6678 data $= 0.094$, GOF $= 1.019$, largest hole and peak $= -2.72$ and $2.38\ e\text{Å}^{-3}$. The refinement of the occupancies for the Ga and Zn positions gave the tentative composition $Mn_8Ga_{\approx 27}Zn_{\approx 14}$ which coincides with the Ga/Zn ratio of the reaction mixture. Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-410318.

[13] The neutron scattering lengths of Ga and Zn differ by about 20%. Time-of-flight neutron powder diffraction data was collected at room temperature using the POLARIS diffractometer at the ISIS Facility, UK. The backscattering detector bank which covers the scattering angles $130^\circ < 2\theta < 160^\circ$ was used, providing data over the d-spacing range $0.2 < d < 3.2$ Å with a resolution of $\Delta d d^{-1} = 5 \times 10^{-3}$. The normalized diffraction data was corrected for absorption.

[14] Rietveld analysis was carried out using the program GSAS (A. C. Larson, R. B. von Dreele, M. Lujan, *GSAS: The General Structure Analysis System*, Los Alamos National Laboratory, Los Alamos, NM, **1994**). The refined parameters included an extinction correction. Due to a strong correlation between temperature factors and occupancies, only two temperature factors, for the Mn and Ga atoms and for Zn atoms, respectively, were refined (3687 data points, $R_p = 0.0452$, $R_{wp} = 0.0216$, $\chi^2 = 1.982$ (for 38 variables), $R_p = \Sigma |y_{oi} - y_{ci}| / \Sigma |y_{oi}|$, $R_{wp} = (\Sigma w |y_{oi} - y_{ci}|^2 / \Sigma w |y_{oi}|^2)^{0.5}$.

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Helical Coordination Polymers with Large Chiral Cavities**

Kumar Biradha, Corey Seward, and
Michael J. Zaworotko*

The concept of crystal engineering[1, 2] owes much to recent advancements in supramolecular chemistry and recognition, understanding, and exploitation of supramolecular synthons.[3] Crystal engineering offers the intriguing promise of facile development of a new generation of functional solids that have been designed from first principles. Therefore, a degree of control over substrates, structure and, ultimately, bulk properties that is not inherently present in naturally occurring compounds is potentially offered. Furthermore, it is already clear that the construction of architectures that are unprecedented in naturally occurring solids becomes feasible. In the context of metal-organic solids, infinite molecular brick walls,[4] ladders,[5] bilayers,[6] and helices[7, 8] represent just four examples of this new generation of solids. Of particular current interest are these and other examples of open framework metal-organic[9, 10] and organic[11, 12] zeolite mimics which incorporate organic guests and "organic clay mimics" which are able to exchange metal cations.[13] Herein we report on a new class of host compound, helical coordination polymers that spontaneously resolve to generate chiral cavities that are large enough to contain supramolecular complexes of organic guest molecules. Significantly, these chiral architectures are generated from simple and inexpensive achiral building blocks.

A weak but commonly encountered supramolecular synthon is the T-shape or edge-to-face stacking interaction.[14] This type of C–H$\cdots\pi$ interaction[15] occurs, for example, in the crystal structure of benzene and appears to be the key driving force for the architecture that is exhibited by the simple and facile to synthesize compound **1**. Crystals of **1** were grown by dissolving [Ni(acetate)$_2$] and benzoic acid in MeOH and layering with a solution of 4,4′-dipy in MeOH [Eq. (1); 4,4′-dipy = 4,4′-bipyridine].

$$Ni(CH_3COO)_2 \cdot 4\,H_2O + 4{,}4'\text{-dipy} \xrightarrow{\text{ArCOOH, MeOH}} [\{Ni(4{,}4'\text{-dipy})(ArCOO)_2(MeOH)_2\}_n] \quad (1)$$

1: Ar = C_6H_5
2: Ar = 2-(OH)C_6H_4
3: Ar = 3-(NO_2)C_6H_4

An X-ray structure analysis[16] reveals that **1** acts as a host compound if crystals are grown in the presence of the guest molecules nitrobenzene, benzene, veratrole, phenol, chloroform, and dioxane to generate the inclusion compounds **1a–f**, respectively. These exhibit isostructural helical architectures with large chiral cavities. The helices are generated around crystallographic 4_1 or 4_3 screw axes and each coil of the helix therefore contains four residues (Figure 1). The distance between coils corresponds to the unit cell length, which ranges from 27.02 to 27.91 Å. As revealed by Scheme 1, this architecture is one of at least three possible architectures that might reasonably exist for **1**. Square boxes based upon 4,4′-dipy have attracted considerable recent attention,[17] but we are un-

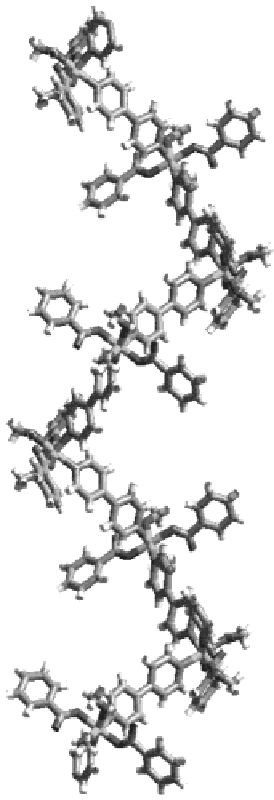

Figure 1. A portion of the helical structure exhibited by compounds **1a–f**.

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[*] Prof. Dr. M. J. Zaworotko, Dr. K. Biradha, C. Seward
Department of Chemistry, The University of Winnipeg
515 Portage Avenue, Winnipeg, Manitoba, R3B 2E9 (Canada)
Fax: (+1) 204-783-7981
E-mail: mike.zaworotko@uwinnipeg.ca

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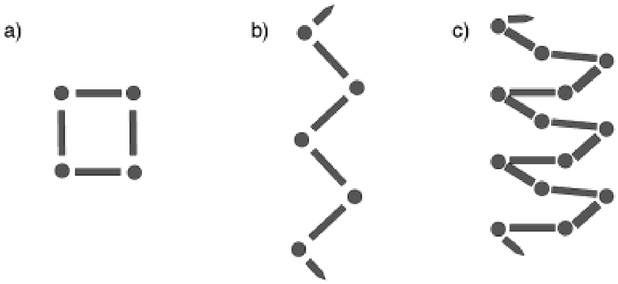

Scheme 1. Possible supramolecular isomers for compounds constituted from a *cis*-octahedral or square-planar coordinated metal ion and a linear "spacer" ligand. a) square box, b) zigzag, c) helix. Circle: metal ion, rod: ligand.

aware of any other examples of helical structures sustained by 4,4′-dipy.

Examination of the crystal packing in **1a–f** reveals the existence of T-shape stacking interactions between benzoate ligands of each helix and the 4,4′-dipy ligands on adjacent helices. The stacking is inherently directional and appears to manifest itself in two salient ways. First, the 3D nature of the crystal packing induces spontaneous resolution of the helices, that is they align in the same direction. Second, adjacent helices are staggered by half the length of the unit cell. Consequently, large chiral cavities that are suitable for incorporation of organic guest molecules exist in between the helices (Figure 2).

The cavities that exist in **1a–f** deserve special attention. They are large in both absolute and relative terms (about 400–500 Å^3 in volume and 24–28% of unit cell volume, respectively) and they are inherently disymmetric. Indeed, the cavity is large enough to enclose aromatic dimers and few examples of cavities greater than this size have been reported in existing crystalline solids.[18] Furthermore, there is very little difference in the crystal packing amongst **1a–f**. Indeed, the six compounds are in effect isostructural and exhibit almost identical cell parameters.[16] Predictably, given the coil nature of a helix, the only significant variation is the about 1 Å range observed in the length of the helical axis. Within a particular batch of crystals the collection of datasets on several suitable crystals revealed that individual crystals are randomly left-handed or right-handed. The inherent chirality of the cavity appears to induce chirality into the supamolecular adducts that are formed by the achiral guest molecules. Figure 3 illustrates the disymmetric C_2 dimer of nitrobenzene molecules that occurs in **1a** and its environment. The primary interaction between the nitrobenzene guest molecules and the walls of the cavities results from C–H⋯O hydrogen bonding between benzoate ligands and nitro groups. These molecular recognition features mean that the cavity has a profound effect upon the structure of the face-to-face dimer, and it would be reasonable to call this cavity a primitive analogue of the type of cavity that can be observed in enzymes. Interestingly, loss of guest molecules is slow under ambient conditions and does not appear to result in loss of crystallinity.

That C–H⋯π stacking is an important factor in determining and sustaining the crystalline architecture is supported by our observations in two related compounds in which the benzoate ligands are functionalized. First, replacement of the key benzoate C–H functionality by a nitro group, thereby sterically and chemically precluding edge-to-face aromatic stacking, results in another interesting but dramatically different supramolecular isomer of **1**. The crystal structure of **2** consists of linear chains which stack to generate a trigonal architecture (space group $P3_1$, $a = 11.2989(5)$, $c = 17.5432(10)$ Å, $V = 1936.6(2)$ Å^3). Second, replacement of a less critical C–H moiety affords the same architecture as **1a–f**. Specifically, **3** exhibits C–H⋯π interactions and crystallizes with an almost identical structure, including cavities, to that of **1a–f** (space group $I4_122$, $a = 14.8633(10)$, $c = 27.494(3)$ Å, $V = 6074.0(8)$ Å^3).

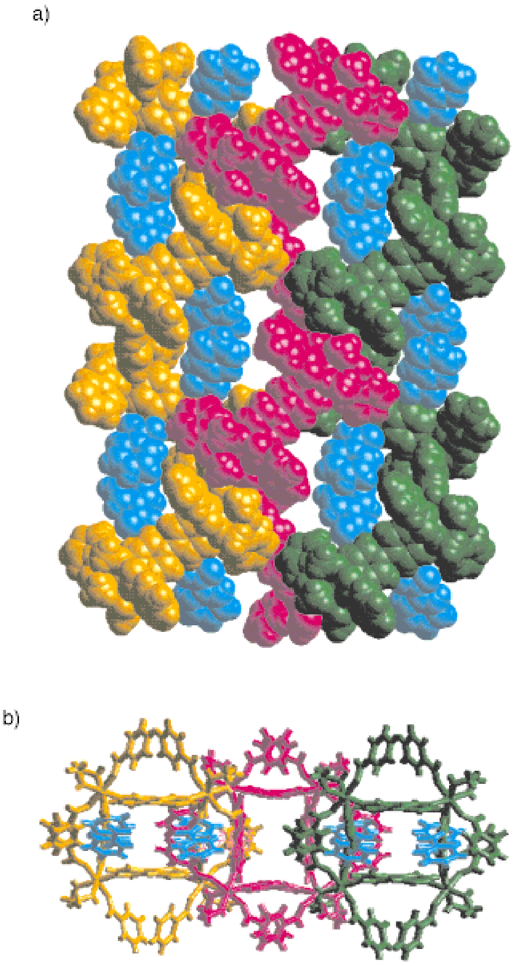

Figure 2. Illustrations of the crystal packing in compound **1a**: a) A space-filling view of the crystallographic *ac* plane in **1a**. Crystals of **1a** are randomly left-handed or right-handed. The right-handed helices presented in the illustration are staggered but orient parallel to one another. Nitrobenzene guest molecules are colored turquoise and form face-to-face dimers. b) A view of the crystallographic *ab* plane in **1a**.

There are several observations and conclusions that we consider of particular relevance concerning the results reported herein:

- It is becoming abundantly clear that *chiral* crystalline architectures and cavities or channels[19, 20] can be achieved by using the most simple of *achiral* molecular components. Furthermore, the nature of the cavities means that achiral guests are induced to form chiral adducts.

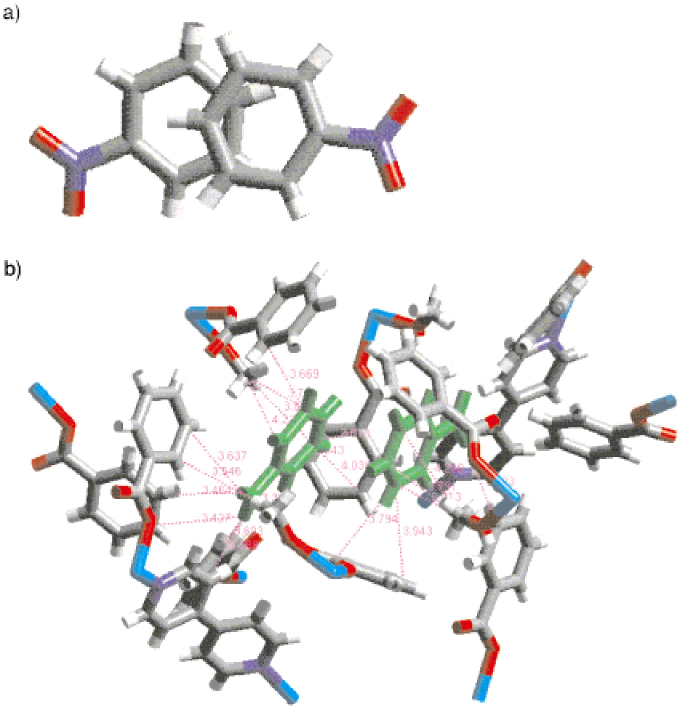

Figure 3. a) A perspective view of the disymmetric (nitrobenzene)$_2$ adduct that occurs in **1a**. b) A view of this adduct and its environment in the chiral cavity. Note the presence of pairs of C–H···O hydrogen bonds between benzoate ligands and nitro groups.

- Chiral and/or chiral porous materials clearly have implications for the developing fields of stereospecific synthesis[21] and enantioselective separations. Furthermore, the bulk properties of helical urea inclusion compounds have already drawn attention.[20]
- We confirm[3] that even the weakest of intermolecular attractive forces, C–H···π interactions, can profoundly and, more importantly, rationally influence crystalline architecture (parallel, staggered alignment of helices and the generation of large cavities) and sustain robust and reproducible networks.
- It appears likely that the compounds reported herein are prototypal for a plethora of similar compounds based upon helices generated from a range of *cis*-metal moieties, counterions, and linear spacer ligands. We consider it important to note that the synthetic procedures described herein involve a "one-pot synthesis", utilize simple and inexpensive substrates, and are relatively trivial.

In summary, the compounds reported herein represent prototypes of a new class of compounds: helical coordination polymers with large chiral cavities that are suitable for the incorporation of several organic guest molecules. They therefore effectively combine the presence of polarity and porosity in the solid state, both of which are of significant relevance to applications in chemistry and materials science.

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Crystallographic Data Centre as supplementary publication nos. CCDC-102586 and CCDC-102587 (**1a** and **1e**, respectively). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

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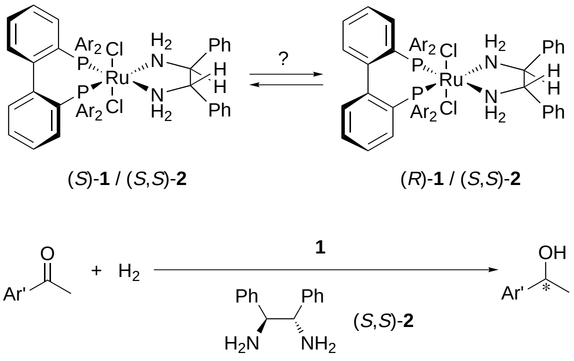
Conformationally Flexible Biphenylphosphane Ligands for Ru-Catalyzed Enantioselective Hydrogenation[**]

Koichi Mikami,[*] Toshinobu Korenaga, Masahiro Terada, Takeshi Ohkuma, Trang Pham, and Ryoji Noyori[*]

In asymmetric catalytic reactions,[1] racemic catalysts inherently give only racemic products, whereas nonracemic catalysts generate nonracemic products with or without a nonlinear relationship.[2] Conversely, we reported a conceptually new strategy for asymmetric catalysis using racemic catalysts wherein a chiral additive selectively activates,[3] rather than deactivates,[4] one enantiomer of the racemic catalyst. We here describe an advanced strategy that uses conformationally flexible bis(phosphanyl)biphenyl ligands (BIPHEP)[5] for a Ru catalyst which, following activation by a chiral diamine,[3d, 6] achieves high enantioselectivity in the hydrogenation of carbonyl compounds (see Scheme 1). Combination of a racemic BINAP/RuCl$_2$ species (BINAP = 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl) with an equimolar amount of an enantiomerically pure diamine gives a 1:1 mixture of two diastereomeric diphosphane/diamine complexes.[3d] When the BINAP ligand is replaced by the flexible and proatropisomeric BIPHEP, diastereomeric complexes are formed, in principle, in unequal amounts. Here, if the major diastereomer shows higher chiral efficiency than does the minor isomer, this strategy becomes more beneficial than the use of structurally similar BINAP analogues.

The hydrogenation of a carbonyl compound by the complex formed from [RuCl$_2$(dm-biphep)(dmf)$_n$] (**1**; DM-BIPHEP = 2,2′-[(3,5-dimethylphenyl)phosphanyl]biphenyl) and enantiopure (*S*,*S*)-1,2-diphenylethylenediamine ((*S*,*S*)-DPEN; (*S*,*S*)-**2**)[7] is shown in Scheme 1. Conformational flexibility of the BIPHEP/RuCl$_2$/diamine complexes was proven by ^{1}H NMR spectroscopic analysis. A mixture of **1** and **2** in CDCl$_3$ at room temperature showed a ^{1}H NMR spectrum that is quite similar to that of the racemic DM-BINAP/RuCl$_2$/(*S*,*S*)-DPEN complex.[8, 9] This indicated the initial formation of an equimolar mixture of *S*- and *R*-fixed DM-BIPHEP/RuCl$_2$/(*S*,*S*)-DPEN diastereomers in this solvent (^{1}H NMR (CDCl$_3$): (*S*)-DM-BIPHEP/RuCl$_2$/(*S*,*S*)-DPEN: $\delta = 3.42, 3.43, 4.33$; (*R*)-DM-BIPHEP/RuCl$_2$/(*S*,*S*)-DPEN: $\delta = 3.28, 4.06, 4.59$). However, when this mixture was diluted with [D$_8$]2-propanol (CDCl$_3$/(CD$_3$)$_2$CDOD 1/2) and allowed to stand at room temperature for 3 h or at 80 °C for 30 min, a 3:1 mixture of the *S*/*S*,*S* and *R*/*S*,*S* diastereomers was formed (Figure 1, Scheme 2; ^{1}H NMR



Scheme 1. Enantioselective hydrogenation of carbonyl compounds to optically active alcohols catalyzed by Ru complexes containing conformationally flexible BIPHEP ligands. In each case, (*S*)-**1** and (*R*)-**1** (Ar = 3,5-dimethylphenyl) is fixed in the respective configuration. The chiral amine (*S*,*S*)-**2** is added as activator to complex **1** prior to the hydrogenation.

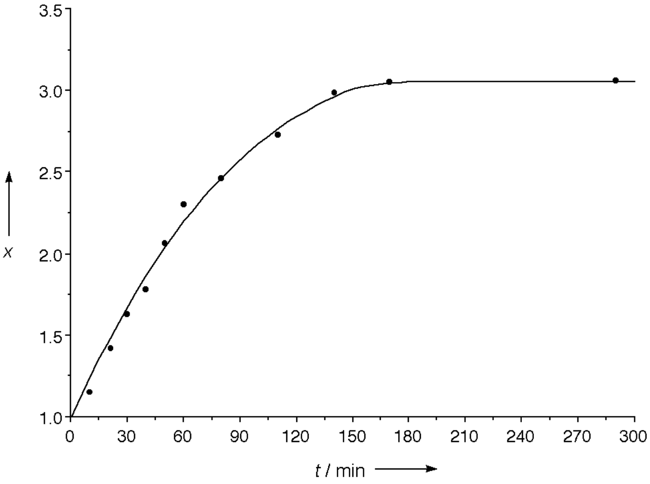


Figure 1. Stereomutation of DM-BIPHEP/RuCl$_2$/(*S*,*S*)-DPEN diastereomers in CDCl$_3$/(CD$_3$)$_2$CDOD (1/2) at 25 °C. x = ratio of (*S*)-DM-BIPHEP/RuCl$_2$/DPEN to (*R*)-DM-BIPHEP/RuCl$_2$/DPEN.

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[*] Prof. Dr. K. Mikami, T. Korenaga, Dr. M. Terada
Department of Chemical Technology
Tokyo Institute of Technology
Ookayama, Meguro-ku, Tokyo 152–8552 (Japan)
Fax: (+81)3-5734-2776
E-mail: kmikami@o.cc.titech.ac.jp

Prof. Dr. R. Noyori, Prof. Dr. T. Ohkuma, Dr. T. Pham
Department of Chemistry and Molecular Chirality
Research Unit, Nagoya University
Chikusa, Nagoya 464–8602 (Japan)
Fax: (+81)52-783-4177
E-mail: noyori@chem3.chem.nagoya-u.ac.jp

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