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 Kα radiation (λ = 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).

\[\text{[NiCl}_2\text{(4-PhPy)}_4\text{]}\cdot2\text{m-xylene}\]

**Fig. S1** Packing diagram of [NiCl₂(4-PhPy)_₄]·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$_2$(4-PhPy)$_4$]·4o-xylene

**Fig. S2** Packing diagram of [NiCl$_2$(4-PhPy)$_4$]·4o-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$_2$(4-PhPy)$_4$]·4p-xylene

**Fig. S3** Packing diagram of [NiCl$_2$(4-PhPy)$_4$]·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.
**[NiCl₂(4-PhPy)₄]·4m-xylene**

Fig. S4 Packing diagram of [CoCl₂(4-PhPy)₄]·4m-xylene as viewed along the b axis. The m-xylene guest molecules occupy the guest-accessible channels.

**[CoCl₂(4-PhPy)₄]·4o-xylene**

Fig. S5 Packing diagram of [CoCl₂(4-PhPy)₄]·4o-xylene as viewed along the a axis. The o-xylene guest molecules are situated in the guest-accessible channels.
[CoCl$_2$(4-PhPy)$_4$]$\cdot$4$p$-xylene

Fig. S6 Packing diagram of [CoCl$_2$(4-PhPy)$_4$]$\cdot$4$p$-xylene as viewed along the $a$ axis. The $p$-xylene guest molecules occupy the guest-accessible channels.

3 Mechanochemical synthesis

[NiCl$_2$(4-PhPy)$_4$]: 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$_2$(4-PhPy)$_4$]: 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$_2$(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.

\[[\text{NiCl}_2(\text{4-PhPy})_4] \cdot 2m\text{-xylene}\]: 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.

\[[\text{NiCl}_2(\text{4-PhPy})_4] \cdot 4o\text{-xylene}\]: 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.

\[[\text{NiCl}_2(\text{4-PhPy})_4] \cdot 4p\text{-xylene}\]: 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.

\[[\text{CoCl}_2(\text{4-PhPy})_4] \cdot 4o\text{-xylene}\]: 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.

\[[\text{CoCl}_2(\text{4-PhPy})_4] \cdot 4m\text{-xylene}\]: 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.

\[[\text{CoCl}_2(\text{4-PhPy})_4] \cdot 4p\text{-xylene}\]: 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}]·4o-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}]·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}]·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.
5 Thermogravimetric analysis

Fig. S7 The TGA of compounds 1, 2 and 3.
6 Powder X-Ray diffraction

Fig. S8 PXRD comparison for the α 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 α 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 α 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 α 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 α 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 α 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 α 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 α 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 α 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-Kα radiation. The temperature was controlled using an Oxford Cryostream cooler. Data reduction and absorption corrections were carried out using the SAINT\textsuperscript{1} and SADABS\textsuperscript{2,3} programmes, respectively. The structures were solved by direct methods or a combination of Patterson and partial structure expansion using SHELXS-97\textsuperscript{4}. Non-hydrogen atoms were refined anisotropically by means of full-matrix least squares calculations on $F^2$ using SHELXL-97\textsuperscript{4} within the X-Seed\textsuperscript{5} 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\textsuperscript{6}. 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: \( \text{C}_{76}\text{H}_{62}\text{Cl}_2\text{N}_4\text{Ni}, \ M = 1150.83, 0.32 \times 0.26 \times 0.18 \text{ mm}^3 \), monoclinic, space group \( \text{C}2/c \) (No. 15), \( a = 9.6749(5), b = 23.1727(12), c = 28.2174(15) \text{ Å}, \beta = 95.5260(10)^\circ, V = 6296.8(6) \text{ Å}^3, Z = 4, D_c = 1.214 \text{ g/cm}^3, F_{000} = 2392, \text{Bruker Duo CCD Area Detector, MoK}\alpha \text{ radiation,} \lambda = 0.71073 \text{ Å, } T = 100(2)\text{K, } 2\theta_{\text{max}} = 56.7^\circ, 23418 \text{ reflections collected, 7832 unique (} \text{R}_{\text{int}} = 0.0260). \text{Final } \text{GooF} = 1.036, \text{ } R1 = 0.0616, wR2 = 0.1774, \text{ } R \text{ indices based on 6285 reflections with } I >2\text{sigma}(I) \text{ (refinement on } F^2), 428 \text{ parameters, 134 restraints. } \text{Lp and absorption corrections applied, } \mu = 0.439 \text{ mm}^{-1}.\)

1-m-xylene: \( \text{C}_{60}\text{H}_{46}\text{Cl}_2\text{N}_4\text{Ni}, \ M = 952.62, 0.46 \times 0.33 \times 0.12 \text{ mm}^3 \), triclinic, space group \( \text{P}-1 \) (No. 2), \( a = 12.6484(13), b = 12.7069(13), c = 15.9544(17) \text{ Å}, \alpha = 89.157(2), \beta = 77.167(2), \gamma = 88.118(2)^\circ, V = 2498.8(4) \text{ Å}^3, Z = 2, D_c = 1.266 \text{ g/cm}^3, F_{000} = 992, \text{Bruker Duo CCD Area Detector, MoK}\alpha \text{ radiation,} \lambda = 0.71073 \text{ Å, } T = 100(2)\text{K, } 2\theta_{\text{max}} = 61.9^\circ, 37396 \text{ reflections collected, 14495 unique (} \text{R}_{\text{int}} = 0.0378). \text{Final } \text{GooF} = 1.030, \text{ } R1 = 0.0459, wR2 = 0.1135, \text{ } R \text{ indices based on 10915 reflections with } I >2\text{sigma}(I) \text{ (refinement on } F^2), 599 \text{ parameters, 0 restraints. } \text{Lp and absorption corrections applied, } \mu = 0.538 \text{ mm}^{-1}.\)

1-p-xylene: \( \text{C}_{76}\text{H}_{76}\text{Cl}_2\text{N}_4\text{Ni}, \ M = 1175.02, 0.33 \times 0.18 \times 0.12 \text{ mm}^3 \), monoclinic, space group \( \text{C}2/c \) (No. 15), \( a = 9.5570(9), b = 23.8992(2), c = 27.482(3) \text{ Å}, \beta = 97.806(2)^\circ, V = 6218.9(10) \text{ Å}^3, Z = 4, D_c = 1.255 \text{ g/cm}^3, F_{000} = 2488, \text{Bruker Duo CCD Area Detector, MoK}\alpha \text{ radiation,} \lambda = 0.71073 \text{ Å, } T = 100(2)\text{K, } 2\theta_{\text{max}} = 61.2^\circ, 24858 \text{ reflections collected, 8844 unique (} \text{R}_{\text{int}} = 0.0415). \text{Final } \text{GooF} = 1.036, \text{ } R1 = 0.0428, wR2 = 0.0968, \text{ } R \text{ indices based on 6462 reflections with } I >2\text{sigma}(I) \text{ (refinement on } F^2), 383 \text{ parameters, 0 restraints. } \text{Lp and absorption corrections applied, } \mu = 0.445 \text{ mm}^{-1}.\)

2-o-xylene: \( \text{C}_{73,34}\text{H}_{56}\text{Cl}_2\text{CoN}_4, \ M = 1123.43, 0.35 \times 0.22 \times 0.07 \text{ mm}^3 \), monoclinic, space group \( \text{C}2/c \) (No. 15), \( a = 9.7131(18), b = 23.5664(4), c = 28.1675(5) \text{ Å}, \beta = 96.357(3)^\circ, V = 6408(2) \text{ Å}^3, Z = 4, D_c = 1.165 \text{ g/cm}^3, F_{000} = 2340.4, \text{Bruker Duo CCD Area Detector, MoK}\alpha \text{ radiation,} \lambda = 0.71073 \text{ Å, } T = 100(2)\text{K, } 2\theta_{\text{max}} = 56.7^\circ, 23171 \text{ reflections collected, 7934 unique (} \text{R}_{\text{int}} = 0.0803). \text{Final } \text{GooF} = 1.028, \text{ } R1 = 0.0997, wR2 = 0.2618, \text{ } R \text{ indices based on}
4039 reflections with I > 2σ(I) (refinement on $F^2$), 459 parameters, 17 restraints. Lp and absorption corrections applied, $\mu = 0.395$ mm$^{-1}$.

2-p-xylene: C$_{76}$H$_{56}$Cl$_2$CoN$_4$, $M =$ 1175.24, 0.33 × 0.15 × 0.09 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$^3$, $Z =$ 4, $D_c =$ 1.245 g/cm$^3$, $F_{000} =$ 2484, Bruker SMART APEX CCD Area Detector, MoKα radiation, $\lambda =$ 0.71073 Å, $T =$ 100(2)K, $2\theta_{\text{max}} =$ 50.0$^\circ$, 16087 reflections collected, 5519 unique ($R_{\text{int}} =$ 0.1056). Final $GooF =$ 0.954, $R1 =$ 0.0598, $wR2 =$ 0.1196, $R$ indices based on 3022 reflections with I > 2σ(I) (refinement on $F^2$), 384 parameters, 0 restraints. Lp and absorption corrections applied, $\mu =$ 0.406 mm$^{-1}$.

2 m-xylene: C$_{76}$H$_{56}$Cl$_2$CoN$_4$, $M =$ 1175.24, 0.41 × 0.33 × 0.20 mm$^3$, 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$^3$, $Z =$ 4, $D_c =$ 1.252 g/cm$^3$, $F_{000} =$ 2484, Bruker Duo CCD Area Detector, MoKα radiation, $\lambda =$ 0.71073 Å, $T =$ 173(2)K, $2\theta_{\text{max}} =$ 50.0$^\circ$, 5304 reflections collected, 5304 unique ($R_{\text{int}} =$ 0.0000). Final $GooF =$ 1.101, $R1 =$ 0.0682, $wR2 =$ 0.1891, $R$ indices based on 4687 reflections with I > 2σ(I) (refinement on $F^2$), 381 parameters, 0 restraints. Lp and absorption corrections applied, $\mu =$ 0.408 mm$^{-1}$.

1-MeOH: C$_{44}$H$_{38}$H$_8$Cl$_2$N$_4$NiO$_8$, $M =$ 775.67, 0.45 × 0.23 × 0.11 mm$^3$, orthorhombic, space group P2$_1$/2$_1$/2$_1$ (No. 19), $a =$ 12.3778(17), $b =$ 16.212(2), $c =$ 19.398(3) Å, $\alpha =$ 98.020(6)$^\circ$, $\beta =$ 91.59$^\circ$, $\gamma =$ 91.59$^\circ$, $V =$ 3892.7(9) Å$^3$, $Z =$ 4, $D_c =$ 1.324 g/cm$^3$, $F_{000} =$ 16160, Bruker APEX CCD Area Detector, MoKα radiation, $\lambda =$ 0.71073 Å, $T =$ 100(2)K, $2\theta_{\text{max}} =$ 109.9$^\circ$, 23493 reflections collected, 9086 unique ($R_{\text{int}} =$ 0.0296). Final $GooF =$ 1.174, $R1 =$ 0.0512, $wR2 =$ 0.1071, $R$ indices based on 8306 reflections with I > 2σ(I) (refinement on $F^2$), 480 parameters, 0 restraints. Lp and absorption corrections applied, $\mu =$ 0.675 mm$^{-1}$. Absolute structure parameter = 0.052(16) (Flack, H. D. *Acta Cryst.* 1983, A39, 876-881).

2-MeOH: C$_{44}$H$_{36}$Cl$_2$CoN$_4$, $M =$ 750.60, 0.44 × 0.37 × 0.28 mm$^3$, monoclinic, space group C2/c (No. 15), $a =$ 9.273(2), $b =$ 23.801(5), $c =$ 21.313(5) Å, $\alpha =$ 98.130(4)$^\circ$, $\beta =$ 91.59$^\circ$, $\gamma =$ 91.59$^\circ$, $V =$ 4656.8(18) Å$^3$, $Z =$ 4, $D_c =$ 1.071 g/cm$^3$, $F_{000} =$ 1556, Bruker Duo CCD Area Detector, MoKα radiation, $\lambda =$ 0.71073 Å, $T =$ 100(2)K, $2\theta_{\text{max}} =$ 56.9$^\circ$, 16686 reflections collected, 5825 unique ($R_{\text{int}} =$ 0.0422). Final $GooF =$ 1.041, $R1 =$ 0.0477, $wR2 =$ 0.1170, $R$ indices based on 3848 reflections with I > 2σ(I) (refinement on $F^2$), 235 parameters, 0 restraints. Lp and absorption corrections applied, $\mu =$ 0.513 mm$^{-1}$.

References
