Molecular chairs, zippers, zigzag and helical chains: chemical enumeration of supramolecular isomerism based on a predesigned metal–organic building-block†

Jie-Peng Zhang, Yan-Yong Lin, Xiao-Chun Huang and Xiao-Ming Chen*

Received (in Cambridge, UK) 19th October 2004, Accepted 7th January 2005
First published as an Advance Article on the web 2nd February 2005
DOI: 10.1039/b416095a

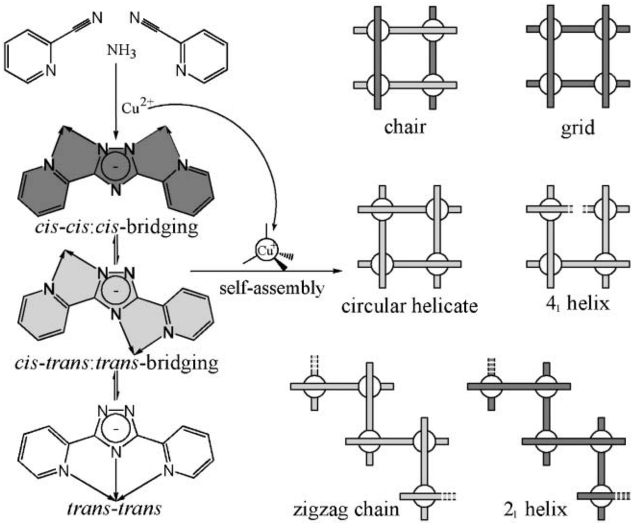
A predesigned metal–organic building-block [Cu^{I}(2-pytz)] (2-Hpytz = 3,5-di-2-pyridyl-1,2,4-triazole) has been successfully used to synthesize four genuine supramolecular isomers.

Supramolecular isomerism and polymorphism is widely encountered in the field of crystal engineering.[1–4] The most famous and simplest system of supramolecular isomers may be the 0D ring-like, 1D zigzag and helical chains derived from a stoichiometry of 1 : 1 metal/ligand molar ratio.[1a] Although some intriguing 0D/1D coordination polymers have been reported in the context of this system, they should be categorised as being pseudo-polymorphic owing to the co-existence of different guest components,[3] including our recent observation in Cu^{I} 2-methylimidazolates.[3d] In fact, no genuine examples of this type of low-dimensional supramolecular isomerism with all three isomers as proposed a long time ago are known, while a few examples of true supramolecular isomerism for higher-dimensional coordination polymers have been reported.[4] Herein we report a successful approach to a genuine example of supramolecular isomerism of 0D/1D coordination polymers.

A binary Cu^{I} triazolate [Cu^{I}(2-pytz)]$_x$ (2-Hpytz = 3,5-di-(2-pyridyl)-1,2,4-triazole) was chosen as the candidate for the following reasons: i) It can be prepared easily *via* our recently established method (copper ion assisted cycloaddition of organonitriles and ammonia).[5] ii) Based on general coordination principles (the bidentate chelating mode is more stable than unidentate, and the tridentate chelating mode is apparently not suitable for Cu^{I}), robust coordination environments can be predicted as illustrated in Scheme 1. iii) The possible supramolecular superstructures cover the desired ones. iv) The large aromatic 2-pytz ligand and hydrothermal condition may favour close packing. The lack of strong hydrogen bonding donor/acceptor can also reduce additional guest/solvent components.

As accurate prediction of the final superstructures is impossible, we tried different synthetic routes by varying the reaction time and temperature (100–160 °C), concentration, as well as additive (anions and/or solvents) to study the possible supramolecular isomerism of this system, and four types of air stable crystals with different colors and/or shapes have been isolated. Crystallographic studies‡ reveal that they are true supramolecular isomers bearing a fixed stoichiometry of Cu^{I} : 2-pytz = 1 : 1. Expected coordination environments were found for both Cu^{I} (distorted tetrahedral, Cu–N 1.928(2)–2.338(2) Å) and 2-pytz ligands (bis-bidentate).

Red polyhedral **I** possesses a centrosymmetrical, chair-like tetrameric superstructure bearing both *cis–cis* and *cis–trans* 2-pytz ligands (Fig. 1 and Scheme 1). Although the squares, grids, and circular helicates have been extensively studied,[6] no such chair-like tetrameric metallomacrocycle has been described previously. Two crystallorgraphically independent Cu^{I} centers are in distorted tetrahedral coordination environments (Cu1: Cu–N



Scheme 1 Synthesis and three possible conformations of 2-pytz (left) and some hypothetical supramolecular isomers [Cu^{I}(2-pytz)] (right).

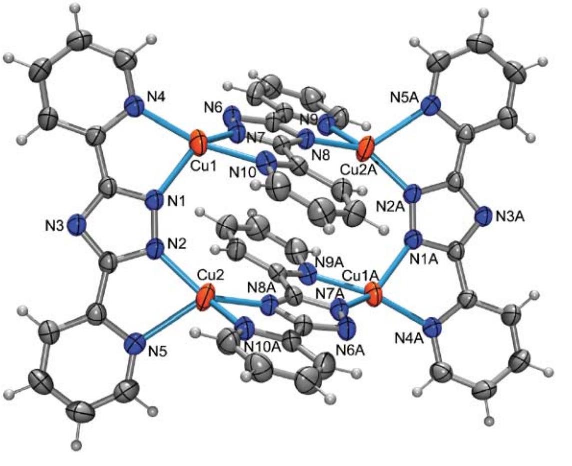


Fig. 1 ORTEP drawing of **I** (at 50% probability; A: $1 - x, 1 - y, 1 - z$).

---

† Electronic supplementary information (ESI) available: synthetic details, photographs of the crystals, PXRD patterns, and additional plots of the structures. See http://www.rsc.org/suppdata/cc/b4/b416095a/

*cescxm@zsu.edu.cn

2.017(2)–2.099(2) Å, N–Cu–N 80.74(8)–147.60(9)°; Cu2: 1.934(2)–2.323(2) Å, N–Cu–N 77.35(9)–134.01(9)°), and the difference between Cu1 and Cu2 is correlated to the unsymmetrical nature of the *cis–trans* 2-pytz ligands. Compared with the commonly expected grid-like [2 × 2] architectures,[6b] chair-like **I** displays some unique structural features. The four metal centers in **I** define a quasi-rectangle (Cu1···Cu2 4.325 Å, Cu1···Cu2A 5.972 Å, Cu2···Cu1···Cu2A 90.7°). The two inversely-related *cis–trans* ligands possess an intramolecular face-to-face π–π interaction (*ca*. 3.5 Å), which may be responsible for the significant deviation (29°) of the dehedral angles between adjacent coordinated ligand planes from the ideal 90°. However, such face-to-face separations should be close to the intermetallic distances in the regular (square) grid-like structures, but can be shortened when the square distorts into a rhomb.[6b] The grid-like structure may be possible for [Cu^I(2-pytz)] since the tetrahedral coordination requirement is not so strict for Cu^I. However, so far we have not been able to synthesise the grid or other hypothetical circular helicates. The unique structure of 2-pytz could be responsible for these observations, in which two bidentate chelating sites are fused to a five-membered ring, but a six-membered one is commonly observed for the grid or a long and flexible one is required for the helicate. The intramolecular π–π stacking within the chair may give additional stabilisation energy in the competition with other isomers such as the grid.[6b]

There is one *cis–trans* and half a *cis–cis* 2-pytz ligand in the unsymmetrical unit of red column-like **II**. Cu1 is chelated by two *cis–trans* 2-pytz ligands (dihedral angle 55.6°) in a highly distorted tetrahedral environment (Cu–N 2.048(2)–2.058(2) Å, N–Cu–N 81.90(7)–138.45(7)°). Cu2 is chelated by two 2-pytz ligands in different conformations (dihedral angle 70.0°) and its coordination environment should be described as linearly coordinated by two triazolate donors (Cu–N 1.928(2) and 1.932(2) Å, N–Cu–N 163.76(8)°) distorted by two additional pyridyl donors (Cu–N 2.280(2) and 2.338(2) Å). As the linkages of the building blocks distort greatly from ideal ones, the extended chain possesses an unexpected saw-toothed geometry and further dimerizes to a zipper-like double chain *via* face-to-face π–π interactions (3.43 Å) between the teeth (*cis–trans* ligands) (Fig. 2).[8] Parallel zippers in **II** further stack to form 3D structures *via* van der Waals interactions.

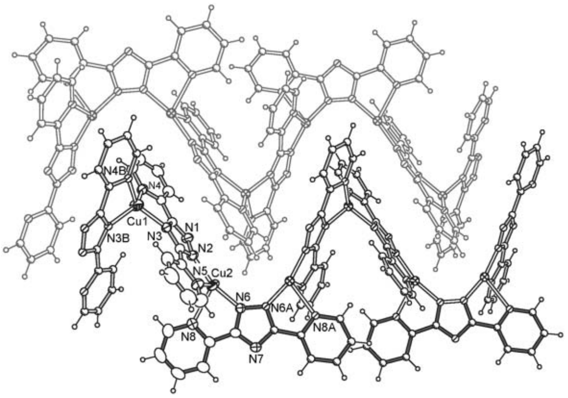


Fig. 2 Zipper-like double chain of **II**, one of the crystallographic independent units is shown in thermal ellipsoid mode (50%; A: $-x$, y, $2.5 - z$; B: $-x$, y, $1.5 - z$).

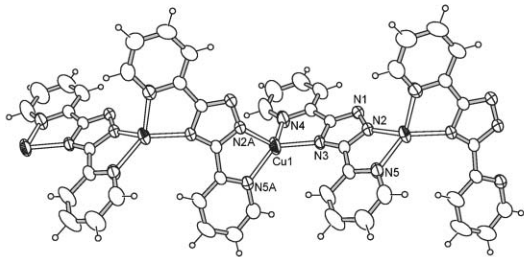


Fig. 3 ORTEP drawing of **III** (50%; A: x, $0.5 - y$, $-0.5 + z$).

Only one *cis–trans* 2-pytz and a distorted tetrahedral Cu^I atom (Cu–N 2.006(2)–2.130(2) Å, N–Cu–N 81.24(7)–130.71(7)°) exists in the orange column-like **III**. The [Cu^I(2-pytz)] building blocks (dihedral angle 74.3°) interlink to each other along the *c*-axis to give a polar zigzag chain, which is generated by the head-to-tail alignments of the unsymmetrical organics. However, the whole crystal structure of **III** is centrosymmetric ($P2_1/c$) since anti-parallel chains stack with each other *via* π–π, C–H···π and C–H···N interactions (Fig. 3). The diverse superstructures of **I**–**III** should be categorised as conformational supramolecular isomers since the ligand conformations are different.[1a]

The local structure of orange needle-like **IV** is very similar to that of **III** (Cu–N 1.999(2)–2.118(2) Å, N–Cu–N 81.37(9)–127.98(9)°). The dihedral angle between adjacent ligands (*cis–trans*) in **IV** is very close to the ideal one (89.4° *vs*. 90°) compared to those in the other isomers. Although the zigzag chain in **III** is widely encountered, the 1D polymer in its structural supramolecular isomer **IV** is a rare example of a single-stranded 4_1 helix[7] (Fig. 4a), whereas other types of helix are quite common, especially the 2_1 ones.[8,9] Helical structures are one of the most interesting superstructures in the context of spontaneous chiral resolution from achiral components.[1a,7–9] The whole packing structure of **IV** comprises left-handed helices only, giving a homochiral

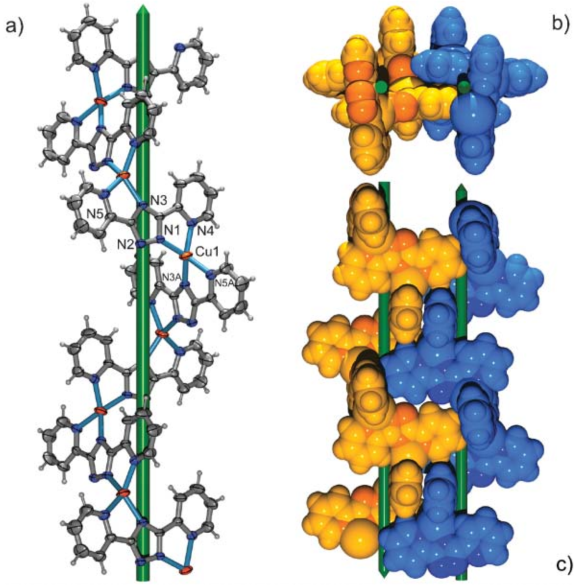


Fig. 4 ORTEP drawing (50%; A: $0.5 - y$, $x - 0.5$, $z - 0.25$) of a single 4_1 helix in **IV** (a). Top (b) and side (c) views of two adjacent helical chains in space filling modes (arrows represent the different orientations of the triazolato rings along the *c*-axis).

superstructure. However, known coordination helices are usually packed in a racemic fashion.[8,9b] Detailed analysis reveals that adjacent chains in **IV** match with each other *via* π–π, C–H···π and C–H···N supramolecular interactions in the packing. In fact, we were unable to reach an efficient packing model with heterochiral helices by using the structural parameters of **IV**, implying that it may be impossible for **IV** to crystallize in a centric space group. Similar, but more complicated recognition-driven proccesses are also responsible for most examples of chiral information transfer from metal–organic helices to the crystal.[7,9] Chemists who desire a designed synthesis for homochiral crystals may be enlightened from the simple, neutral **IV**, which reduces the uncertainty and complexity of the structural prediction of the packing target.[1d] One should notice that the zig-zag and helical chains have additional polarities as all unsymmetrical organics in a single chain are uniformly arranged. Such additional polarities are counteracted as the adjacent chains are opposite to each other in **III** and **IV**, although those in **IV** are homochiral. The lack of separated polarity in the helices mentioned in the literature mainly arises from the fact that most of the helices are nonpolar,[7–9] or from the easy confusion of chirality and polarity (chiral molecules are not necessarily polar, such as those with D_n symmetry).

From an energetic point-of-view, discrete superstructures should be the most favorable species among the possible types of structures (finite and infinite coordination oligo- and polymers).[1a,6] On the other hand, infinite polymers are kinetically favored for crystal growth. **I** is found to be the most easily prepared compared with the other three isomers, which is indicated by the isolated frequencies and yields among our various experimental conditions. Discrete **I** is virtually insoluble in common solvents at room temperature, while such behaviour is unsurprising for the other three polymeric isomers. **I** can be observed under most synthetic conditions from 100–160 °C including addition of different anions (carbonate, nitrate, and sulfate) in the starting materials. In contrast, **II** can also be synthesised from 100–160 °C on addition of the above mentioned cations, but without addition of anions (using $Cu(OH)_2$ as the Cu^{II} source). Although we hardly observe **I** and **II** as contaminants, **III** usually appears as a byproduct of **I** or **II** (manual separation, *ca.* 5–10%) under these conditions. It is interesting that pure **I** or **II** can be prepared by reduced concentration of the starting agents upon addition of more water, while pure **III** can be prepared by addition of carbonate and benzene only. **IV** can only be synthesized by the use of a fixed proportion of $Cu_2(OH)_2CO_3$, aqueous ammonia and 2-cyanopyridine over a reduced reaction time (2 days) in low yield, while **I**–**III** are not sensitive to time (2–3 days) and the yields are relatively high. Large amounts of water soluble colourless crystals[10] were found to coexist with **IV**. However, this reaction was not fully repeatable in our 20 trials (successful in only 5 trials). The amazing phenomena of disappearing polymorphs were also observed for some organic compounds.[1c,2a,2b]

In summary, the four simple and straightforward isomers without the presence of any guest component represent the first examples of low-dimensional supramolecular isomerism in coordination polymers. We have also established synthetic methods for the controlled crystallization of individual isomers.

This work was supported by NSFC and MOE of China, and Guangdong Provincial Science and Technology Bureau.

Jie-Peng Zhang, Yan-Yong Lin, Xiao-Chun Huang and Xiao-Ming Chen*
School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou, 510275, China. E-mail: cescxm@zsu.edu.cn;
Fax: +86 20 8411-2245; Tel: +86 20 8411-3986

Notes and references

‡ Crystal data for **I**: monoclinic, space group $P2_1/c$ (no. 14), a = 13.2428(9), b = 19.557(1), c = 9.1855(7) Å, β = 106.530(9)° V = 2280.6(3) Å^3, Z = 8, D_c = 1.665 g cm^{-3}, F(000) = 1152, μ = 1.90 mm^{-1}, 17968 reflections measured, 5479 unique (R_{int} = 0.033), final R_1 = 0.0648, wR_2 = 0.1076, S = 1.029 for all data; **II**: monoclinic, space group $C2/c$ (no. 15), a = 16.215(1), b = 18.521(1), c = 12.5482(8) Å, β = 115.506(1)°, V = 3401.2(4) Å^3, Z = 12, D_c = 1.674 g cm^{-3}, F(000) = 1728, μ = 1.91 mm^{-1}, 11455 reflections measured, 3806 unique (R_{int} = 0.026), final R_1 = 0.0492, wR_2 = 0.0946, S = 1.016 for all data; **III**: monoclinic, space group $P2_1/c$ (no. 14), a = 11.6326(9), b = 9.6838(7), c = 11.1798(9) Å, β = 108.410(2)°, V = 1194.9(2) Å^3, Z = 4, D_c = 1.589 g cm^{-3}, F(000) = 576, μ = 1.82 mm^{-1}, 9255 reflections measured, 2874 unique (R_{int} = 0.024), final R_1 = 0.0515, wR_2 = 0.1058, S = 1.048 for all data; **IV**: tetragonal, space group $P4_32_12$ (no. 96), a = 11.532(1), c = 18.290(1) Å, V = 2432.3(3) Å^3, Z = 8, D_c = 1.561 g cm^{-3}, F(000) = 1152, μ = 1.78 mm^{-1}, 15744 reflections measured, 2934 unique (R_{int} = 0.035), final R_1 = 0.0485, wR_2 = 0.0926, S = 1.060 for all data, Flack parameter 0.001(2). Data collections of **I**–**IV** were performed with Mo-Kα radiation (λ = 0.71073 Å) at T = 293 K on a Bruker SMART Apex CCD diffractometer ($2\theta \leqslant 56°$), the structures were solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F^2 using the SHELXTL program.[11] CCDC 246255–246258. See http://www.rsc.org/suppdata/cc/b4/b416095a/ for crystallographic data in .cif or other electronic format.

1 (*a*) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; (*b*) J. Bernstein, R. J. Davey and J. O. Henck, *Angew. Chem. Int. Ed.*, 1999, **38**, 3441; (*c*) J. D. Dunitz and J. Bernstein, *Acc. Chem. Res.*, 1995, **28**, 193; (*d*) G. R. Desiraju, *Nat. Mater.*, 2002, **1**, 77.
2 (*a*) L. Yu, G. A. Stephenson, C. A. C. Mitchell, A. Bunnell, S. V. Snovek, J. J. Bowyer, T. B. Borchardt, J. G. Stowell and S. R. Byrn, *J. Am. Chem. Soc.*, 2000, **122**, 585; (*b*) V. S. S. Kumar, A. Addlagatta, A. Nangia, W. T. Robinson, C. K. Broder, R. Mondal, I. R. Evans, J. A. K. Howard and F. H. Allen, *Angew. Chem. Int. Ed.*, 2002, **41**, 3848; (*c*) J.-O. Henck, J. Bernstein, A. Ellern and R. Boese, *J. Am. Chem. Soc.*, 2001, **123**, 1834; (*d*) P. Bombicz, M. Czugler, R. Tellgren and A. Kálmán, *Angew. Chem. Int. Ed.*, 2003, **42**, 1957.
3 (*a*) T. L. Hennigar, D. C. MacQuarrie, P. Loiser, R. D. Rogers and M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 972; (*b*) D. V. Soldatov, J. A. Ripmeester, S. I. Shergina, I. E. Sokolov, A. S. Zanina, S. A. Gromilov and Yu. A. Dyadin, *J. Am. Chem. Soc.*, 1999, **121**, 4179; (*c*) H. Abourahma, B. Moulton, V. Kravtsov and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2002, **124**, 9990; (*d*) X.-C. Huang, J.-P. Zhang and X.-M. Chen, *J. Am. Chem. Soc.*, 2004, **126**, 13218.
4 (*a*) S. Masaoka, D. Tanaka, Y. Nakanishi and S. Kitagawa, *Angew. Chem. Int. Ed.*, 2004, **43**, 2530; (*b*) N. Masciocchi, S. Bruni, E. Cariati, F. Cariati, S. Galli and A. Sironi, *Inorg. Chem.*, 2002, **40**, 5897.
5 J.-P. Zhang, S.-L. Zheng, X.-C. Huang and X.-M. Chen, *Angew. Chem. Int. Ed.*, 2004, **43**, 206.
6 (*a*) S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853; (*b*) M. Ruben, J. Rojo, F. J. Romero-Salguero, L. H. Uppadine and J. M. Lehn, *Angew. Chem. Int. Ed.*, 2004, **43**, 3644.
7 (*a*) K. Biradha, C. Seward and M. J. Zaworotko, *Angew. Chem. Int. Ed.*, 1999, **38**, 492; (*b*) E. V. Anokhina and A. J. Jacobson, *J. Am. Chem. Soc.*, 2004, **126**, 3044; (*c*) T. Ezuhara, K. Endo and Y. Aoyama, *J. Am. Chem. Soc.*, 1999, **121**, 3279; (*d*) F. M. Tabellion, S. R. Seidel, A. M. Arif and P. J. Stang, *Angew. Chem. Int. Ed.*, 2001, **40**, 1529; (*e*) U. Siemeling, I. Scheppelmann, B. Neumann, A. Stammler, H.-G. Stammler and J. Frelek, *Chem. Commun.*, 2003, 2236.
8 X.-M. Chen and G.-F. Liu, *Chem. Eur. J.*, 2002, **8**, 4811.
9 (*a*) L. Pérez-García and D. B. Amabilino, *Chem. Soc. Rev.*, 2002, **31**, 342; (*b*) C. Janiak, *Dalton Trans.*, 2003, 2781.
10 Cell parameters are similar to those of α-picolinamide reported by: T. Takano, Y. Sasada and M. Kakudo, *Acta Crystallogr.*, 1966, **21**, 514.
11 *SHELXTL 6.10*, Bruker Analytical Instrumentation, Madison, WI, USA, 2000.