

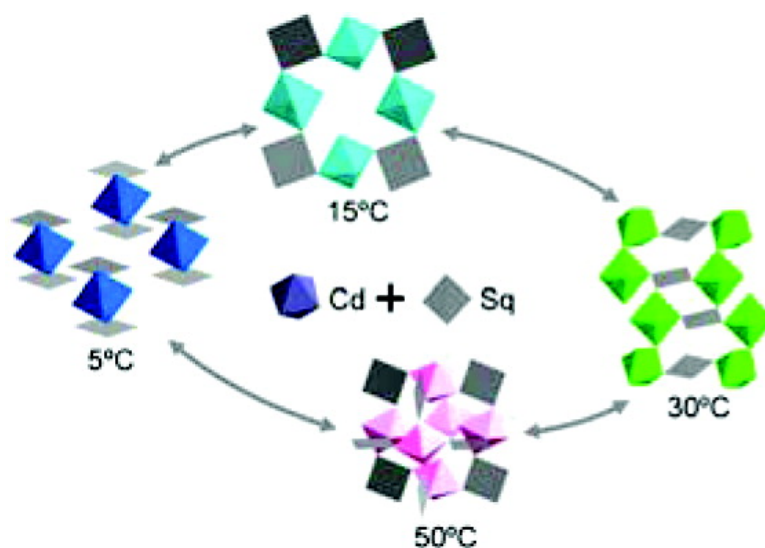
Communication

Temperature Controlled Reversible Change of the Coordination Modes of the Highly Symmetrical Multitopic Ligand To Construct Coordination Assemblies: Experimental and Theoretical Studies

Bo Zheng, Hao Dong, Junfeng Bai, Yizhi Li, Shuhua Li, and Manfred Scheer

J. Am. Chem. Soc., **2008**, 130 (25), 7778-7779 • DOI: 10.1021/ja800439p • Publication Date (Web): 30 May 2008

Downloaded from <http://pubs.acs.org> on February 8, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

Temperature Controlled Reversible Change of the Coordination Modes of the Highly Symmetrical Multitopic Ligand To Construct Coordination Assemblies: Experimental and Theoretical Studies

Bo Zheng,[†] Hao Dong,[‡] Junfeng Bai,^{*,†} Yizhi Li,[†] Shuhua Li,^{*,‡} and Manfred Scheer^{*,§}

State Key Laboratory of Coordination Chemistry and Institute of Theoretical and Computational Chemistry, Nanjing University, Nanjing 210093, PR China, and Institut für Anorganische Chemie der Universität Regensburg, D-93040 Regensburg, Germany

Received January 23, 2008; E-mail: bjunfeng@nju.edu.cn; shuhua@nju.edu.cn; manfred.scheer@chemie.uni-regensburg.de

Coordination assemblies are of high interest due to their fascinating topologies and interesting properties.¹ However, controllable synthesis of MOFs is a great challenge because many factors may affect self-assembly of them, such as the chemical structure of the ligands chosen,^{2a} the coordination geometry preferred by the metal,^{2b} reaction temperature, the counterions,^{2c} the solvent system,^{2d} pH value,^{2e} the metal-to-ligand ratio,^{2f} and the methods of the crystallization.^{2g} Among them, temperature is a crucial parameter in influencing the formation of the MOFs, leading to their structural and dimensional variations,^{3a–e} supramolecular isomerism,^{3f} and new topologies based upon the variation of the conformations of ligand.^{3g} However, systematical investigation of the effect of temperature on coordination modes of the highly symmetrical multitopic ligands still remains unexplored. Furthermore, reversible change of them by temperature also has not been reported.

We are interested in constructing coordination polymers with novel topologies from highly symmetrical multitopic units.⁴ By varying the different concentrations of the solution, we have isolated the inorganic fullerene-like molecules, 1D or 2D coordination polymers based on the highly symmetrical [Cp*Fe(η^5 -P₅)].^{4a} Herein, we present a systematic investigation of temperature on the coordination modes of the squarate ligand. By fine-tuning the reaction temperature to 5, 15, 30, and 50 °C, respectively, four complexes, [Cd(HC₄O₄)₂(H₂O)₄] (**1**), [Cd₄(C₄O₄)₄(H₂O)₁₆]·(H₂O)₂ (**2**), [Cd(C₄O₄)(H₂O)₂] (**3**), and [Cd(C₄O₄)(H₂O)₂] (**4**), were formed successfully with the identical initial mixture (Figure 1), in which the coordination mode of the squarate is changed step by step from monodentate in **1**, bisonodentate in **2**, and trisonodentate in **3**, to tetramonodentate in **4**. It should be emphasized that, in contrast to those reactions of other groups,^{3,5} the lower reaction temperatures (5–50 °C) are in a very limited range with the narrow temperature intervals, which may be easily neglected. Moreover, the unprecedented reversible interconversion among the four complexes at the corresponding reaction temperatures mediated by the mother liquor was also observed (Figure 1). Calculations of their total energies helped us to deeply understand this interesting phenomenon of the formations of these structures. This unprecedented result will contribute to the further development of our knowledge to substantially influence supramolecular chemistry and crystal engineering processes concerning the highly symmetrical multitopic ligands.

By fine-tuning the reaction temperature to 5, 15, 30, and 50 °C, a stoichiometric reaction using cadmium hydroxid, squaric acid, and water in approximately a 1:1.8:579 ratio led to the formations

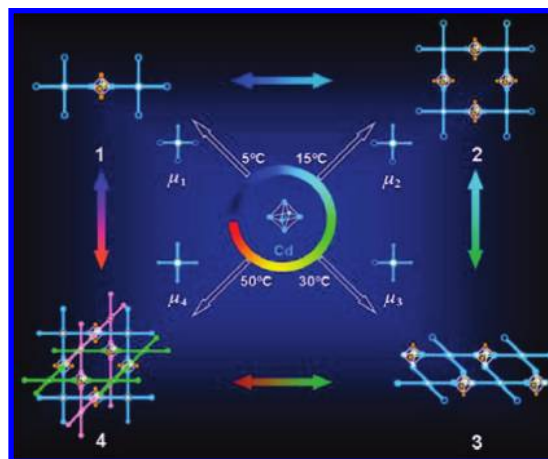


Figure 1. Schematic illustrations of complex **1–4** that can form at 5, 15, 30, and 50 °C and transform to each other reversibly, including four coordination modes of the squarate. Blue octahedra are drawn around cadmium centers. Blue crosses denote squarate ligands. Blue spheres denote coordinated oxygen atoms of squarate. Hollow spheres are uncoordinated oxygen atoms. Coordinated water molecules are orange spheres.

of the complexes **1**, **2**, **3**, or **4**, respectively. X-ray diffraction analysis reveals that complex **1** represents a cadmium squarate monomer, which is isostructural to [Mn(HC₄O₄)₂(H₂O)₄] reported by Yaghi et al.^{6a} Each cadmium atom is coordinated in a perfect octahedral geometry by two squarate oxygen atoms which are trans to each other and four water molecules (Figure S1 in Supporting Information). The squarate acts as a monodentate ligand, connecting to one metal center. Complex **2** is a rare molecular square derived from the two pairs of Cd(II) ions and squarate ligands. As shown in Figure S2 in the Supporting Information, there are two crystallographically independent Cd(II) ions (Cd1 and Cd2) in the fundamental building unit. Each cadmium atom adopts perfect octahedral coordination geometry on the edge of the square, coordinated by four water molecules at the basal positions and two squarates at the apical positions. The squarate acts as a μ_2 -1,2-bisonodentate ligand to span as a bridge between metal centers on the corner of the square since its coordination sites are oriented $\sim 90^\circ$. In contrast, the vast majority of the molecular squares reported so far are based on *cis*-coordinated metal ion or bimetal unit corners and difunctional linear ligand edges.⁷ Complex **3** is a novel 3D network, in which each cadmium atom is coordinated by six oxygen atoms from three squarate ligands, two μ_2 -bridging water molecules, and a terminal water molecule in a slightly distorted octahedral geometry (Figure S3a in Supporting Information). Each squarate ligand acting as μ_3 -1,2,3-trisonodentate linker bridges three Cd atoms to form a 1D infinite ladder-like chain along the

[†] State Key Laboratory of Coordination Chemistry, Nanjing University.

[‡] Institute of Theoretical and Computational Chemistry, Nanjing University.

[§] Universität Regensburg.

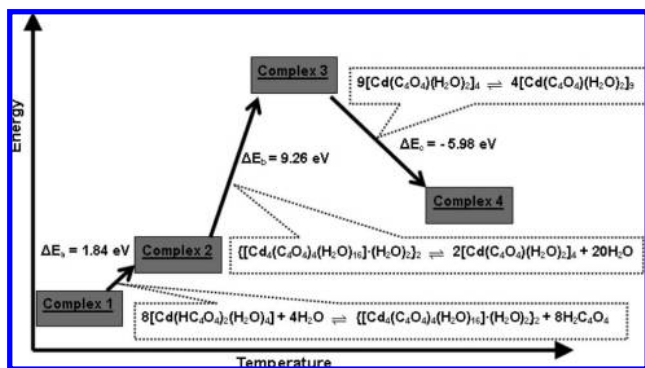


Figure 2. Comparison of the relative stability of the structures (1–4) based upon each formula as a function of temperature and energy.

a-axis. These chains are cross-linked with the 1D zigzag chains (Cd–Ow–Cd) along the *c*-axis by sharing the μ_2 -bridging water molecules. The topology of the network may be simplified by considering the squarate ligands and metal ions as three-connected and five-connecting nodes. This generates an unusual 3D binodal (3,5)-connected network with the Schläfli symbol of $(4^2.6)(4^2.6^5.8^3)$ (Figure S3b in Supporting Information). To the best of our knowledge, 3D networks based upon mixed three- and five-connected nodes are rare.⁸ Complex 4 is a 3D network structure with the typical NbO topology and was first reported by Maji et al.,^{6b} in which each cadmium atom adopts a slightly distorted octahedral coordination geometry (Figure S4 in Supporting Information), coordinated by four squarates at the basal positions and two water molecules at the apical positions. Every squarate binds to four different cadmium centers, that is, each squarate functions as a μ_4 -1,2,3,4-tetramonodentate bridging ligand.

In our case, the temperature was observed to have an approximately linear effect on the coordination modes of the squarate, which consequently influences on the structure of the complexes. When the temperature increases, the coordination mode of the squarate is changed step by step, such as monodentate in 1, bimonodentate in 2, trimonodentate in 3, and tetramonodentate in 4. As a result, the oxygen atoms of the squarate ligands substitute the aqua ligands around the metal center in that system gradually, resulting in the transformations from the $\text{Cd}(\text{H}_2\text{O})_4^{2+}$ units (1 and 2) and the $\text{Cd}(\text{H}_2\text{O})_3^{2+}$ units (3) to the $\text{Cd}(\text{H}_2\text{O})_2^{2+}$ units (4) and the increase of the dimensionality of the complexes from 0D mononuclear complex (1) and 0D tetranuclear complex (2), to 3D MOFs (3 and 4). When the temperature decreases, the transformation process follows inverted sequence with that of the increase of the temperature.

In order to get further insight into the formations of the different structures of the products 1–4 depending on reaction temperature, one can formulate the chemical reactions based on the unit cell of the corresponding product to estimate the relative stability of the four complexes (Figure 2). The total energies of all the structures (1–4) were calculated using CASTEP⁹ (see Supporting Information). The results show that the transformations from 1 to 2 and from 2 to 3 are endothermic processes, which are consistent with the experimental observations and indicate that the enthalpic factor may be the driving force of such transformations. However, our calculations show that complex 4 has a ground state energy lower than that of complex 3. This is in contrast to the fact that complex 3 appears at 30 °C, and complex 4 is obtained at a higher

temperature (50 °C). Thus, entropic and kinetic factors contribute to a large extent in the transformation processes.¹⁰

In summary, for the first time, temperature in the limited range (5–50 °C) was reported to control finely and reversibly the coordination modes of the ligands and coordination assemblies. Interestingly, along with this investigation, the rare example of molecular square and the unusual (3,5)-connected 3D network has been obtained. This unprecedented result will contribute to the further development of our knowledge to substantially influence supramolecular chemistry and crystal engineering processes concerning the highly symmetrical multitopic ligands.

Acknowledgment. The authors gratefully acknowledge supports from the Major State Basic Research Development Programs (Nos. 2006CB806104 and 2007CB936302), the NSFC (No. 20771058), and the Science Foundation of Innovative Research Team of NSFC (No. 20721002).

Supporting Information Available: Detailed experimental procedures, crystallographic data and cif files, structural description, crystal photographs, and PXRD patterns of 1–4. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334–2375. (b) Rao, C. N. R.; Natarajan, S.; Vaidhyanathan, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 1466–1496. (c) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F. *Acc. Chem. Res.* **2005**, *38*, 217–225. (d) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629–1658. (e) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reinecke, T. M.; O’Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319–330.
- (2) (a) Wang, Y. T.; Fan, H. H.; Wang, H. Z.; Chen, X. M. *Inorg. Chem.* **2005**, *44*, 4148–4150. (b) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Rizzuto, S. *New J. Chem.* **2003**, *27*, 483–489. (c) Cui, G. H.; Li, J. R.; Tian, J. L.; Bu, X. H.; Batten, S. R. *Cryst. Growth Des.* **2005**, *5*, 1775–1780. (d) Lee, I. S.; Mokshin, D.; Chung, Y. K. *Chem.—Eur. J.* **2004**, *10*, 3158–3165. (e) Wu, S. T.; Long, L. S.; Huang, R. B.; Zheng, L. S. *Cryst. Growth Des.* **2007**, *7*, 1746–1752. (f) Lu, X. Q.; Jiang, J. J.; Chen, C. L.; Kang, B. S.; Su, C. Y. *Inorg. Chem.* **2005**, *44*, 4515–4521. (g) Shin, D. M.; Lee, I. S.; Cho, D.; Chung, Y. K. *Inorg. Chem.* **2003**, *42*, 7722–7724.
- (3) (a) Forster, P. M.; Burbank, A. R.; Livage, C.; Férey, G.; Cheetham, A. K. *Chem. Commun.* **2004**, 368–369. (b) Tong, M. L.; Kitagawa, S.; Chang, H. C.; Ohba, M. *Chem. Commun.* **2004**, 418–419. (c) Go, Y. B.; Wang, X. Q.; Anokhina, E. V.; Jacobson, A. J. *Inorg. Chem.* **2005**, *44*, 8265–8271. (d) Thirumurugan, A.; Rao, C. N. R. *J. Mater. Chem.* **2005**, *15*, 3852–3858. (e) Mahata, P.; Sundaresan, A.; Natarajan, S. *Chem. Commun.* **2007**, 4471–4473. (f) Masaoka, S.; Tanaka, D.; Nakanishi, Y.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2530–2534. (g) Dong, Y. B.; Jiang, Y. Y.; Li, J.; Ma, J. P.; Liu, F. L.; Tang, B.; Huang, R. Q.; Batten, S. R. *J. Am. Chem. Soc.* **2007**, *129*, 4520–4521.
- (4) (a) Bai, J.; Virovets, A. V.; Scheer, M. *Science* **2003**, *300*, 781–783. (b) Bai, J.; Virovets, A. V.; Scheer, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 1737–1740. (c) Johnson, B. P.; Dielmann, F.; Balázs, G.; Sierka, M.; Scheer, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 2473–2475. (d) Scheer, M.; Gregoriades, L. J.; Virovets, A. V.; Kunz, W.; Neueder, R.; Krossing, I. *Angew. Chem., Int. Ed.* **2006**, *45*, 5689–5693.
- (5) (a) Solans, X.; Aguiló, M.; Gleizes, A.; Faus, J.; Julve, M.; Verdager, M. *Inorg. Chem.* **1990**, *29*, 775–784. (b) Müller, A.; Röhlfing, R.; Krichemeyer, E.; Bgge, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 909–912. (c) Khan, M. I.; Chang, Y.-D.; Chen, Q.; Salta, J.; Lee, Y.-S.; O’Connor, C. J.; Zubieta, J. *Inorg. Chem.* **1994**, *33*, 6340–6350. (d) Gutschke, S. O. H.; Molinier, M.; Powell, A. K.; Wood, P. T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 991–992.
- (6) (a) Yaghi, O. M.; Li, G. M.; Groy, T. L. *J. Chem. Soc., Dalton Trans.* **1995**, 727–732. (b) Maji, T. K.; Mostafa, G.; Sain, S.; Prasad, J. S.; Chaudhuri, N. R. *CrystEngComm* **2001**, *37*, 1–4.
- (7) (a) Leininger, S.; Stang, P. J.; Olenyuk, B. *Chem. Rev.* **2000**, *100*, 853–908. (b) Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B. *Acc. Chem. Res.* **2005**, *38*, 369–378. (c) Holliday, B. J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2022–2043. (d) Cotton, F. A.; Lin, C.; Murillo, C. A. *Acc. Chem. Res.* **2001**, *34*, 759–771.
- (8) Batten, S. R.; Hoskins, B. F.; Robson, R. *Chem.—Eur. J.* **2000**, *6*, 156–161.
- (9) Segall, M. D.; Lindan, P. L. D.; Probert, M. J.; Pickard, C. J.; Hasnip, P. J.; Clark, S. J.; Payne, M. C. *J. Phys.: Condens. Matter* **2002**, *14*, 2717–2744.
- (10) Nielsen, A. E. *Kinetics of Precipitation*; Pergamon: Oxford, 1964.

JA800439P