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Xylene Separation

Solid–Vapor Sorption of Xylenes: Prioritized Selectivity as a Means of Separating All Three Isomers Using a Single Substrate**

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Xylenes occur in the three isomeric forms (*ortho*, *meta*, and *para*), hereafter referred to as **ox**, **mx** and **px**, respectively. Together with ethylbenzene, they constitute the so-called C8 aromatic compounds derived from crude oil that serve as starting materials for the synthesis of many important chemical intermediates. These include terephthalic acid, phthalic anhydrides, phthalonitriles, and styrene, which are used in the production of polymers, plastics, resins, pigments, and fungicides. Moreover, xylenes are often added to motor fuel as an anti-knocking agent.[1] Owing to their similar physical properties (boiling points of 144.5, 139.1, and 138.2 °C for **ox**, **mx**, and **px**, respectively), separation of the three isomers is an expensive and inefficient undertaking. Distillation with a view to producing commercial-grade reagents requires more than 150 theoretical plates to isolate the higher-boiling **ox** and up to 360 plates to further separate **mx** and **px**. Viable alternative methods include crystallization, absorption, sieving, complexation, isomerization, and a number of hybrid strategies that involve solid–liquid separation. Some of these processes involve the use of highly reactive chemicals. For example, Mitsubishi Gas-Chemical Company isolates **mx** by means of complexation with tetrafluoroboric acid (HBF_4). More recently, methods that exploit zeolites to separate the *para* isomer from a vapor mixture have been explored but, owing to low efficiency, they have not yet been implemented on an industrial scale.[2] Indeed, in this type of application the amount of xylene adsorbed (and separated) in each cycle could be relatively small in comparison to the adsorbent (1% by weight)[3] and the use of a desorbent is often necessary.[4] Related methods that employ metal–organic frameworks have been reviewed by Zhou et al.[5] and attempts to engineer hydrogen-bonded assemblies for the selective inclusion of xylenes have also been reported.[6] A summary of the main industrial separation methods currently used is given in the Supporting Information.

More than fifty years ago, a method for the separation of xylenes from the liquid phase was suggested that involves enclathration by octahedral metal complexes with the general formula $[ML_4X_2]$ (where M is a transition metal, X is an anion, and L is a pyridine derivative).[7] These so-called Werner clathrates were not deemed sufficiently viable for industrial applications but they were implemented for chromatographic separation.[8] Indeed, crystallization from solution involves a costly recovery process and also leads to the formation of byproducts that reduce selectivity.[9] Subsequent studies showed that Werner complexes could also effect isotopic[10] and enantiomeric[11] separations when applied to other compounds. From a solid-state structural perspective these host systems are interesting because of the often profound structural differences between their apohost and guest-included forms, thus necessitating significant phase transformations to enclathrate the guest molecules.

In its pure form, the octahedral metal complex typically exists as a nonporous phase (α), and the formation of a host–guest adduct generally involves entrapment of the guest during crystallization of the host from solution. Therefore, the majority of studies report solvent-mediated enclathration processes[12] while solid–vapor inclusion reactions have received little attention in this particular context. The guest-included forms can exhibit a variety of structural arrangements; cage-, layer-, and channel-inclusion compounds (referred to as β, γ, and δ phases, respectively) are all possible, depending on the geometric relationship between the host and the guest.[13] In some cases the host arrangement is preserved after guest removal and the sorption–desorption processes can be cycled by means of solid–vapor reactions.[14] Herein we 1) report new solution-state and solid-vapor preparations of the xylene clathrates of $[Ni(NCS)_2(ppp)_4]$ (**1**)[15] (ppp = *para*-phenylpyridine); 2) describe the previously unknown structure of $[Ni(NCS)_2(ppp)_4]\cdot 3p$-xylene (**1px**); 3) demonstrate significant selectivity of **1** for **ox** over **mx** and **px** from a ternary mixture, and then similar selectivity for **mx** over **px** from a binary mixture; and 4) identify the reason of such selectivity.

The pure octahedral metal complex **1** (Scheme 1) was precipitated by slow evaporation of a methanolic solution as previously reported.[16] The quality and dimensions of the crystals appear to depend on the initial concentration of the solution as well as the rate of evaporation. Microcrystalline **1** can be redissolved in an appropriate solvent and layered with a number of organic liquids to yield various inclusion compounds. For example, when a DMSO solution is layered with a commercial C8 mixture, $[Ni(NCS)_2(ppp)_4]\cdot 2o$-xylene (**1ox**) and $[Ni(NCS)_2(ppp)_4]\cdot 2m$-xylene (**1mx**) are formed together with a $Ni(NCS)_2(ppp)_4]\cdot 2DMSO\cdot p$-xylene (**1pxd**) mixed clathrate.[15] Similar experiments have previously yielded additional products, such as $[Ni(NCS)_2(ppp)_4]$

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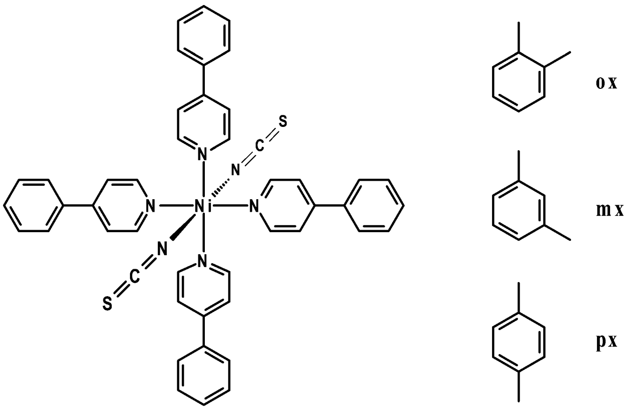

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Scheme 1. $[Ni(NCS)_2(para\text{-phenylpyridine})_4]$ and *ortho*-, *meta*-, and *para*-xylene.

$\cdot 2DMSO$[17] and $[Ni(NCS)_2(ppp)_2(DMSO)_2]$,[16] which have been identified by means of single-crystal X-ray diffraction (SCD) analyses. Indeed, the concomitant crystallization of different species might well be expected for such reactions owing to the complex equilibria that most likely occur in solution.[9]

The pure known phases **1ox** and **1mx** were formed directly by evaporation of a mixture of methanol and **ox** or **mx**, respectively, as confirmed by powder X-ray diffraction (PXRD) analysis. An analogous procedure affords the previously unknown crystalline phase $[Ni(NCS)_2(ppp)_4]\cdot 3p$-xylene (**1px**) when **px** is used as the co-solvent with methanol. PXRD also indicates that an as-yet unidentified phase is produced concomitantly with **1px** (see the Supporting Information).

During our exploration of solid–vapor reactions as a means of forming the respective xylene clathrates, polycrystalline **1** was exposed to the pure isomers in separate experiments, and the extent of guest uptake was recorded gravimetrically as a function of time (Figure 1). Sorption of the guest occurred slowly in air, but the rate of uptake was significantly enhanced when the reaction chamber was evacuated prior to admitting the vapor. After each experiment, the product was analyzed by means of PXRD, which confirmed the formation of the corresponding phase resulting from solution growth. We note that the apohost **1** consists of a close-packed nonporous phase[15] and that guest sorption therefore involved a rearrangement of the host molecules upon enclathration. The three inclusion compounds prepared by solid–vapor reactions were subjected to thermogravimetric analysis (TGA) to investigate guest release as a function of temperature (Figure 2). The inclusion compound **1px** appears to be the least robust, as the guest molecules are released with an onset temperature of approximately 46.1 °C. The release of the *meta* isomer commences at 72.5 °C and that for the *ortho* isomer at 74.8 °C (Figure 2), which shows that **1ox** is only slightly more thermally stable than **1mx**. The thermogram for **1ox** shows a small loss (0.3 %) between 20 and 30 °C, and this observation is in agreement with the sorption experiment, which shows that the reaction proceeds to slightly over 100 % completion for the expected host–guest stoichiometry. The excess solvent is most likely adsorbed onto the crystallite surfaces; interestingly, this phenomenon is not observed for the other two isomers.

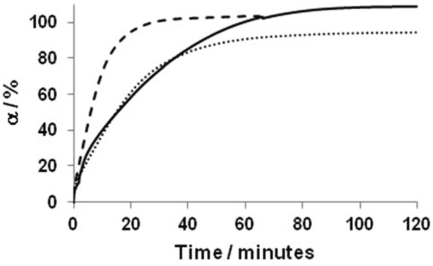

Figure 1. Sorption kinetics (recorded at 22 °C) showing extent of reaction α as a function of time for the uptake of the three isomers of xylene by **1** (—— *o*-xylene, ----- *m*-xylene, ••••• *p*-xylene).

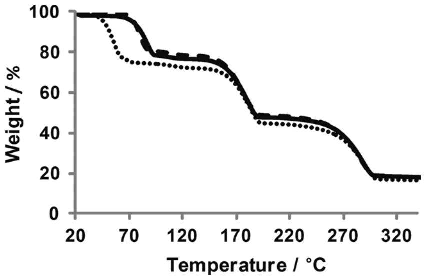

Figure 2. Thermogravimetric analyses for **1ox** (——), **1mx** (-----), and **1px** (•••••). See the Supporting Information for further details.

Competition experiments were carried out by exposing polycrystalline **1** to the vapors derived from liquid mixtures of the xylene isomers (Table 1). Whenever **ox** is present in the mixture, the PXRD pattern of the bulk product compellingly matches that simulated from the SCD structure of **1ox** (see the Supporting Information). Before each sorption experiment, the composition of the liquid xylene mixture was determined by means of gas chromatography (GC; see the Supporting Information for experimental details). After each experiment, the xylene guest molecules were extracted from the polycrystalline products using hexane (see the Supporting Information) and their composition was determined using GC analysis. The results are consistent with the PXRD analyses,

Table 1: Summary of competition experiments.

Solution	*omp*	*om*	*op*	*mp*
ox:**mx**:**px**	1:1:1	1:1:0	1:0:1	0:1:1
PXRD	**1ox**	**1ox**	**1ox**	**1mx**
in liquid[b]	33.1:36.9:30.0	50.3:49.6:0.1	50.1:0.0:49.9	0.0:55.7:44.3
in crystals[b]	94.9:3.5:1.5	97.2:2.8:0.0	97.6:0.0:2.4	0.0:94.1:5.9

[a] More accurate values and standard deviations are reported in the Supporting Information. [b] Percentage composition (GC analysis).

confirming that the Werner complex **1** shows remarkable discrimination in favor of **ox** in the presence of **mx** and/or **px**. In the absence of **ox**, **1** reprioritizes its preference, becoming highly selective towards **mx**. The selectivity trend **ox** $\gg$ **mx** $\gg$ **px** (selectivity coefficients $o/m = 34.2$, $o/p = 40.5$, and $m/p = 12.7$) does not comport well with the trend in thermal stability (as determined by TGA; note the relatively small difference in guest-loss onset temperature for **ox** and **mx**), and not at all with the kinetics of sorption (rate constants of 1.35×10^{-2}, 4.72×10^{-2}, and $2.73 \times 10^{-2}\,\text{min}^{-1}$ were determined for **ox**, **mx**, and **px**, respectively; see the Supporting Information). We therefore believe that the isomeric selectivity exhibited by **1** is dominated by thermodynamic rather than kinetic factors.

Although it would be useful to rationalize the selectivity trends in terms of packing interactions, any such evaluation would be merely speculative; we recognize that many subtle factors may influence selectivity and that any simplistic approach based on comparing densities, interactions, and so on would be inadequate in providing a holistic explanation for the observed trend in guest preferences.

The trend in efficient occupation of the guest-accessible volume is **1mx** < **1px** < **1ox** (see the Supporting Information); this observation does not correlate with the observed trend in vapor sorption selectivity, but it does agree with the kinetics (that is, the least densely packed guest is most rapidly sorbed).

A cursory inspection of their crystal structures, determined at 273 K, reveals that the metal complexes deviate from ideal octahedral geometry (Figure 3). It should be noted that the phenyl carbon atoms in **1m** and **1p** have large anisotropic displacement parameters (thermal ellipsoids); in the case of **1p**, disorder of one of the phenyl rings is also present. Density function theory (DFT) calculations were carried out; to reduce the effect of crystallographic artifacts on the energy calculations and the positions of the phenyl carbon atoms, and all of the hydrogen atoms in each complex were allowed to optimize. The metal complex in **1o** appears to be 4.04 and 5.10 kcal mol^{-1} more stable than that in **1m** and **1p**, respectively. This trend is consistent with that observed for the competition experiments. From these results it appears that the guest selectivity may be based on factors that allow the complex to assume the most relaxed conformation, although supramolecular interactions, packing energy, and entropy may also play a minor role.

We have shown that host **1** readily absorbs any of the three xylene isomers as a solid–vapor process, but that significant differences in selectivity are observed when the isomers are mixed. The observed trend in isomeric selectivity appears to be a consequence of the conformation that the metal complex must assume in the host–guest structure. This implies that it would be difficult to formulate a design strategy (that is, crystal engineering) to identify a metal complex with high selectivity towards a specific guest. Nevertheless, a trial-and-error approach could be used to optimize a metal complex for the desired multiple separation.

Conceptually, this implies that in cases where there is a large difference in selectivity x for three guests **A**, **B**, and **C** such that $x_\mathbf{A} \gg x_\mathbf{B} \gg x_\mathbf{C}$, then it is possible to utilize a single procedure (even the same device) to first separate **A** from **B** and **C**, and then to repeat the process to separate **B** and **C**. This is important for implementing separation technologies in commercial applications where such selectivity is required, as is indeed the case for xylenes. The proof of concept demonstrated herein should be amenable to applications involving pressure-swing adsorption technology, modified for solvent vapor recovery (PSA-SVR operating at low pressure, for example, 0.2–0.5 atm),[18] whereby a single solventless process can be implemented, in principle, to effect complete separation of three or more isomers. Previously reported methods of separating xylenes using Werner clathrates were not industrially viable[19] because they required dissolution, crystallization and solvent extraction; each of these steps reduces the yield and increases the cost of the process.

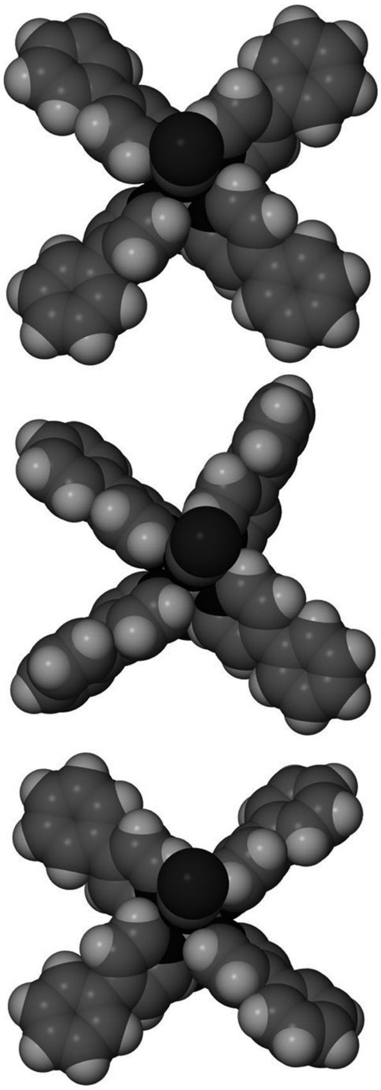

Figure 3. Metal complex conformation in **1ox** (top), **1mx** (center), and **1px** (bottom) at 273 K.

The method presented herein shows that the energy-intensive, time-consuming, and costly liquid-phase steps could be eliminated and appears promising for implementation in industrial scale applications, such as PSA processes that employ a substrate with prioritized selectivity.

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[19] Werner clathrates are viable for the chromatographic separation of xylenes. However, such techniques usually involve minute amounts of sample and do not require large differences in selectivity for the target molecules. As the objectives of chromatography and pressure-swing adsorption separations are quite different, the two methods are not directly comparable in terms of their viability.