Inorganic Chemistry Communications 32 (2013) 68–73

Contents lists available at SciVerse ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Cation-exchange-induced single-crystal-to-single-crystal transformations of a nanoporous coordination complex

Chao Huang, Yao Wang, Changsen Wei, Na Li, Feixiang Ji, Jie Wu *, Hongwei Hou **

The College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450052, PR China

ARTICLE INFO

Article history:
Received 22 January 2013
Accepted 25 March 2013
Available online 29 March 2013

Keywords:
Single-crystal-to-single-crystal
Ion exchange reaction
Cobalt complex

ABSTRACT

Use of a rigidly conjugated clamp-like bis-pyridyl-bis-amide ligand *N,N*-bis-(3-pyridyl)isophthalamide (L), complex $[CoLCl_2]_2$ (**1**) with porous macrocycle structure was obtained under solvothermal conditions. When single crystals of **1** were immersed into the methanol solution of $HgCl_2$ and $CdSO_4$, new crystals of a bimetallic macrocyclic complex $[HgLCl_2]_2$ (**2**) and a two-dimensional (2D) corrugated sheet complex $[CdLSO_4(H_2O)_2]_n$ (**3**) were attained, respectively. All these phenomena are observed through single crystal to single crystal (SCSC) transformations along with the metal–ligand bond breaking and the new metal–ligand bond formation. In addition, the determination of Scanning Electron Microscope (SEM) and Energy-Dispersive X-ray Spectrometry (EDS) reveals that the exchange is a recurrent dissolving-exchange-crystallization process of solvent-mediated mechanism.

Single-crystal-to-single-crystal (SCSC) transformations have received considerable interest in crystal engineering [1–7]. The characteristic which differentiates a SCSC reaction from all other solid-state reactions is that the single crystal maintains its integrity during the reaction. Thus, the SCSC transformation is highly desirable and opens routes to the systematic study of gas storage, separation, and solid state reaction mechanisms, since it allows direct visualization of how the crystal structure is changing during the transformation process and of the location and orientation of guest molecules in the voids.

In recent years, our group has focused on SCSC transformation by cation exchange, which can afford various substituted products through simultaneous metal–ligand bond breaking/formation along with exchange of lattice metal center by external metal ions [8–10]. The previous investigations indicate that the cation exchange reaction mechanism can be classified into two kinds. One is solid-state diffusion mechanism with a nonhomogeneous phase exchange process [11–14], and the other is solvent-mediated mechanism with an initial coordination polymer recurrent dissolving-exchange-crystallization process [15–17]. For example, a few metal–organic frameworks (MOFs) are reported where the process of guest desorption–resorption [18–21], guest-exchange [22,23], and photochemical cycloaddition reactions [24] has been observed in solid-state diffusion fashion. However, only a few documented cases of SCSC transformations in solvent-mediated mechanism involving the dimensionality changes of coordination polymers or cleavage of coordination bonds have been reported by several groups including ours [19,25]. Recently, we have reported the dissolving-exchange-crystallization processes with solvent-mediated mechanism from a tetranuclear Ni^{II} cage to a decanuclear Cu^{II} "pocket", as well as from a 1D meso-helical chain to 2D zigzag chain [26,27], et al.

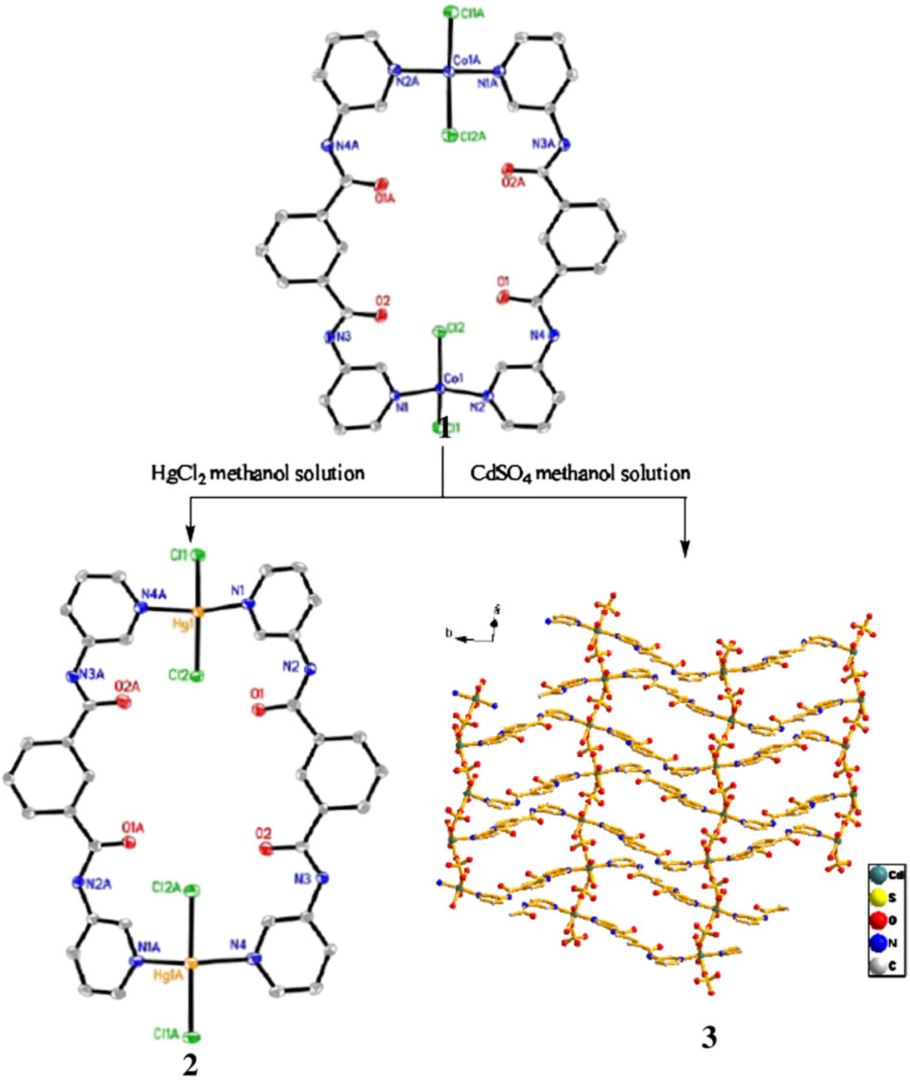
Unfortunately, the poor crystallinity of the final product often prevents the structural determination after solid-state transformations, especially those involving the breakage/formation of metal–ligand bonds. As a continuous research program of our laboratory developing the solvent-mediated mechanism, in this work, we report a SCSC transformation from a binuclear complex $[CoLCl_2]_2$ (**1**) to a binuclear complex $[HgLCl_2]_2$ (**2**), and from **1** to a two-dimensional (2D) corrugated sheet complex $[CdLSO_4(H_2O)_2]_n$ (**3**) (Scheme 1). Furthermore, we employ SEM and EDS to observe the dissolving-exchange-crystallization processes and describe the solvent-mediated mechanism.

Complex $[CoLCl_2]_2$ (**1**) was obtained by heating a mixture of $CoCl_2$ and L in methanol at 120 °C for three days and cooled to room temperature at 5 °C/h [28]. X-ray diffraction study indicates that **1** belongs to the triclinic space group $P\bar{1}$ and the symmetric unit contains two Co(II) atoms with the same coordination environments and two ligands as shown in Fig. 1a. Each Co atom is coordinated in a distorted tetrahedron geometry by two nitrogen atoms (N1 and N2) from the terminal pyridine of two ligands and two chlorine atoms (Cl1 and Cl2). The rigidly conjugated clamp-like bis-pyridyl-bis-amide ligand L acts as a bridging linker which coordinates with two Co(II) ions to form a 28-memberd macrocycle with Co···Co distance of 13.6709(47) Å. The metallomacrocycle has an oval shaped pore wherein all the amide carbonyls are pointed inward. The two terminal pyridyl rings and central benzene rings in the ligand are not co-planar, which is presumably due to the

---

* Corresponding author. Tel.: +86 371 67781588.
** Corresponding author. Tel.: +86 371 67761744.
E-mail addresses: wujie@zzu.edu.cn (J. Wu), houhongw@zzu.edu.cn (H. Hou).

1387-7003/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.inoche.2013.03.025



Scheme 1. Structures of pre- and post-exchanged products. (a) Building unit structure of complex **1**. (b) The $HgCl_2$-exchange-induced complex **2**. (c) The $CdSO_4$-exchange-induced complex **3**.

interaction of $N_{amide}-H\cdots N_{pyridyl}$. The dihedral angles between the central benzene rings and the terminal pyridyl rings are 28.7 and 163.3°, respectively. In addition, the amide group is a fascinating functional group because it possesses two types of hydrogen bonding sites: the –NH moiety acts as an electron acceptor and the $-C{=}O$ group acts as an electron donor. Thus, the amide functionalities are expected to be involved in hydrogen bonding interactions with the counter anions, with itself and with the solvent. As respected, the $N-H\cdots O$ ($N2-H\cdots O2 = 3.008$ Å) hydrogen bonds link complex molecules into one-dimensional (1D) chains. The chains are further connected by the $N-H\cdots Cl$ ($N3-H\cdots Cl1 = 3.380$ Å) hydrogen bonds to form a porous macrocycle structure along the *a*-axis (Fig. 1b).

It is worthy of note that complex **1** is infinitesimally soluble and can stay crystalline state well in methanol solution. This is an important condition for the SCSC transformation by solvent-mediated cation exchange. The subtle dissolved crystals can react with the metal ions in the solution to produce new crystals with different structures along with the simultaneous metal–ligand bond breaking and the new metal–ligand bond formation. Furthermore, the porous macrocycle structure of compound **1** is also conducive to cation exchange reaction.

Aimed at adjusting structure by the cation exchange reactions, we immersed the single crystals of **1** in methanol solution of $HgCl_2$ (0.05 mol/L) at ambient temperature. After about 15 days, the blue crystals started turning colorless and some new tiny colorless crystals were observed on the surface of parent crystals upon microscope. EDS determination to the crystals shows that the metal ions are both Hg(II) and Co(II) ions (Fig. 2b). One month later, the parent crystals disappeared absolutely and the newly formed crystals became suitable for X-ray single crystal diffraction [29]. X-ray diffraction study indicates that the new crystal obtained by SCSC transformation exhibits a binuclear Hg(II) structure. Followed SEM and EDS further indicate that all metal ions are Hg(II) ions (Fig. 2c). Such phenomenon demonstrates that parent crystals act as crystalline supporter to assist the crystallization of new crystals. The crystal growth of the new phase isn't a surface mechanism, but a recurrent dissolving-exchange-crystallization process of solvent-mediated mechanism, which makes the parent crystals convert to the new Hg(II) complex gradually.

The complex $[HgLCl_2]_2$ **2** is isostructural with complex **1**. The crystal structure can be described as a bimetallic macrocycle formed by coordinating two Hg(II) metal centers with two ligands in *syn–syn* conformation [30]. The central metal Hg(II) ion exhibits a distorted tetrahedral