Coordination polymers formed in solution and in solvent-free environment. Structural transformation due to interstitial solvent removal revealed by X-ray powder diffraction†

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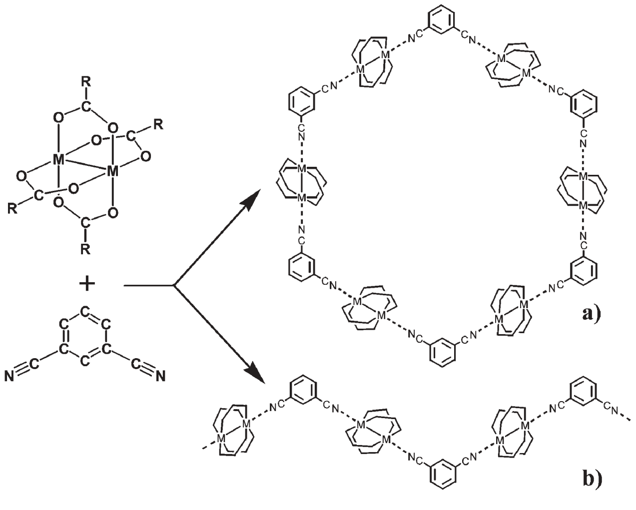
The crystal-to-powder transformation induced by solvent removal has been examined through a direct comparison of the structures of the solvated and the unsolvated coordination products determined by single crystal and powder X-ray diffraction, respectively.

There has been extensive interest in controlled formation of metal–organic frameworks having different topologies due to possible applications in gas storage, separation, guest recognition, catalysis, and magnetism.[1] Various synthetic procedures utilizing the preconstructed building blocks for self-assembling are usually carried out in solutions. In this case the formation of multi-dimensional structures is often accompanied by incorporation of solvent molecules into open cavities or channels. Moreover, a template effect of various solvents in self-assembling reactions is well recognized.[2] Solvents are known to affect formation, structures and properties of supramolecular architectures.[3] The evacuation of guest solvent molecules often causes structural transformations including a total collapse of porous networks. While X-ray powder diffraction (XRPD) is widely used as a general method to detect these changes, an application of XRPD for structural characterization of powders formed as a result of such transformations is very rare.[4] Importantly, the recent developments in XRPD method and programming can now be utilized for direct elucidation of the structures of microcrystalline materials formed after the solvent- or temperature-induced structural transitions which are often accompanied by the loss of single crystalline properties. Herein, to study such solvent-determined transformation we applied a combination of single crystal and powder X-ray diffraction techniques. This allowed us to examine an interesting solvent-directing effect in the syntheses of coordination polymers by directly comparing the structures of the solvated and unsolvated products.

For this study we have selected a model system composed of a strongly-coordinating angular bidentate dicyanobenzene ligand, 1,3-$C_6H_4(CN)_2$, and very electrophilic bidentate linear metal complex, $[Rh_2(O_2CCF_3)_4]$. This system is of interest since the interaction of the above building blocks may afford coordination isomers.[5] Thus, for a 1 : 1 composition, a hexagon comprised of six dimetal units and six ligands as well as various conformations of the 1D chain can be envisioned (Scheme 1). To attempt targeted synthesis of such isomers, we tested two synthetic approaches: solution and solvent-free coordination reactions. The former technique may favor the formation of closed architectures (dilute systems, slow crystal growth, low temperatures), while the high temperature solid state reactions should inevitably yield the infinite chain motif. This is due to the fact that assembling processes for discrete and extended products from the starting building units are essentially different. For a polymer, each assembling step exactly repeats the previous one, and therefore, high temperatures should favor this indiscriminatory process. For a discrete structure, there is a unique "intelligent" step that requires closing of a cycle that may happen at low temperatures in solution. While dicyanobenzenes were widely used as bidentate angular spacers in solution assembling reactions, mainly extended coordination networks have been isolated as products.[6] The only metallotriangle was reported for 1,2-phenylene diisocyanide.[7]

From solution coordination reaction between the dirhodium complex and 1,3-dicyanobenzene, single crystals of **1** have been isolated in good yield. When removed from solution crystals were losing solvent quickly, and that prevented obtaining the accurate chemical analysis data for **1**. IR spectra of **1** confirmed the presence of both building units: the stretches at 1664 and 1478/1460 cm^{-1} are due to $\nu_{asym}(CO)$ and $\nu_{sym}(CO)$ of carboxylates, while weak bands at 2275 and 2239 cm^{-1} correspond to $\nu(CN)$ vibrations. The single crystal X-ray structural characterization revealed a 1D chain



Scheme 1 Discrete hexagon (a) *vs.* 1D polymer (b) in 1 : 1 complex of dimetal tetracarboxylate with *m*-dicyanobenzene.

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† Electronic Supplementary Information (ESI) available: Synthesis, characterization, X-ray details, XRPD patterns, and additional plots of the structures. See http://www.rsc.org/suppdata/cc/b5/b503748d/
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structure of **1**, $[Rh_2(O_2CCF_3)_4{\cdot}C_6H_4(CN)_2]{\cdot}0.5CH_2Cl_2{\cdot}1.75C_6H_6$, with solvent molecules filling the interchain voids (Fig. 1a,c,e). The 1D chains in **1** run in two different directions (69.3°) to leave interstitial cavities that are occupied by the disordered benzene and dichloromethane molecules. Each hybrid chain composed of alternating dimetal units and organic spacers is build on strong Rh···N axial interactions of 2.197(4) Å. The Rh–Rh–N and Rh–N–C angles are both close to linear, being 179.5(1) and 175.6(4)°, respectively. The Rh–Rh distance within the dimetal unit of 2.4137(6) Å is comparable with that in other dirhodium(II) trifluoroacetate adducts having axially bound N-donors.[8]

The defining feature of the solid state structure of **1** is intermolecular interactions between the solvent and the ligand π-systems. Although benzene molecules are not coplanar with the aromatic planes of the ligands, close C···C contacts of 3.36(2)–3.45(2) Å exist between the edges of the rings. The characteristic parameters for these interactions, following the criteria of Janiak,[9] are presented in the ESI.†

The TGA data for **1** indicate that partial loss of solvent (probably CH_2Cl_2) starts at room temperature. A complete removal of solvents from the single crystalline material is achieved around 85 °C corresponding to the weight loss of 15.8% (assuming that all benzene is removed only upon heating, this value also includes the loss of residual dichloromethane, *ca.* 25.4%, based on the crystal structure). The polymeric product **1** starts to decompose at temperatures above 225 °C. Using these data, we obtained the desolvated product **2** in the form of fine microcrystalline powder by heating the crystals of **1** under reduced pressure at 85 °C. The process of solvent removal from **1** was accompanied by a noticeable structural transformation, as recorded by X-ray powder diffraction (ESI). Importantly, the same powder product **2** was obtained in quantitative yield by direct solid state reaction of the 1 : 1 mixture of the dirhodium complex and 1,3-dicyanobenzene in the absence of solvents in an evacuated ampoule at 70 °C (Scheme 2). The XRPD patterns of the desolvated and the unsolvated powders obtained by different synthetic routes were identical (Fig. 2).

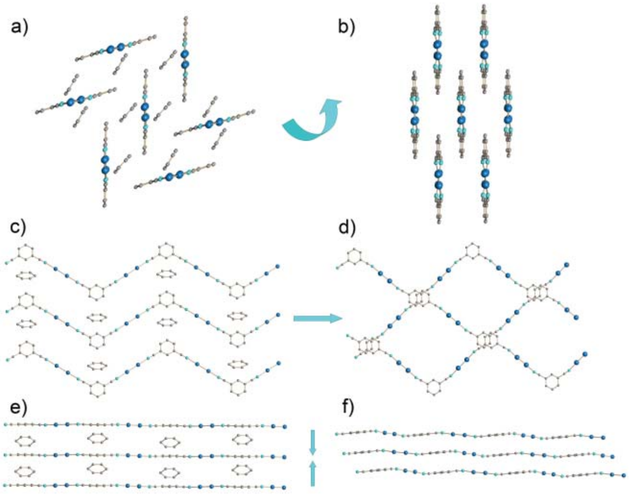
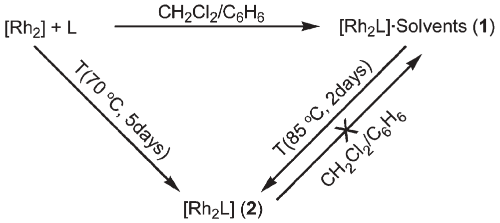


Fig. 1 Representation of the structural transformation from **1** to **2** upon solvent evacuation. Perspective views are arbitrary chosen for three almost perpendicular directions to show: rotation of the $[Rh_2L]_\infty$ chains (a,b); chain shift (c,d); and contraction of the interchain space (e,f) in the structures of **1** and **2**, respectively. Only Rh atoms (dark blue) of metal complex are shown. N light blue, C grey, H-atoms are removed for clarity.



Scheme 2 Syntheses and transformations of **1** and **2**.

To understand the above crystal-to-powder transformation upon solvent evacuation from **1**, the structural characteristics of the microcrystalline product **2** were needed. It is noteworthy that **2**, having the ratio of building units of 1 : 1, as determined by elemental analysis, is insoluble in common organic solvents and cannot be melted without decomposition thus precluding the use of single crystal X-ray diffraction. Recently, we have successfully applied XRPD for structural characterization of coordination polymers that resisted single crystal growth techniques.[10] Herein, the structure of **2** was solved based on XRPD data using procedures described in the ESI. This application provided a unique opportunity to follow the desolvation process and to understand the role of solvent in the structure.

The hybrid powder **2** is comprised of rigid building blocks, $[Rh_2(O_2CCF_3)_4]$ and $C_6H_4(CN)_2$, and the knowledge of geometries of both units[11,12] facilitated the structure solution based on the rigid body approach. The Rietveld plot for **2** showed good correspondence between the model and the observed data (Fig. 3). The structure features zig-zag chains $[Rh_2(O_2CCF_3)_4{\cdot}C_6H_4(CN)_2]_\infty$ that have the same conformation as those in **1** but run parallel to each other (Fig. 1b). The major geometric characteristics of these 1D chains are very close in both structures, although the parameters obtained from powder diffraction data for **2** are not as accurate as those extracted from the single crystal X-ray analysis of **1**. A noticeable feature of the solid state packing in **2** is weak off-centered π–π interactions between the 1,3-dicyanobenzene molecules of the neighboring chains. The arene planes of ligands exhibit parallel displacement so that the shortest contacts of 3.33 and 3.37 Å occur between the ring edges and carbon atoms of the cyano-groups. The estimated interplanar distance between the arene rings of 3.33 Å in **2** is even shorter than that in the solid stacks of 1,3-dicyanobenzene itself (3.47 Å).[11] Recent analysis of π–π interactions in metal complexes with N-containing aromatic ligands[9] shows that such non-covalent interactions play a very

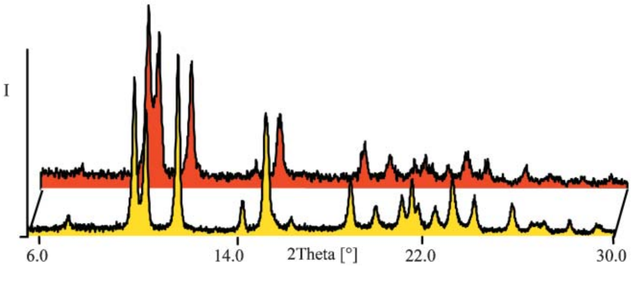


Fig. 2 Observed X-ray powder patterns for the desolvated (yellow) and unsolvated (red) powders **2** at room temperature.

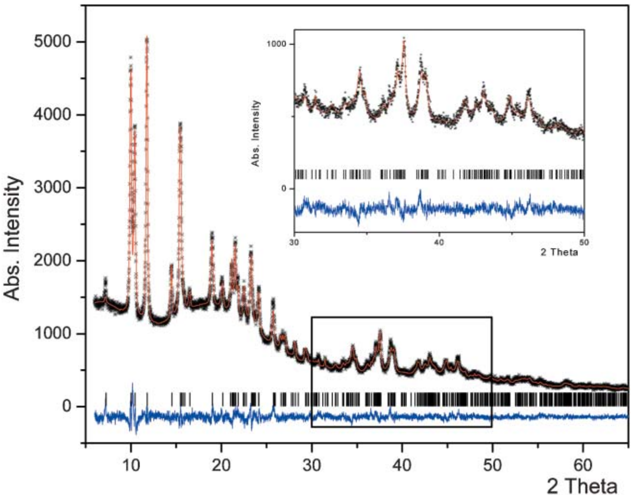


Fig. 3 The Rietveld plot of the powder diffraction pattern for $[Rh_2(O_2CCF_3)_4{\cdot}C_6H_4(CN)_2]$ (**2**) at 293 K. The observed pattern (black crosses), the best calculated fit (red), and the difference profile (blue) are given. The black lines at the bottom show the allowed peak positions.

important role in crystal packing due to their low π-electron density. Experimental investigations confirmed that electron withdrawing substituents or N-heteroatoms in aromatic systems feature the strongest π–π interactions. Moreover, metal coordination to a nitrogen heteroatom should enhance the electron-withdrawing effect and increase the tendency to stack even further.

A relationship between the solid state structures of **1** and **2** is shown in Fig. 1. Upon losing solvent molecules, the $[Rh_2L]_\infty$ chains rotate by 69.3° to align parallel in the structure of **2** (Fig. 1a,b). In addition, the chains undergo a shift relative to each other by *ca.* 12.4 Å (Fig. 1 c,d). Finally, the chains move closer to each other by *ca.* 1.6 Å so that the interchain space is contracted (Fig. 1 e,f). A direct comparison of the structures **1** and **2** provides a classic example of the solvent exerting a significant effect on the solid state packing of the same 1D hybrid chains. Weak intermolecular π–π interactions of the solvent-ligand *vs.* ligand-ligand type seem to be responsible for the observed solid state packing of the polymeric chains in **1** and **2**, respectively. The removal of solvent from **1** results in the irreversible chain rearrangement that is accompanied by a decrease of the calculated volume per $[Rh_2L]$ unit by 29.4% in **2**. In this manner, the voids in **2** having no interstitial solvent are effectively reduced and, consequently, a more closely packed structure is formed.

In summary, the removal of guest solvent molecules involved in weak π-interactions with the ligand in single crystals of **1** triggered the collective reorientation of the hybrid chains $[Rh_2(O_2CCF_3)_4{\cdot}C_6H_4(CN)_2]_\infty$ in **2**. This irreversible desolvation process was accompanied by the loss of single crystalline properties, however retention of the product crystallinity has made the direct structure solution of **2** by powder diffraction possible. With the use of the model system studied in this work we demonstrated that an application of XRPD for structural characterization of products that can only be obtained as microcrystalline phases should greatly advance the field of metal–organic framework materials. In particular, a better understanding of the role of solvents as the structure-directing templates in such frameworks should promote formation of desirable compounds and structural types.‡

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Notes and references

‡ *Crystal data* for **1**: $C_{27}H_{15.5}ClF_{12}N_2O_8Rh_2$, M = 965.18, orthorhombic, *Pnma* (no. 62), a = 16.3302(10), b = 24.7253(15), c = 8.7079(5) Å, V = 3516.0(4) Å^3, Z = 4, T = 173(2) K, μ(Mo–Kα) = 1.126 mm^{-1}, 4260 reflections measured, 3849 unique (R_{int} = 0.0550). The final $R1$ = 0.0595, $wR2$ = 0.1437 for all data. For **2**: the data were collected on an automated STADI-P (STOE) diffractometer, Cu Kα1-radiation, λ = 1.5406 Å, 2θ = 6–65.0°, step 0.01°, $C_{16}H_4F_{12}N_2O_8Rh_2$, M = 786.03, monoclinic, *C 2/c* (no. 15), a = 19.411(20), b = 16.879(19), c = 8.348(4) Å, β = 114.91(2)°, V = 2481(4) Å^3, Z = 4, T = 293(2) K, 438 reflections used in calculations. The final R_p = 0.0324, R_{wp} = 0.0426, and χ^2 = 1.246. CCDC 266399–266400. See http://www.rsc.org/suppdata/cc/b5/b503748d/ for crystallographic data in CIF or other electronic format.

1 G. B. Gardner, D. Venkataraman, J. S. Moore and S. Lee, *Nature*, 1995, **374**, 792; C. Rovira, *Chem. Eur. J.*, 2000, **6**, 1723; W. Lin and H. L. Ngo, *Chem. Nanostruct. Mater.*, 2003, 261; D. Maspoch, D. Ruiz-Molina and J. J. Veciana, *Mater. Chem.*, 2004, **14**, 2713; J. L. C. Rowsell and O. M. Yaghi, *Microporous Mesoporous Mater.*, 2004, **73**, 3; W. Mori, S. Takamizawa, C. N. Kato, T. Ohmura and T. Sato, *Microporous Mesoporous Mater.*, 2004, **73**, 31.
2 Y. Tokunaga, D. M. Rudkevich, J. Santamaria, G. Hilmersson and J. Rebek, Jr., *Chem. Eur. J.*, 1998, **4**, 1449; W. Zhao, H.-F. Zhu, T.-A. Okamura, W.-Y. Sun and N. Ueyama, *Supram. Chem.*, 2003, **15**, 345; A. Bacchi, E. Bosetti, M. Carcelli, P. Pelagatti, D. Rogolino and G. Pelizzi, *Inorg. Chem.*, 2005, **44**, 431.
3 K. A. Hirsch, S. R. Wilson and J. S. Moore, *Inorg. Chem.*, 1997, **36**, 2960; A. J. Blake, N. R. Champness, P. A. Cooke and J. E. B. Nicolson, *Chem. Commun.*, 2000, 665; K. Aoki, M. Nakagawa, T. Seki and K. Ichimura, *Chem. Lett.*, 2002, 378; R. García-Zarracino and H. Höpfl, *J. Am. Chem. Soc.*, 2005, **127**, 3120.
4 C. Boudaren, T. Bataille, J.-P. Auffredic and D. Louër, *Solid State Sci.*, 2003, **5**, 175.
5 N. Masciocchi, G. A. Ardizzoia, G. Lamonica, A. Maspero and A. Sironi, *Angew. Chem., Int. Ed.*, 1998, **37**, 3366; B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629.
6 D. Venkataraman, G. B. Gardner, A. C. Covey, S. Lee and J. S. Moore, *Acta Crystallogr., Sect. C*, 1996, **C52**, 2416; T. Kuroda-Sowa, T. Horino, M. Yamamoto, Y. Ohno, M. Maekawa and M. Munakata, *Inorg. Chem.*, 1997, **36**, 6382; T. Niu, J. Lu, G. Crisci and A. J. Jacobson, *Polyhedron*, 1998, **17**, 4079; F. A. Cotton, C. Lin and C. A. Murillo, *Chem. Commun.*, 2001, 11; K. Uehara, S. Hikichi and M. Akita, *J. Chem. Soc., Dalton Trans.*, 2002, 3529.
7 P. Espinet, K. Soulantica, J. P. H. Charmant and A. G. Orpen, *Chem. Commun.*, 2000, 915.
8 A. Cogne, A. Grand, P. Rey and R. Subra, *J. Am. Chem. Soc.*, 1989, **111**, 3230; F. A. Cotton and Y. Kim, *Eur. J. Solid State Inorg. Chem.*, 1994, **31**, 525; H. Miyasaka, C. S. Campos-Fernandez, R. Clerac and K. R. Dunbar, *Angew. Chem., Int. Ed.*, 2000, **39**, 3831; F. A. Cotton, E. V. Dikarev, M. A. Petrukhina, M. Schmitz and P. J. Stang, *Inorg. Chem.*, 2002, **41**, 2903.
9 C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, 3885.
10 E. V. Dikarev, R. V. Shpanchenko, K. W. Andreini, E. Block, J. Jin and M. A. Petrukhina, *Inorg. Chem.*, 2004, **43**, 5558; E. V. Dikarev, V. V. Chernyshev, R. V. Shpanchenko, A. S. Filatov and M. A. Petrukhina, *Dalton Trans.*, 2004, 4120.
11 J. Janszak and R. Kubiak, *J. Mol. Struct.*, 2000, **553**, 157.
12 F. A. Cotton, E. V. Dikarev and X. Feng, *Inorg. Chim. Acta*, 1995, **237**, 19.