# A mechanochemically synthesised solid solution enables engineering of the sorption properties of a Werner clathrate

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### 1 Materials and methods

Thermal analyses were carried out under nitrogen at a heating rate of 10 °C per minute using a TA instruments Q500 TGA. Diffraction patterns were recorded on a PANalytical XPERT-PRO diffractometer system using Bragg-Brentano geometry and an incident beam of Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å).

### 2 Solution synthesis

The inclusion compounds were prepared by dissolving the host material in methanol, and then layering with the intended guest (o-, m- or p-xylene).

### [NiCl<sub>2</sub>(4-PhPy)<sub>4</sub>]·2*m*-xylene



Fig. S1 Packing diagram of  $[NiCl_2(4-PhPy)_4]\cdot 2m$ -xylene as viewed along the *c* axis. The *m*-xylene guest molecules occupy the guest-accessible channels. Hydrogen atoms have been omitted for clarity

#### [NiCl<sub>2</sub>(4-PhPy)<sub>4</sub>]·4*o*-xylene



**Fig. S2** Packing diagram of [NiCl<sub>2</sub>(4-PhPy)<sub>4</sub>]·4*o*-xylene as viewed along the *a* axis. The *o*-xylene guest molecules occupy the guest-accessible channels. Hydrogen atoms have been omitted for clarity

### [NiCl<sub>2</sub>(4-PhPy)<sub>4</sub>]·4*p*-xylene



**Fig. S3** Packing diagram of  $[NiCl_2(4-PhPy)_4]\cdot 4p$ -xylene as viewed along the *a* axis. The *p*-xylene guest molecules occupy the guest-accessible channels. Hydrogen atoms have been omitted for clarity

### [NiCl<sub>2</sub>(4-PhPy)<sub>4</sub>]·4*m*-xylene



**Fig. S4** Packing diagram of  $[CoCl_2(4-PhPy)_4]\cdot 4m$ -xylene as viewed along the *b* axis. The *m*-xylene guest molecules occupy the guest-accessible channels.

### [CoCl<sub>2</sub>(4-PhPy)<sub>4</sub>]·4*o*-xylene



**Fig. S5** Packing diagram of [**CoCl**<sub>2</sub>(**4-PhPy**)<sub>4</sub>]**·4***o***-xylene** as viewed along the *a* axis. The *o*-xylene guest molecules are situated in the guest-accessible channels.

### [CoCl<sub>2</sub>(4-PhPy)<sub>4</sub>]·4*p*-xylene



**Fig. S6** Packing diagram of [**CoCl<sub>2</sub>(4-PhPy)<sub>4</sub>]·4***p***-xylene** as vied along the *a* axis. The *p*-xylene guest molecules occupy the guest-accessible channels.

#### **3** Mechanochemical synthesis

[NiCl<sub>2</sub>(4-PhPy)<sub>4</sub>]: A mixture of 4-phenylpyridine (62 mg; 0.4 mmol), nickel (II) chloride hexahydrate (23.71 mg; 0.1 mmol) and a few drops of methanol were ground together using a mortar and pestle. The paste was then allowed to dry in open air.

[CoCl<sub>2</sub>(4-PhPy)<sub>4</sub>]: A mixture of 4-phenylpyridine (62 mg; 0.4 mmol), cobalt (II) chloride hexahydrate (23.71 mg; 0.1 mmol) and a few drops of methanol were ground together using a mortar and pestle. The paste was then allowed to dry in open air.

 $[Ni_{0.5}Co_{0.5}Cl_{2}\cdot(4-PhPy)_{4}]$ : A mixture of 4-phenylpyridine (62 mg; 0.4 mmol), nickel (II) chloride hexahydrate (11.85 mg; 0.05 mmol), cobalt (II) chloride hexahydrate (11.85 mg: 0.05 mmol) and a few drops of methanol were ground together using a mortar and pestle. The paste was then allowed to dry in open air.

### 4 Solid-vapour reactions

The solid vapour reactions were carried out using a microbalance, which monitors weight change as a function of time under controlled conditions of temperature and pressure.

 $[NiCl_2(4-PhPy)_4]\cdot 2m$ -xylene: 25.350 mg (0.034 mmol) of 1 were weighed on a microbalance under vacuum at 20 °C. 2 ml of *m*-xylene was injected into the microbalance and the weight equilibrated for 220 minutes to 32.540 mg, corresponding to 0.107 mmol of *m*-xylene sorbed.

 $[NiCl_2(4-PhPy)_4]\cdot 4o$ -xylene: 21.540 mg (0.029 mmol) of 1 were weighed on a microbalance under vacuum at 20 °C. 2 ml of *o*-xylene was injected into the microbalance and the weight equilibrated for 220 minutes to 31.354 mg, corresponding to 0.116 mmol of *o*-xylene sorbed.

[NiCl<sub>2</sub>(4-PhPy)<sub>4</sub>]·4*p*-xylene: 23.834 mg (0.032 mmol)) of **1** were weighed on a microbalance under vacuum at a controlled temperature of 20 °C. 2 ml of *p*-xylene was injected into the microbalance and the weight equilibrated for 220 minutes to 35.210 mg, corresponding to 0.150 mmol of *p*-xylene sorbed.

 $[CoCl_2(4-PhPy)_4]$ ·4*o*-xylene: 11.055 mg (0.0147 mmol) of **2** were weighed on a microbalance under vacuum at 20° C. 2 ml of *o*-xylene was injected into the microbalance and the weight equilibrated for 220 minutes to 16.484 mg, corresponding to 0.0511 mmol of *o*-xylene sorbed.

 $[CoCl_2(4-PhPy)_4]$ ·4*m*-xylene: 22.876 mg (0.0305 mmol) of **2** were weighed on a microbalance under vacuum at 20 °C. 2 ml of *m*-xylene was injected into the microbalance and the weight equilibrated for 220 minutes to 32.540 mg, corresponding to 0.0910 mmol of *m*-xylene sorbed.

 $[CoCl_2(4-PhPy)_4]$ -4*p*-xylene: 23.768 mg (0.032 mmol)) of **2** were weighed on a microbalance under vacuum at 20 °C. 2 ml of *p*-xylene was injected into the microbalance and the weight equilibrated for 220 minutes to 31.835 mg, corresponding to 0.076 mmol of *p*-xylene sorbed.

 $[Ni_{0.5}Co_{0.5}Cl_2(4-PhPy)_4]$ ·4*o*-xylene : 21.609 mg (0.029 mmol) of **3** were weighed on a microbalance under vacuum at 20° C. 2 ml of *o*-xylene was injected into the microbalance and the weight equilibrated for 220 minutes to 32.553 mg, corresponding to 0.103 mmol of *o*-xylene sorbed.

 $[Ni_{0.5}Co_{0.5}Cl_2(4-PhPy)_4]\cdot 4m$ -xylene: 24.513 mg (0.033 mmol) of **3** were weighed on a microbalance under vacuum at a controlled temperature of 20 °C. 2 ml of *m*-xylene was injected into the microbalance and the weight equilibrated for 220 minutes to 35. 418 mg, corresponding to 0.103 mmol of *m*-xylene sorbed.

 $[Ni_{0.5}Co_{0.5}Cl_2(4-PhPy)_4]\cdot 4p$ -xylene: 18.407 mg (0.0245 mmol)) of 3 were weighed on a microbalance under vacuum at a controlled temperature of 20 °C. 2 ml of *p*-xylene was injected into the microbalance and the weight equilibrated for 220 minutes to 19.788 mg, corresponding to 0.01 mmol of p-xylene sorbed.

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## 5 Thermogravimetric analysis



Fig. S7 The TGA of compounds 1, 2 and 3.

6 Powder X-Ray diffraction



Fig. S8 PXRD comparison for the  $\alpha$  phase of compound 1, the *m*-xylene clathrate resulting from the solid vapour synthesis and the simulated pattern of the *m*-xylene clathrate resulting from solution synthesis.



Fig. S9 PXRD comparison for the  $\alpha$  phase of compound 1, the *o*-xylene clathrate resulting from the solid vapour synthesis and the simulated pattern of the *o*-xylene clathrate resulting from solution synthesis.



Fig. S10 PXRD comparison for the  $\alpha$  phase of compound 1, the *p*-xylene clathrate resulting from the solid vapour synthesis and the simulated pattern of the *p*-xylene clathrate resulting from solution synthesis.



Fig. S11 Comparison of the PXRD patterns for the  $\alpha$  phase for 2, *m*-xylene clathrate obtained from solid vapour synthesis and the simulated pattern of the *m*-xylene clathrate obtained from solution synthesis.



Fig. S12 Comparison of the PXRD patterns for the  $\alpha$  phase for compound 2, *p*-xylene clathrate obtained from solid vapour synthesis and the simulated pattern of the *p*-xylene clathrate obtained from solution synthesis.



Fig. S13 Comparison of the PXRD patterns for the  $\alpha$  phase for compound 2, *o*-xylene clathrate obtained from solid vapour synthesis and the *o*-xylene clathrate obtained from solution synthesis.



Fig. S14 PXRD analysis for the  $\alpha$  phase of compound 3, the *m*-xylene clathrate prepared by solid vapour synthesis and the simulated pattern for *m*-xylene phase for compound 1.



Fig. S15 PXRD analysis for the  $\alpha$  phase of compound 3, the *o*-xylene clathrate prepared by solid vapour synthesis and the simulated pattern of *o*-xylene phase for compound 1.



Fig S16. PXRD analysis for the  $\alpha$  phase of compound 3, the *p*-xylene clathrate prepared by solid vapour synthesis and the simulated pattern of *p*-xylene clathrate of compound 1.

### 6 Crystallographic data

Single crystal X-ray diffraction data were collected on a Bruker Apex II Duo diffractometer employing Mo-K $\alpha$  radiation. The temperature was controlled using an Oxford Cryostream cooler. Data reduction and absorption corrections were carried out using the SAINT<sup>1</sup> and SADABS<sup>2,3</sup> programmes, respectively. The structures were solved by direct methods or a combination of Patterson and partial structure expansion using SHELXS-97.<sup>4</sup> Non-hydrogen atoms were refined anisotropically by means of full-matrix least squares calculations on  $F^2$ using SHELXL-97<sup>4</sup> within the X-Seed<sup>5</sup> graphical user interface. Hydrogen atoms were placed on calculated positions.

In the **1**-*m*-**xylene** structure one of the *m*-xylene molecules was refined as disordered over two positions in a ratio of 0.64 to 0.36. The **2**-*m*-**xylene** structure was a non-merohedral twin which was integrated in two twin domains after identification of the orientation matrices using the program CELL\_NOW<sup>6</sup>. The twin law is a twofold rotation about [0 1 0]. In the **1**-*o*-**xylene** and **2**-*o*-**xylene** structures there is disorder of both the ligand and the guest molecules. In **1**-*o*-**xylene** the phenyl substituent of the ligand could be modelled as disordered over two positions of 60-40% occupancy, while the various positions of the disordered *o*-xylene could not be resolved. Therefore, the highest populated orientation was refined as a full occupancy

molecule for both the *o*-xylene molecules in the asymmetric unit. In the **2**·*o*-xylene structure one of the ligand molecules is disordered and was modelled as two components in a 0.55 to 0.45 ratio. In one of the *o*-xylene molecules, the highest populated orientation was modelled as a full occupancy molecule, while the second *o*-xylene molecule was modelled as a three part disorder in a 0.33 to 0.34 to 0.32 ratio.

In the **1·MeOH** structure the methanol has an occupancy of 88% (as determined from an electron density summation in SQUEEZE), and it is disordered over two positions. However, an attempt to model the methanol as a two part disorder did not yield a satisfactory model, therefore only the highest populated orientation was refined. In the **2·MeOH** structure the unresolved electron density in the channels was treated with SQUEEZE which resulted in a *R1* of 0.0478.

**1**•*o*-xylene:  $C_{76}H_{52}Cl_2N_4Ni$ , M = 1150.83,  $0.32 \times 0.26 \times 0.18 \text{ mm}^3$ , monoclinic, space group C2/c (No. 15), a = 9.6749(5), b = 23.1727(12), c = 28.2174(15) Å,  $\beta = 95.5260(10)^\circ$ , V = 6296.8(6) Å<sup>3</sup>, Z = 4,  $D_c = 1.214$  g/cm<sup>3</sup>,  $F_{000} = 2392$ , Bruker Duo CCD Area Detector, MoK $\alpha$  radiation,  $\lambda = 0.71073$  Å, T = 100(2)K,  $2\theta_{max} = 56.7^\circ$ , 23418 reflections collected, 7832 unique (R<sub>int</sub> = 0.0260). Final *GooF* = 1.036, *R1* = 0.0616, *wR2* = 0.1774, *R* indices based on 6285 reflections with I >2sigma(I) (refinement on  $F^2$ ), 428 parameters, 134 restraints. Lp and absorption corrections applied,  $\mu = 0.439$  mm<sup>-1</sup>.

**1**•*m*-**xylene**: C<sub>60</sub>H<sub>46</sub>Cl<sub>2</sub>N<sub>4</sub>Ni, M = 952.62, 0.46 × 0.33 × 0.12 mm<sup>3</sup>, triclinic, space group *P*-1 (No. 2), a = 12.6484(13), b = 12.7069(13), c = 15.9544(17) Å,  $\alpha = 89.157(2)$ ,  $\beta = 77.167(2)$ ,  $\gamma = 88.118(2)^{\circ}$ , V = 2498.8(4) Å<sup>3</sup>, Z = 2,  $D_c = 1.266$  g/cm<sup>3</sup>,  $F_{000} = 992$ , Bruker Duo CCD Area Detector, MoK $\alpha$  radiation,  $\lambda = 0.71073$  Å, T = 100(2)K,  $2\theta_{max} = 61.9^{\circ}$ , 37396 reflections collected, 14495 unique (R<sub>int</sub> = 0.0378). Final *GooF* = 1.030, *R1* = 0.0459, *wR2* = 0.1135, *R* indices based on 10915 reflections with I >2sigma(I) (refinement on  $F^2$ ), 599 parameters, 0 restraints. Lp and absorption corrections applied,  $\mu = 0.538$  mm<sup>-1</sup>.

**1**·*p*-xylene:  $C_{76}H_{76}Cl_2N_4Ni$ , M = 1175.02,  $0.33 \times 0.18 \times 0.12 \text{ mm}^3$ , monoclinic, space group C2/c (No. 15), a = 9.5570(9), b = 23.899(2), c = 27.482(3) Å,  $\beta = 97.806(2)^\circ$ , V = 6218.9(10) Å<sup>3</sup>, Z = 4,  $D_c = 1.255 \text{ g/cm}^3$ ,  $F_{000} = 2488$ , Bruker Duo CCD Area Detector, MoK $\alpha$  radiation,  $\lambda = 0.71073$  Å, T = 100(2)K,  $2\theta_{max} = 61.2^\circ$ , 24858 reflections collected, 8844 unique (R<sub>int</sub> = 0.0415). Final *GooF* = 1.036, *R1* = 0.0428, *wR2* = 0.0968, *R* indices based on 6462 reflections with I >2sigma(I) (refinement on  $F^2$ ), 383 parameters, 0 restraints. Lp and absorption corrections applied,  $\mu = 0.445 \text{ mm}^{-1}$ .

**2**·*o*-xylene: C<sub>73.34</sub>H<sub>56</sub>Cl<sub>2</sub>CoN<sub>4</sub>, M = 1123.43, 0.35 × 0.22 × 0.07 mm<sup>3</sup>, monoclinic, space group *C*2/*c* (No. 15), a = 9.7131(18), b = 23.566(4), c = 28.167(5) Å,  $\beta = 96.357(3)^{\circ}$ , V = 6408(2) Å<sup>3</sup>, Z = 4,  $D_c = 1.165$  g/cm<sup>3</sup>,  $F_{000} = 2340.4$ , Bruker Duo CCD Area Detector, MoK $\alpha$  radiation,  $\lambda = 0.71073$  Å, T = 100(2)K,  $2\theta_{max} = 56.7^{\circ}$ , 23171 reflections collected, 7934 unique (R<sub>int</sub> = 0.0803). Final *GooF* = 1.028, *R1* = 0.0997, *wR2* = 0.2618, *R* indices based on

4039 reflections with I >2sigma(I) (refinement on  $F^2$ ), 459 parameters, 17 restraints. Lp and absorption corrections applied,  $\mu = 0.395 \text{ mm}^{-1}$ .

**2**·*p*-xylene:  $C_{76}H_{76}Cl_2CoN_4$ , M = 1175.24,  $0.33 \times 0.15 \times 0.09 \text{ mm}^3$ , monoclinic, space group C2/c (No. 15), a = 9.555(4), b = 24.019(9), c = 27.580(10) Å,  $\beta = 98.020(6)^\circ$ , V = 6268(4) Å<sup>3</sup>, Z = 4,  $D_c = 1.245 \text{ g/cm}^3$ ,  $F_{000} = 2484$ , Bruker SMART APEX CCD Area Detector, MoK $\alpha$  radiation,  $\lambda = 0.71073$  Å, T = 100(2)K,  $2\theta_{max} = 50.0^\circ$ , 16087 reflections collected, 5519 unique (R<sub>int</sub> = 0.1056). Final *GooF* = 0.954, RI = 0.0598, wR2 = 0.1196, R indices based on 3022 reflections with I >2sigma(I) (refinement on  $F^2$ ), 384 parameters, 0 restraints. Lp and absorption corrections applied,  $\mu = 0.406 \text{ mm}^{-1}$ .

**2** *m*-xylene: C<sub>76</sub>H<sub>76</sub>Cl<sub>2</sub>CoN<sub>4</sub>, M = 1175.24, 0.41 × 0.33 × 0.20 mm<sup>3</sup>, monoclinic, space group C2/c (No. 15), a = 23.480(5), b = 11.315(2), c = 23.479(3) Å,  $\beta = 91.59^{\circ}$ , V = 6235.4(19) Å<sup>3</sup>, Z = 4,  $D_c = 1.252$  g/cm<sup>3</sup>,  $F_{000} = 2484$ , Bruker Duo CCD Area Detector, MoK $\alpha$  radiation,  $\lambda = 0.71073$  Å, T = 173(2)K,  $2\theta_{max} = 50.0^{\circ}$ , 5304 reflections collected, 5304 unique (R<sub>int</sub> = 0.0000). Final *GooF* = 1.101, RI = 0.0682, wR2 = 0.1891, R indices based on 4687 reflections with I >2sigma(I) (refinement on  $F^2$ ), 381 parameters, 0 restraints. Lp and absorption corrections applied,  $\mu = 0.408$  mm<sup>-1</sup>.

**1.MeOH:**C<sub>44.82</sub>H<sub>38.45</sub>Cl<sub>2</sub>N<sub>4</sub>NiO<sub>0.82</sub>, M = 775.67,  $0.45 \times 0.23 \times 0.11 \text{ mm}^3$ , orthorhombic, space group  $P2_12_12_1$  (No. 19), a = 12.3778(17), b = 16.212(2), c = 19.398(3) Å, V = 3892.7(9) Å<sup>3</sup>, Z = 4,  $D_c = 1.324 \text{ g/cm}^3$ ,  $F_{000} = 1616.0$ , Bruker APEX CCD Area Detector, MoK $\alpha$  radiation,  $\lambda = 0.71073$  Å, T = 100(2)K,  $2\theta_{\text{max}} = 109.9^\circ$ , 23493 reflections collected, 9086 unique (R<sub>int</sub> = 0.0296). Final *GooF* = 1.174, RI = 0.0512, wR2 = 0.1071, R indices based on 8306 reflections with I >2sigma(I) (refinement on  $F^2$ ), 480 parameters, 0 restraints. Lp and absorption corrections applied,  $\mu = 0.675 \text{ mm}^{-1}$ . Absolute structure parameter = 0.052(16) (Flack, H. D. Acta Cryst. **1983**, A39, 876-881).

**2·MeOH**: C<sub>44</sub>H<sub>36</sub>Cl<sub>2</sub>CoN<sub>4</sub>, M = 750.60, 0.44 × 0.37 × 0.28 mm<sup>3</sup>, monoclinic, space group C2/c (No. 15), a = 9.273(2), b = 23.801(5), c = 21.313(5) Å,  $\beta = 98.130(4)^{\circ}$ , V = 4656.8(18) Å<sup>3</sup>, Z = 4,  $D_c = 1.071$  g/cm<sup>3</sup>,  $F_{000} = 1556$ , Bruker Duo CCD Area Detector, MoK $\alpha$  radiation,  $\lambda = 0.71073$  Å, T = 100(2)K,  $2\theta_{max} = 56.9^{\circ}$ , 16686 reflections collected, 5825 unique (R<sub>int</sub> = 0.0422). Final *GooF* = 1.041, *R1* = 0.0477, *wR2* = 0.1170, *R* indices based on 3848 reflections with I >2sigma(I) (refinement on  $F^2$ ), 235 parameters, 0 restraints. Lp and absorption corrections applied,  $\mu = 0.513$  mm<sup>-1</sup>.

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