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## COMMUNICATION

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

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**Mechanochemical synthesis has been used to obtain two Werner complexes and their solid solution that could not be obtained by conventional “wet” chemistry; remarkably, despite the structural and chemical similarity, the solid solution exhibits sorption properties that differ from those of the pure compounds.**

Mechanochemistry refers to processes in which solids undergo a chemical reaction by the application of mechanical energy.<sup>1,2</sup> This can be achieved by ball milling or manual grinding with a mortar and pestle. Manual grinding is used for reactions that do not require overcoming a large energy barrier, while ball milling is employed for reactions that require longer reaction times.<sup>1,3</sup> During the mechanochemical process, a series of transformations take place, viz. crystal size reduction, formation of point defects and formation of new reaction sites on crystal surfaces.<sup>1,4</sup> In some cases, catalytic amounts of solvent are required to initiate or to accelerate the reaction. In such instances the reactions are often termed “kneading”, “solvent drop grinding” or “liquid assisted grinding” (LAG).<sup>5</sup>

Apart from being a simple and economical method of synthesis, mechanochemistry has another major advantage in that it is environmentally friendly since no solvent waste is generated.<sup>6</sup> It has recently been shown how solvent-free processes can yield homogeneous solid solutions that are inaccessible by common wet chemistry. The formation of the solid solution phase allowed control of some structural and physical properties such as polymorphism,<sup>7</sup> photoemission spectra and unit cell dimensions.<sup>8,9</sup> In these examples, the physical parameters assume values of either of the pure phases or a linear combination of both depending on whether the considered property can assume only certain values (e.g. space group) or can vary continuously (e.g. unit cell volume or emission band). In the latter case the physical parameter can be tuned by varying the solid solution composition. These studies concerned 2-D coordination polymers but the present work focuses on octahedral 0-D Werner complexes, which usually have the

general formula  $\text{MX}_2\text{L}_4$ , where M is a divalent metal salt (M = Co, Ni, Mn, Fe, Cu, Cd), X is an anion (X = Cl, SCN,  $\text{NO}_2$ , CN,  $\text{NO}_3$ ) and L is an organic ligand (L = substituted pyridine,  $\alpha$ -arylalkylamine, isoquinoline).<sup>10,11</sup> These compounds are generally known for their ability to enclathrate a variety of aromatic guests and have therefore been employed in chromatographic separation of mixtures of aromatic compounds.<sup>12</sup> The  $\alpha$  form refers to the empty phase whereas the clathrate phases are referred to as  $\beta$ ,  $\gamma$ ,  $\delta$ ... depending on the structural features.<sup>13</sup>

Thus far, the most widely studied compounds have the general formula  $[\text{Ni}(\text{NCS})_2(4\text{-RPy})_4]$ , where R is an alkyl or aryl group and Py is a pyridyl group.<sup>14–18</sup> More specifically, the host compound  $[\text{Ni}(\text{NCS})_2(4\text{-MePy})_4]$  has been studied extensively; a review by Lipkowski describes several crystal structures and the physico-chemical properties of this host compound with a variety of guest molecules.<sup>13</sup> The majority of the reported inclusion compounds were prepared by dissolving the host material in a suitable solvent and layering the guest, which would then be included upon crystallisation. Recently, our group reported a solid–vapour inclusion process of the host compound  $[\text{Ni}(\text{NCS})_2(4\text{-PhPy})_4]$  as a means of separating the three isomers of xylene.<sup>19</sup> Here we report (i) the mechanochemical synthesis of  $[\text{NiCl}_2(4\text{-PhPy})_4]$  (**1**),  $[\text{CoCl}_2(4\text{-PhPy})_4]$  (**2**) and the solid solution  $[\text{Ni}_{0.5}\text{Co}_{0.5}\text{Cl}_2(4\text{-PhPy})_4]$  (**3**) (PhPy = phenyl pyridine), (ii) structures of the xylene clathrates obtained from solution synthesis and (iii) the vapour sorption kinetics for the uptake of xylene isomers by compounds **1–3**.

When either of the products from grinding (**1** or **2**), or a combination of the respective metal salt and ligand are dissolved in methanol, crystals of the Werner clathrates  $[\text{NiCl}_2(4\text{-PhPy})_4]\cdot\text{MeOH}$  (**1·MeOH**) or  $[\text{CoCl}_2(4\text{-PhPy})_4]\cdot\text{MeOH}$  (**2·MeOH**) are obtained. The empty ( $\alpha$ ) phases of **1** and **2** can be prepared by manual grinding of the respective metal chloride and 4-phenyl pyridine (M : L = 1 : 4). The solid solution **3** is produced by mechanochemical grinding of the ligand with a mixture of  $\text{CoCl}_2$  and  $\text{NiCl}_2$  (Co : Ni : L = 0.5 : 0.5 : 4). The three  $\alpha$  phases were analysed by powder X-ray diffraction (PXRD) (Fig. 1) and thermogravimetric analysis (TGA) – see ESI.† PXRD analysis reveals that compound **3** adopts the structure of compound **1** (Fig. 1). Scanning electron microscopy (SEM) in conjunction with energy-dispersive X-ray spectroscopy (EDX) was used to produce elemental mapping images that show the distribution of the elements of interest. Results of this technique are

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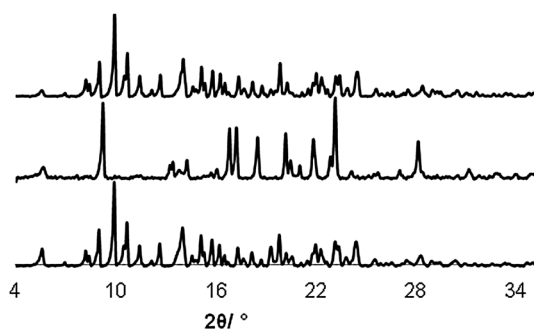


Fig. 1 PXRD patterns of **1** (top), **2** (middle) and **3** (bottom).

presented for the following samples: (1) the product of mechanochemical grinding of  $\text{CoCl}_2$ ,  $\text{NiCl}_2$  and 4-PhPy (**3**); (2) the product of solvent evaporation of  $\text{CoCl}_2$ ,  $\text{NiCl}_2$  and 4-PhPy; (3) the product of solvent evaporation of a 1 : 1 mixture of **1** and **2** and (4) the solid solution after exposure to *p*-xylene. These analyses indicate that both cobalt and nickel ions are evenly distributed throughout the grind product **3** (Fig. 2a). It is also apparent that the methanol solvent evaporation of a 0.5 : 0.5 : 4 mixture of  $\text{CoCl}_2$ ,  $\text{NiCl}_2$  and 4-PhPy, as well as the methanol solvent evaporation of a 1 : 1 mixture of **1** and **2** do not afford the solid solution **3**. Indeed, both of these solution crystallisation techniques yielded a mechanical mixture of crystals of **1**·MeOH and **2**·MeOH (Fig. 2b and c). Exposure of **3** to *p*-xylene also did not induce any phase separation, and the solid solution is maintained after the solid–vapour sorption reaction (Fig. 2d).

The xylene clathrates of compounds of **1** and **2** were prepared by layering a methanolic solution of the host with the intended guest. The  $[\text{NiCl}_2(4\text{-PhPy})_4]\cdot 4p\text{-xylene}$  and

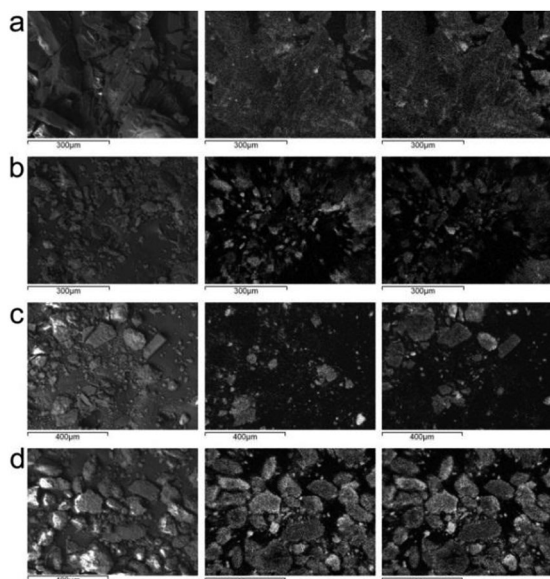


Fig. 2 From left to right: SEM, cobalt and nickel elemental mapping images for (a) the product of grinding  $\text{CoCl}_2$ ,  $\text{NiCl}_2$  and 4-PhPy in a 0.5 : 0.5 : 4 ratio, (b) the product of solvent evaporation of  $\text{CoCl}_2$ ,  $\text{NiCl}_2$  and 4-PhPy in a 0.5 : 0.5 : 4 ratio, (c) the product of solvent evaporation of a 1 : 1 mixture of **1** and **2** and (d) the product of grinding  $\text{CoCl}_2$ ,  $\text{NiCl}_2$  and 4-PhPy in a 0.5 : 0.5 : 4 ratio which was then exposed to *p*-xylene.

$[\text{NiCl}_2(4\text{-PhPy})_4]\cdot 2m\text{-xylene}$  clathrates have been reported elsewhere.<sup>20</sup> Except for  $[\text{NiCl}_2(4\text{-PhPy})_4]\cdot 2m\text{-xylene}$ , which crystallises in the space group  $P\bar{1}$ , the clathrates crystallise in the monoclinic space group  $C2/c$  with similar unit cell parameters and packing features (see ESI†). The host : guest ratio in the  $C2/c$  clathrates is 1 : 4 whereas it is 1 : 2 in the  $P\bar{1}$  clathrate. In the monoclinic phases, the guest molecules occupy channels along the crystallographic *a* axis and there are slight differences in the molecular conformations and the relative positions of the molecules with respect to overlap of adjacent 4-phenyl pyridine ligands (see ESI†).

Solid–vapour sorption reactions were carried out using a microbalance that monitors weight change as a function of time under controlled conditions of temperature and pressure.<sup>21</sup> The solid–vapour reactions of compounds **1**–**3** with the three xylene isomers were recorded in separate experiments at 20 °C. In each case the reaction chamber was first evacuated until a constant weight was achieved. Then the liquid guest was injected and the weight increase was monitored until saturation, after which the resulting clathrates were analysed using TGA and PXRD. For compound **1** the solid–vapour preparation of the *m*-xylene clathrate reaches 100% completion while those for the *o*- and *p*-xylene clathrates reach approximately 80% completion (Fig. 3). PXRD analysis confirms that, upon exposure of **1** to each of the three xylene isomers, the apohost  $\alpha$  phase transforms into the corresponding  $\beta$  phase, and these PXRD patterns are consistent with the simulated

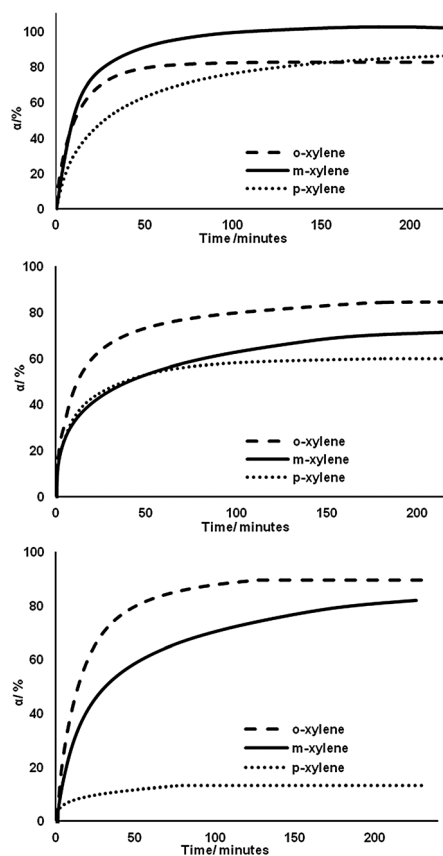
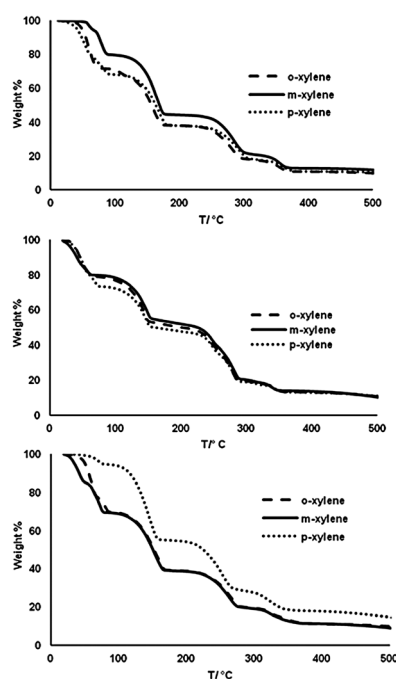


Fig. 3 Sorption kinetics showing the extent of reaction as a function of time for the uptake of the three isomers of xylene by compounds **1** (top), **2** (middle) and **3** (bottom).



**Fig. 4** TGA for the release of absorbed xylene isomers by compounds **1** (top), **2** (middle) and **3** (bottom).

patterns for the clathrates resulting from solution growth. TGA reveals that guest release for the *o*- and *p*-xylene clathrates commences at approximately 25 °C while the *m*-xylene clathrate starts to release the guest at approximately 65 °C (Fig. 4). For compound **2** the solid–vapour preparation of the *p*- and *m*-xylene clathrates reaches about 50% and 60% completion, respectively, while that of the *o*-xylene analogue proceeds to approximately 80% completion (Fig. 3). PXRD analysis of the product of the solid–vapour reactions with *p*- and *m*-xylene reveals the presence of some peaks corresponding to the host  $\alpha$  phase, which confirms only partial conversion of the material to its clathrate form (see ESI†).

TGA shows that guest release commences at 30 °C for all three clathrates and is complete at 60 °C for the *o*- and *m*-xylene clathrates, while for the *p*-xylene clathrate guest release is only complete at 75 °C (Fig. 4). In contrast to compounds **1** and **2**, reaction of the solid solution **3** with *p*-xylene is only 10% complete after 220 minutes while for *o*- and *m*-xylene the reaction proceeds to about 80% completion (Fig. 3).

The PXRD pattern of **3** after exposure to *p*-xylene is very similar to that of the  $\alpha$  phase, indicating that the amount of *p*-xylene absorbed by the host was insufficient to induce a substantial phase transformation to the  $\beta$  phase. PXRD analyses of the *o*- and *m*-xylene clathrates are consistent with the simulated patterns of the structures of the corresponding clathrates of compound **1** (see ESI†). TGA of the xylene clathrates of **3** shows that guest release commences at approximately 50 °C for the *p*-xylene clathrate, 30 °C for the *o*-xylene clathrate and 20 °C for the *m*-xylene clathrate. For all three clathrates guest release is complete at approximately 80 °C (Fig. 4).

In summary we prepared three compounds, namely  $[\text{NiCl}_2(4\text{-PhPy})_4]$  (**1**),  $[\text{CoCl}_2(4\text{-PhPy})_4]$  (**2**) and the solid solution  $[\text{Ni}_{0.5}\text{Co}_{0.5}\text{Cl}_2(4\text{-PhPy})_4]$  (**3**) by grinding. We established that

mechanochemical processing produces a homogeneous solid solution, whereas crystallisation from methanol produces a non-homogeneous product (*i.e.* a mixture of phases **1**·MeOH and **2**·MeOH). Despite the structural similarity between compounds **1** and **3**, there is a remarkable difference in their sorption behaviour. In particular, the sorption tendency of *o*-xylene is consistent for all three compounds while that of *p*-xylene is significantly reduced for **3**. It has been speculated that, in order to enclathrate a guest, the crystalline Werner complex must exhibit conformational flexibility.<sup>22</sup> For each crystal structure such flexibility depends, among other factors, upon the cooperative reorganization of the metal complex. We believe that, owing to the presence of Co centres, compound **3**, which is isostructural to **1** but different from **2**, is unable to assume the conformation required to host *p*-xylene, thereby preventing sorption. This study highlights the importance of exploring (a) solid solutions as a means of engineering bulk properties of crystalline materials and (b) mechanochemical preparation of phases not accessible by solution synthesis.

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