	90.00	90.00	100.571(14)	90.00
	βÔ	101.0770(10)	108.924(3)	132.3600(10)	102.327(7)	102.859(2)	97.240(13)	91.705(5)
	γÔ	92.0410(11)	90.019(3)	90.0000(9)	90.00	90.00	109.181(13)	90.00
	$V(A^3)$	2328.60(11)	1122.40(13)	2920.11(11)	1433.0(4)	1506.99(13)	734.8(3)	1344.7(2)
	Z	1	1	4	2	2	1	4
	$D_{calc}$ (g cm <sup>-3</sup> )	1.631	1.628	1.751	1.792	1.911	1.969	2.315
	$\mu (mm^{-1})$	2.347	2.430	1.539	1.758	1.491	1.530	11.827
	F (000)	1132	542	1560	784	856	432	872
	Goodness-of-fit	1.050	1.050	1.050	1.093	1,129	1.083	1.136
	Final R indices	$R_1 = 0.0388$ .	$R_1 = 0.0423$	$R_1 = 0.0351$	$R_1 = 0.0294$ .	$R_1 = 0.0258$	$R_1 = 0.0269$	$R_1 = 0.0653$ .
	$[I > 2\sigma(I)]$	$wR_2 = 0.0838$	$wR_2 = 0.0969$	wR <sub>2</sub> =0.0794	$wR_2 = 0.0657$	$wR_2 = 0.0681$	$wR_2 = 0.0602$	$wR_2 = 0.1786$
	R indices (all	$R_1 = 0.0461$ .	$R_1 = 0.0588$ ,	$R_1 = 0.0428$ ,	$R_1 = 0.0385$ .	$R_1 = 0.0349$	$R_1 = 0.0321$	$R_1 = 0.0729$ .
	data)	wR <sub>2</sub> =0.0873	$wR_2 = 0.1033$	$wR_2 = 0.0827$	$WR_2 = 0.0705$	$wR_2 = 0.0717$	$wR_2 = 0.0625$	$wR_2 = 0.1823$
	Largest	1.538 and -	3.274 and -	0.667 and -	0.375 and -	0.733 and -	0.913 and -	4.960 and -
	difference peak	1.340	3.303	0.483	0.358	0.637	0.735	3.191
	and hole (e Å <sup>-3</sup> )							

 Table 2

 Selected bond distances (Å) and angles (°) for 1–4.

				$\mathcal{U}$					•
	1 Cu1-11 Cu1-11 <sup>i</sup> Cu1-N19 Cu1-P1 Cu1-Cu1 Cu2-N41 Cu2-N1 Cu2-P2 Cu2-12	2.674(4) 2.639(4) 2.063(2) 2.230(8) 3.002(7) 2.061(2) 2.097(2) 2.196(7) 2.587(4)	$\begin{array}{c} 2 \\ Cu1-II \\ Cu1-II^{ii} \\ Cu1-NIA \\ Cu1-NIB^{iii} \\ Cu1-NIB^{iii} \\ Cu1-PI \\ Cu1-Cu1^{ii} \end{array}$	2.6712(3) 2.6590(3) 2.052(3) 2.066(3) 2.2234(5) 2.9554(5)	3 Cu1-N5 <sup>iv</sup> Cu1-N3 Cu1-N4 Cu1-O4 Cu1-O1 Cu1-O5	1.9742(14) 1.9777(15) 2.0447(14) 2.1062(13) 2.1743(12) 2.6619(15)	4 Zn1—N3 Zn1—N4 Zn1—N5 Zn1—O1 Zn1—O4 Zn1—O5	2.1259(17) 2.1460(17) 2.0870(17) 2.0899(15) 2.1251(15) 2.4156(17)	
	N19-Cu1-P1 N19-Cu1-I1 <sup>i</sup> N19-Cu1-I1 P1-Cu1-I1 N41-Cu2-N1 N41-Cu2-P2 N1-Cu2-P2 N1-Cu2-P2 N1-Cu2-I2 P2-Cu2-I2	116.92(7) 106.91(7) 100.28(7) 108.50(2) 112.73(2) 80.67(9) 121.30(7) 115.28(7) 106.18(7) 119.94(6) 110.70(2)	II-Cu1-II <sup>ii</sup> P1-Cu1-II P1-Cu1-II <sup>ii</sup> P1-Cu1-N1A P1-Cu1-N1B <sup>iii</sup>	112.653(8) 111.676(13) 112.193(13) 117.66(13) 113.53(14)	N3-Cu1-N4 N3-Cu1-N5 O1-Cu1-N3 O1-Cu1-N3 O1-Cu1-N4 O1-Cu1-N5 O4-Cu1-N3 O4-Cu1-N4 O4-Cu1-N5	80.78(6) 75.06(6) 95.63(6) 89.54(5) 132.97(5) 94.13(5) 91.18(6) 145.51(5) 90.89(5)	N4-Zn1-N5 N3-Zn1-N4 O1-Zn1-N3 O1-Zn1-N4 O1-Zn1-N5 O4-Zn1-N3 O4-Zn1-N3 O5-Zn1-N3 O5-Zn1-N4 O5-Zn1-N5	93.67(6) 77.05(7) 92.36(6) 127.95(6) 91.85(6) 89.89(6) 147.28(6) 56.23(5) 90.06(6) 93.44(6) 92.51(6)	
	P2-Cu2-I2	110.70(2)			NP		O5-Zn1-N5	92.51(6)	
5			2						

**Table 3** Selected bond distances (Å) and angles (°) for 5-7

5 Cd1—N3 Cd1—N4 Cd1—N5 <sup>i</sup> Cd1—O1 Cd1—O2	2.3088(13) 2.3432(13) 2.2728(14) 2.3420(13)	6 Cd1—N3 Cd1—N4 Cd1—N5 <sup>vii</sup> Cd1—Q1	2.313(2) 2.338(2) 2.316(2) 2.428(2)	7 Hg1—Cl1 Hg1—Cl2 Hg1—N3	2.471(5) 2.486(5) 2.514(15)	Ó
Cd1—N3 Cd1—N4 Cd1—N5 <sup>i</sup> Cd1—O1 Cd1—O2	2.3088(13) 2.3432(13) 2.2728(14) 2.3420(13)	Cd1—N3 Cd1—N4 Cd1—N5 <sup>vii</sup> Cd1—O1	2.313(2) 2.338(2) 2.316(2) 2.428(2)	Hg1—Cl1 Hg1—Cl2 Hg1—N3	2.471(5) 2.486(5) 2.514(15)	Ő
Cd1—N4 Cd1—N5 <sup>i</sup> Cd1—O1 Cd1—O2	2.3432(13) 2.2728(14) 2.3420(13)	Cd1—N4 Cd1—N5 <sup>vii</sup> Cd1—O1	2.338(2) 2.316(2)	Hg1—Cl2 Hg1—N3	2.486(5) 2.514(15)	
Cd1—N5 <sup>i</sup> Cd1—O1 Cd1—O2	2.2728(14) 2.3420(13)	Cd1—N5 <sup>vii</sup> Cd1—O1	2.316(2)	Hg1—N3	2.514(15)	
Cd1—O1 Cd1—O2	2.3420(13)	Cd1-01	0 420(0)			
Cd1-02		cui oi	2.438(2)	Hg1—N4	2.345(16)	K
01 02	2.6403(14)	Cd1O2	2.458(2)	Hg1—N5 <sup>vii</sup>	2.376(19)	
Cd1—04	2.3369(13)	Cd104	2.4789(19)			
Cd1—05	2.4977(14)	Cd105	2.382(2)			
N3-Cd1-N4	71.91(5)	N3-Cd1-N4	72.93(8)	Cl1—Hg1—Cl2	120.74(18)	
N3-Cd1-N5 <sup>vi</sup>	168.30(5)	N3-Cd1-N5 <sup>vii</sup>	168,26(8)	Cl1—Hg1—N3	107.9(4)	
N4-Cd1-N5 <sup>vi</sup>	96.78(5)	N4-Cd1-N5 <sup>vii</sup>	116.33(8)	Cl2—Hg1—N3	131.3(4)	
O1-Cd1-N3	92.72(5)	O1-Cd1-N3	84.52(7)	Cl1—Hg1—N4	108.1(4)	
O1-Cd1-N4	131.09(4)	O1-Cd1-N4	91.65(8)	Cl2—Hg1—N4	92.3(4)	
D1-Cd1-N5 <sup>v1</sup>	92.66(5)	O1-Cd1-N5 <sup>vii</sup>	87.90(7)	Cl1—Hg1—N5 <sup>viii</sup>	95.6(5)	
04-Cd1-N3	88.62(5)	O4-Cd1-N3	106.25(7)	Cl2—Hg1—N5 <sup>vm</sup>	94.3(5)	
J4-Cd1-N4	144.19(5)	O4-Cd1-N4	80.42(7)	N3—Hg1—N4	68.7(5)	
J4-Cd1-N5	102.66(5)	04-Cd1-N5	83.14(7)	N3—Hg1—N5 <sup>m</sup>	83.4(6)	
J5-Cd1-N3	92.96(5)	05-Cd1-N3	90.15(7)	N4—Hg1—N5	147.0(6)	
J5-Cd1-N4	96.99(5)	05-Cd1-N4	123.90(8)			
05-Cal-N5	91.39(4) 51.10(4)	03-Cd1-N3	90.03(7)			
01-Cd1-04	78.04(5)	01-Cd1-04	163.84(6)			
51-Cu1-0+	70.04(5)	01-041-04	105.04(0)			
6	R					
	Cd1—O5 N3-Cd1-N4 N3-Cd1-N5 <sup>vi</sup> N4-Cd1-N5 <sup>vi</sup> D1-Cd1-N3 D1-Cd1-N4 D4-Cd1-N3 D4-Cd1-N5 <sup>vi</sup> D5-Cd1-N4 D5-Cd1-N5 <sup>vi</sup> D5-Cd1-N4 D5-Cd1-N5 <sup>vi</sup> D1-Cd-O2 D1-Cd1-O4	Cd1O5 2.4977(14) N3-Cd1-N4 71.91(5) N3-Cd1-N5 <sup>vi</sup> 168.30(5) N4-Cd1-N5 <sup>vi</sup> 96.78(5) D1-Cd1-N3 92.72(5) D1-Cd1-N4 131.09(4) D1-Cd1-N5 <sup>vi</sup> 92.66(5) D4-Cd1-N3 88.62(5) D4-Cd1-N5 <sup>vi</sup> 102.66(5) D5-Cd1-N3 92.96(5) D5-Cd1-N4 96.99(5) D5-Cd1-N4 96.99(5) D5-Cd1-N5 <sup>vi</sup> 91.39(4) D1-Cd-O2 51.10(4) D1-Cd1-O4 78.04(5)	Cd1O5 2.4977(14) Cd1O5 N3-Cd1-N4 71.91(5) N3-Cd1-N4 N3-Cd1-N5 <sup>vi</sup> 168.30(5) N3-Cd1-N5 <sup>vii</sup> 96.78(5) N4-Cd1-N5 <sup>vii</sup> 91-Cd1-N3 92.72(5) O1-Cd1-N3 D1-Cd1-N4 131.09(4) O1-Cd1-N4 D1-Cd1-N5 <sup>vi</sup> 92.66(5) O4-Cd1-N3 O4-Cd1-N3 88.62(5) O4-Cd1-N3 O4-Cd1-N5 <sup>vi</sup> 102.66(5) O4-Cd1-N5 <sup>vii</sup> D5-Cd1-N3 92.96(5) O5-Cd1-N3 D5-Cd1-N4 96.99(5) O5-Cd1-N4 D5-Cd1-N5 <sup>vi</sup> 91.39(4) O5-Cd1-N5 <sup>vii</sup> D1-Cd-O2 51.10(4) O1-Cd-O2 D1-Cd1-O4 78.04(5) O1-Cd1-O4	Cd1—O5 2.4977(14) Cd1—O5 2.382(2) N3-Cd1-N5 <sup>vi</sup> 168.30(5) N3-Cd1-N5 <sup>vii</sup> 168,26(8) N4-Cd1-N5 <sup>vii</sup> 96.78(5) N4-Cd1-N5 <sup>viii</sup> 116.33(8) D1-Cd1-N3 92.72(5) O1-Cd1-N3 84.52(7) D1-Cd1-N4 131.09(4) O1-Cd1-N4 91.65(8) D1-Cd1-N5 <sup>vii</sup> 92.66(5) O4-Cd1-N3 106.25(7) D4-Cd1-N3 88.62(5) O4-Cd1-N3 106.25(7) D4-Cd1-N3 92.96(5) O5-Cd1-N4 80.42(7) D4-Cd1-N5 <sup>vii</sup> 102.66(5) O4-Cd1-N5 <sup>viii</sup> 83.14(7) D5-Cd1-N3 92.96(5) O5-Cd1-N4 123.90(8) D5-Cd1-N5 <sup>vii</sup> 91.39(4) O5-Cd1-N5 <sup>viii</sup> 90.05(7) D1-Cd-O2 51.10(4) O1-Cd-O2 52.87(6) D1-Cd1-O4 78.04(5) O1-Cd1-O4 163.84(6)	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	

#### Table 4

					U						
#	М	L	$l_2 - l_1$	$I_5 - l_4$	$A_1 - A_2$	$A_4 - A_5$	$l_3 - l_2$	$l_6 - l_5 = A_3$	3 A <sub>6</sub>	Mode $NO_3(1)$	Mode NO <sub>3</sub> (2)
3	Cu	$L_1$	0.81	0.55	33	25	0.03	0.11 1:	58 166	Monodentate	Anisobident
											ate
4	Zn	$L_1$	0.73	0.29	35	13	0.03	0.24 10	60 169	Monodentate	Bidentate
5	Cd	$L_1$	0.30	0.16	13	7	0.26	0.31 1'	72 173	Bidentate	Bidentate
6	Cd	$L_1$	0.02	0.10	1	5	0.37	0.35 1	70 177	Bidentate	Bidentate
4 5 6	Zn Cd Cd	$\begin{array}{c} L_1 \\ L_1 \\ L_1 \end{array}$	0.73 0.30 0.02	0.29 0.16 0.10	35 13 1	13 7 5	0.03 0.26 0.37	0.24 10 0.31 17 0.35 17	601697217370177	Monodentate Bidentate Bidentate	Bidentate Bidentate Bidentate

#### **Figure captions:**

**Fig. 1.** The structure of  $[Cu_2(L_1)(PPh_3)_2I_2]_2$  (1) showing the atom numbering, symmetry operation i = 1-x, 1-y, 1-z.

**Fig. 2.** Part of the structure of  $[Cu_2(L_2)(PPh_3)_2I_2]_n$  (2) showing the atom numbering, symmetry operations ii = -x+1, -y+1, -z+1, iii = -x, -y+2, -z+1. Only one disorder component of the equally disordered ((E)-1-(pyridin-3-yl)-N-(pyridine-4-ylmethylene)methanamine (L<sub>2</sub>) ligand is shown for clarity.

**Fig. 3.** Part of the one dimensional polymer chain formed by **2** with selected atoms numbered. Symmetry operations ii = -x+1, -y+1, -z+1, iii = -x, -y+2, -z+1. Only one disorder component of the equally disordered ((E)-1-(pyridin-3-yl)-N-(pyridine-4-ylmethylene)methanamine (L<sub>2</sub>) ligand is shown for clarity.

**Fig. 4.** The structure of  $[Cu(L_1)(NO_3)_2]_2$  (**3**) showing the atom numbering, symmetry operation iv = -x+1/2, -y+1/2, -z.

**Fig. 5.** Two views of the cavity formed in the structure of **3** (a) perpendicular to the Cu1—N4 bonds. (b) along the mean planes of the 2- and 3-pyridyl rings.

**Fig. 6.** a) The structure of **4** showing the atom numbering scheme with ellipsoids drawn at the 50% probability level, v = -x+1, -y+1, -z+1. b) The structure of **5** showing the atom numbering scheme with ellipsoids drawn at the 50% probability level, vi = -x+2, -y, -z+1. c) The structure of **6** showing the atom numbering scheme with ellipsoids drawn at the 50% probability level, vi = -x+1, -y+2, -z+1.

**Fig. 7.** Parameters used to define the coordination preferences of the nitrato ligands, adapted from Kleywegt *et al* [56].

Fig. 8. (a) The distorted trigonal bipyramidal coordination sphere of 3. (b) The highly distorted octahedral coordination sphere of 4. (c) The distorted pentagonal bipyramidal coordination sphere of 5. (d) The distorted, capped octahedral coordination sphere of 6.

**Fig. 9.** Varying coordination geometries of **3**-**6** with only the central N atoms of the bidentate  $NO_3^-$  ligands displayed. Atoms are drawn as spheres of arbitrary radius and the contacts with the N atoms of the bidentate nitrato ligands shown as dashed lines. (a) **3**, (b) **4**, (c) **5**, (d) **6**.

Fig. 10. The distorted square pyramidal coordination sphere for 7 with atoms drawn as spheres of arbitrary radius.

**Fig. 11.** Polymer chains of **7** propagating along the *b* axis through Hg—N5<sup>viii</sup> bonds, viii = 3/2-x, 1/2+y, 1/2-z.

Fig. 12. A comparison of the structures 4 and 7 (through overlaying the metal atoms and the chelate ring systems in both molecules).



Fig. 1.















Fig. 6.











### Self-assembly of chelating, bridging N, N, N donor ligands and Cu(I), Cu(II), Cd(II), Hg(II): molecular box versus coordination polymer

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A series of molecular boxes and coordination polymers have been synthesized from the reaction of three chelating and bridging N, N, N donor ligands and transition metal salts. The solid state structures of all the compounds were studied by X-ray crystallography. The metal coordination geometries, coordination mode of the nitrato ligands and effects of the chlorido ligands on the structures are discussed

