



Hydrothermal syntheses, crystal structures and magnetic properties of five interpenetrated coordination networks: Effect of reaction conditions



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ARTICLE INFO

Article history:

Received 11 June 2014

Accepted 14 August 2014

Available online 2 September 2014

Keywords:

Coordination network
Flexible bis(imidazole) ligand
Interpenetration
Reaction condition
Magnetic property

ABSTRACT

Five new coordination networks, namely $[\text{Cu}_3(\text{bimb})_3(\text{BTC})_2]$ (**1**), $[\text{M}(\text{H}_2\text{O})_2(\text{bimb})(\text{SUC})]$ [$\text{M} = \text{Co}^{\text{II}}$ (**2**), Mn^{II} (**3**) and Ni^{II} (**4**)] and $[\text{Co}(\text{bimb})_{0.5}(\text{BDC})]$ (**5**) (bimb = 1,4-bis(imidazol-1-yl)-butane, $\text{H}_3\text{BTC} = 1,3,5$ -benzenetricarboxylic acid, $\text{H}_2\text{SUC} = \text{succinic acid}$ and $\text{H}_2\text{BDC} = 1,4$ -benzenedicarboxylic acid) have been synthesized hydrothermally and structurally characterized by elemental analysis, IR spectra and X-ray diffraction analyses. Complex **1** exhibits a binodal 3,4-**tfz** net with 3-fold interpenetration. Complexes **2–4** are isostructural, all showing 3-fold interpenetrated **dia** structures. Complex **5** is a 3-fold interpenetrated 3D network structure of the **pcu** topology that is built from tetra-carboxylate dinuclear Co_2 units with a paddle-wheel structure. We examined all the related known structures containing the same mixed ligands and found that the reaction conditions play an important role in the final structure. Furthermore, the magnetic property of **5** has also been investigated.

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1. Introduction

Interpenetration is one of the common phenomena related to entangled architectures, which has achieved considerable attention in the field of supramolecular chemistry and crystal engineering because of the intriguing aesthetic structures and topological features as well as promising applications as functional materials [1–2]. There are two comprehensive reviews by Robson and Batten on interpenetration, which has been the most investigated type of entanglement [3]. Research on coordination polymers is always being directed toward the design and synthesis of novel entangled networks [4]. Usually, it is widely acknowledged that long spacer ligands often favor the formation of interpenetrated motifs. The flexible long bis(imidazole) ligand 1,4-bis(imidazol-1-yl)-butane (bimb), as a good N-donor ligand, has already been proven to be a good candidate for the organization of polymeric interpenetrated systems in our and other group's previous works [5–6]. Such a ligand, bearing alkyl spacers, can assume different conformations (considering the relative orientations of the four CH_2 groups) when it coordinates to metal center, and this often causes the occurrence of diversified network topologies. In continuation of our work, our synthetic strategy is to select the flexible bimb ligand as an organic linker in the presence of BTC^{3-} , SUC^{2-} and BDC^{2-} anions ($\text{H}_3\text{BTC} =$

1,3,5-benzenetricarboxylic acid, $\text{H}_2\text{SUC} = \text{succinic acid}$ and $\text{H}_2\text{BDC} = 1,4$ -benzenedicarboxylic acid) as co-ligands to react with divalent transitional metal ions in an attempt to assemble interpenetrated frameworks. Fortunately, by selecting suitable reaction conditions, five new coordination networks, $[\text{Cu}_3(\text{bimb})_3(\text{BTC})_2]$ (**1**), $[\text{M}(\text{H}_2\text{O})_2(\text{bimb})(\text{SUC})]$ [$\text{M} = \text{Co}^{\text{II}}$ (**2**), Mn^{II} (**3**) and Ni^{II} (**4**)] and $[\text{Co}(\text{bimb})_{0.5}(\text{BDC})]$ (**5**), were successfully obtained [7]. All the compounds were characterized by elemental analyses, IR spectra and X-ray crystallography. The crystal structures as well as topological analysis of these compounds and the systematic investigation of the effect of the reaction conditions on the ultimate frameworks will be represented and discussed. Furthermore, the magnetic property of **5** has also been investigated.

2. Experimental

2.1. Materials and general procedures

Solvents and starting materials for the syntheses were purchased commercially and used as received. Elemental analysis for C, H and N was performed on a Perkin-Elmer 240 analyzer. The IR spectra were recorded as KBr pellets on a Nicolet Magna-FT-IR 560 spectrometer in the 4000 – 400 cm^{-1} region. Variable-temperature magnetic susceptibility measurements and field dependence magnetization measurements were performed on a Quantum Design MPMS SQUID magnetometer.

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2.2. Preparation

2.2.1. Synthesis of $[Cu_3(bimb)_3(BTC)_2]$ (**1**)

A mixture of $CuCl_2 \cdot 2H_2O$ (0.17 g, 1.0 mmol), H_3BTC (0.21 g, 1.0 mmol) and *bimb* (0.19 g, 1.0 mmol) was dissolved in 8 mL of distilled water. The pH was adjusted to 6.0 by addition of 1 M NaOH solution. Consequently, the resulting mixture was transferred and sealed in a 25 mL Teflon-lined stainless steel vessel, which was heated at 160 °C for 3 days, and then the reaction system was cooled to room temperature. Blue crystals were obtained. Yield: 48% (based on Cu). *Anal. Calc.* for **1**: C, 54.98; H, 4.61; N, 16.03. Found: C, 54.92; H, 4.69; N, 16.09%. Selected IR (KBr) ν (cm^{-1}): 3135(m), 2961(m), 2870(m), 1613(s), 1564(m), 1438(m), 1404(m), 1089(m), 831(m), 758(m), 656(m).

2.2.2. Synthesis of $[Co(H_2O)_2(bimb)(SUC)]$ (**2**)

A mixture of $CoCl_2 \cdot 6H_2O$ (0.24 g, 1.0 mmol), *bimb* (0.19 g, 1.0 mmol) and H_2SUC (0.12 g, 1.0 mmol) was dissolved in 8 mL of distilled water. The pH value was then adjusted to 6.0 with 1 M NaOH. Consequently, the resulting solution was transferred and sealed in a 25 mL Teflon-lined stainless steel vessel, which was heated at 150 °C for 2 days. After the reactor was slowly cooled to room temperature, purple crystals formed, which were filtered off and dried in air. Yield: 62% (Based on Co). *Anal. Calc.* for **2**: C, 41.90; H, 5.53; N, 13.96. Found: C, 41.93; H, 5.61; N, 13.91%. Selected IR (KBr) ν (cm^{-1}): 3448(s), 3028(m), 2963(m), 2830(m), 1582(s), 1408(m), 1080(m), 835(m), 765(m), 675(m).

2.2.3. Synthesis of $[Mn(H_2O)_2(bimb)(SUC)]$ (**3**)

The light yellow block-shaped single crystals of **3** were obtained by adopting a similar synthetic procedure as used for **2**, only using $MnCl_2 \cdot 4H_2O$ (0.20 g, 1.0 mmol) instead of $CoCl_2 \cdot 6H_2O$. Yield: 55% (Based on Mn). *Anal. Calc.* for **3**: C, 42.32; H, 5.58; N, 14.10. Found: C, 42.39; H, 5.64; N, 14.02%. Selected IR (KBr) ν (cm^{-1}): 3450(s), 3031(m), 2960(m), 2830(m), 1585(s), 1405(m), 1082(m), 834(m), 766(m), 675(m).

2.2.4. Synthesis of $[Ni(H_2O)_2(bimb)(SUC)]$ (**4**)

The green block-shaped single crystals of **4** were obtained by adopting a similar synthetic procedure as used for **2**, only using $Ni(OAc)_2 \cdot 4H_2O$ (0.25 g, 1.0 mmol) instead of $CoCl_2 \cdot 6H_2O$. Yield: 61% (Based on Ni). *Anal. Calc.* for **4**: C, 41.92; H, 5.53; N, 13.97. Found: C, 41.85; H, 5.49; N, 13.99%. Selected IR (KBr) ν (cm^{-1}): 3450(s), 3033(m), 2958(m), 2832(m), 1580(s), 1408(m), 1080(m), 836(m), 766(m), 665(m).

2.2.5. Synthesis of $[Co(bimb)_{0.5}(BDC)]$ (**5**)

A mixture of $CoCl_2 \cdot 6H_2O$ (0.24 g, 1.0 mmol), *bimb* (0.19 g, 1.0 mmol) and H_2BDC (0.17 g, 1.0 mmol) was dissolved in 8 mL of distilled water. The pH value was then adjusted to 6.0 with 1 M NaOH. Consequently, the resulting solution was transferred and sealed in a 25 mL Teflon-lined stainless steel vessel, which was heated at 150 °C for 2 days. After the reactor was slowly cooled to room temperature, the dark purple single crystals of **5** were obtained. Yield: 49% (Based on Co). *Anal. Calc.* for **5**: C, 49.07; H, 3.84; N, 8.80. Found: C, 48.89; H, 3.80; N, 9.02%. Selected IR (KBr) ν (cm^{-1}): 3040(s), 2915(m), 1589(s), 1560(m), 1467(m), 1405(m), 1085(m), 837(m), 656(m).

2.3. Crystallographic data collection and refinement

Accurate unit cell parameters for **1–5** were determined by a least-squares fit of 2θ values, and intensity data were measured on a Rigaku τ -axis rapid IP area detector with Mo K α radiation ($\lambda = 0.71073$) at room temperature. The intensities were corrected for Lorentz and polarization effects as well as for empirical

absorptions based on the multi-scan technique. All structures were solved by direct methods and refined by full matrix least-squares fitting on F^2 by SHELX-97. All non-hydrogen atoms were refined with anisotropic thermal parameters. Crystallographic data for the three compounds are summarized in Table 1 and selected bond lengths and angles are listed in Table S1.

3. Results and discussion

3.1. Synthesis

The successful isolation of complexes **1–5** relies on the employment of a one-step hydrothermal technique. This is completely different from the recently reported related Cu-*bimb* complexes [6], which were both obtained by a two steps aqueous solution synthesis method, as shown in Scheme 1. The final products significantly depend on the reaction conditions when the reactants are the same. Under hydrothermal conditions, the reduced viscosity of water enhances the diffusion processes, so that solvent extraction of solids and crystal growth from solution are favored. Since different solubility problems can be minimized, a variety of organic and inorganic precursors can be introduced together, increasing the selectivity for self-assembly of metal ions with various organic ligands. Therefore, hydrothermal reactions are an effective method to synthesize novel coordination polymers with complicated structural features.

We tried to prepare the complexes according to the above-mentioned reported procedure. Unfortunately, we failed to obtain the desired products, suggesting that the crystallization and growth are sensitive to the amount of ammoniacal solution. However, the crystals are well formed with reproducibility on using the hydrothermal method.

3.2. Descriptions of the structures

3.2.1. $[Cu_3(bimb)_3(BTC)_2]$ (**1**)

Single-crystal X-ray diffraction analysis reveals that **1** crystallizes in the monoclinic space group $P2_1/c$. As shown in Fig. 1a, two crystallographically independent Cu(II) cations exist with similar CuO_2N_2 square geometries. Both Cu(II) cations (Cu1 and Cu2) are coordinated by two O atoms from two BTC^{3-} anions and two N atoms from two *bimb* ligands (although the *bimb* ligand to which the Cu2 atom coordinates is disordered). The Cu–O/N bond lengths are in the range 1.953(2)–1.991(2) Å, comparable to that observed in other Cu-based complexes [6]. The completely deprotonated BTC^{3-} ligands display the tri(monodentate) coordinated mode, while the *bimb* ligands perform a *trans* coordinated fashion. The BTC^{3-} anions bridge the Cu(II) cations to form a 2D neutral sheet (Fig. S1). Such layers are then pillared by the bridging, 2-connecting *bimb* ligands via the N(*bimb*)–Cu bonds to generate an extended complicated 3D framework structure (Fig. 1b).

Better insight into such elegant frameworks can be accessed by the topology method. An analysis using TOPOS [8] indicates that the coordination framework of **1** features a binodal 3,4-connected network with the point symbol: $(6^3)_2(6^4 \cdot 8 \cdot 10)_3$, if the metal centers and BTC^{3-} are viewed to be 4- and 3-connected nodes, respectively. This is assigned to a 3,4-**tfz** net. Three equivalent nets adopt 3-fold interpenetration to minimize the large voids in the single net (Fig. 1c). It can be shown using TOPOS that there are 3 interpenetrating nets related by translation vectors, hence the framework is of Class Ia. The full interpenetration vectors are [1, 0, 0] (11.37 Å). The value of PICVR (PICVR = 3) corresponds to the translational degree interpenetration Z_t and $Z = Z_t = 3$. Using the TOPOS TTO collection [8], we can find nine structures of such a topology with RefCodes BUPGID, GUKZUI, HACDUL, KOLWEO, MABFOM,

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