Inorganic Chemistry Communications 46 (2014) 324–328

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

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

Two different Zn(II) interpenetrating networks derived from different dicarboxylate ligands mixed with a flexible imidazole-based ligand

Yajuan Mu [a,*], Yungen Ran [b], Jixing Xie [c], Bo Han [a], Xiaoli Ma [a]

[a] College of Traditional Chinese Medicine, Hebei University, Baoding 071000, PR China
[b] Hebei University, Baoding 071000, PR China
[c] College of Chemistry & Environmental Science, Hebei University, Baoding 071000, PR China

ARTICLE INFO

Article history:
Received 5 May 2014
Accepted 1 July 2014
Available online 2 July 2014

Keywords:
Dicarboxylate acids
Flexible imidazole-based ligand
Photoluminescent properties
Interpenetrating networks

ABSTRACT

Two interpenetrating networks based on 1,4-bis(2-methylimidazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene (bmimx), namely, $\{[Zn_2(bmimx)_2(cba)_2]\cdot 2.5H_2O\}_n$ (**1**) and $\{[Zn(bmimx)(suc)]\cdot 2H_2O\}_n$ (**2**) (H_2cba = 4,4′-carbonyldibenzoic acid, H_2suc = succinic acid) have been prepared at hydrothermal condition by varying the dicarboxylate ligands. Single-crystal X-ray diffraction indicates that complex **1** shows a 4-connected *dmp* net with 3-fold interpenetration which contains 1D $(Zn - cba)_n$ right- and left-handed helical chains; complex **2** shows a *dia* topology with 4-fold interpenetration. The results indicate that the spacers of dicarboxylate coligands have an important effect on the interpenetrating characters and ultimate frameworks. Moreover, the photoluminescence properties of the two complexes were studied in the solid state at room temperature.

Interpenetration has been a major concern in the design and synthesis of metal–organic hybrid materials [1–7]. The peculiar structural character of interpenetrating networks can enhance the skeleton rigidity and interlattice interactions, thus creating materials with unique properties or functions, such as superhard materials, magnetic materials and highly stable materials [8–12]. Although the investigation on interpenetrated networks advanced rapidly, the factors that control the observed degrees of interpenetration in these systems remain largely unknown and/or unproven. According to the literatures, the origin of interpenetration can be ascribed to the presence of large free spaces in a single network [13–16]. Generally, longer ligands will lead to larger voids. In a very loose and general sense, it can be said that the larger the voids in the structure, the more likely the interpenetration occurs and the higher the number of independent nets a particular void is passed through [17–19].

1,4-Bis(2-methylimidazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene (bmimx), as a long flexible ligand, should be an ideal choice for forming interpenetrating networks due to the flexible nature of the two $-CH_2-$ spacers between the phenyl group and 2-methylimidazol group [20]. On the other hand, carboxylate ligands have proven to be of great importance as constructors, which have been extensively employed to construct coordination polymers with high porosity and high dimension [21–23]. And we had earlier observed that ligand bmimx reacted with Cd(II) ions in the presence of H_2tbip (H_2tbip = 5-tert-butyl isophthalic acid) to form a 4-fold interpenetrated framework with *sra* topology [20]. Thus, it was anticipated that employment of the flexible ligand bmimx combined with dicarboxylate as organic linkers would be a feasible method for the construction of coordination polymers with interpenetration and intriguing topologies. Herein, we have reacted bmimx and Zn(II) salts in the regulation of dicarboxylate ligands, and as expected, two interpenetrating complexes, namely, $\{[Zn_2(bmimx)_2(cba)_2]\cdot 2.5H_2O\}_n$ (**1**) and $\{[Zn(bmimx)(suc)]\cdot 2H_2O\}_n$ (**2**) (H_2cba = 4,4′-carbonyldibenzoic acid, H_2suc = succinic acid) were successfully isolated by a hydrothermal reaction. Structural analyses show that the two interpenetrating networks with the same metal component and bmimx ligand exhibit interesting topological variations, which are derived from different spacers of dicarboxylate coligands. In this paper, we report the synthesis, crystal structures as well as photoluminescent properties of the two complexes.

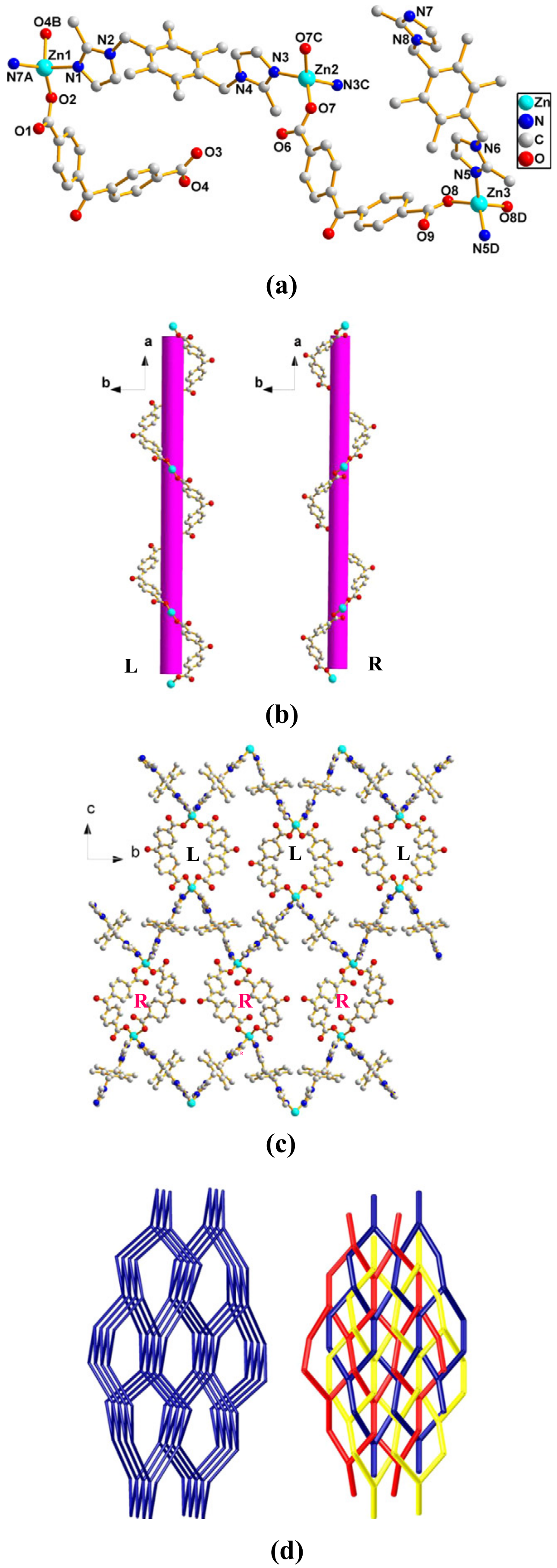
The reaction of $Zn(CH_3COO)_2\cdot 2H_2O$ with bmimx in the presence of dicarboxylate ligands H_2cba and H_2suc led to the formation of complexes **1** and **2**, respectively [24]. The compositions were confirmed by elementary analysis and IR spectra, and the phase purities of the bulk samples for luminescent/thermal measurements were identified by powder X-ray diffraction (PXRD) (please see Fig. S1 in the Supplementary material).

The results of crystallographic analysis [25] revealed that the asymmetric unit of complex **1** contains one and two halves of Zn(II) atoms, two bmimx ligands, two cba^{2-} ligands, and two and a half lattice water molecules. As shown in Fig. 1a, the Zn1, Zn2, and Zn3 centers adopt similar distorted tetrahedral geometry with ZnO_2N_2 coordination environment finished by two nitrogen atoms from two bmimx ligands, and two carboxylate oxygen atoms from two cba^{2-} ligands. The Zn – N

---

* Corresponding author.
E-mail address: muyajuan1027@163.com (Y. Mu).

http://dx.doi.org/10.1016/j.inoche.2014.07.001
1387-7003/© 2014 Published by Elsevier B.V.



distances range from 1.993(8) to 2.023(7) Å and the Zn–O distances are from 1.904(6) to 2.038(11) Å, which are similar to other Zn-based complexes [26]. The two kinds of cba^{2-} ligands adopt the same coordination mode. That is, the two carboxylate groups of each kind of cba^{2-} ligand take the monodentate coordination mode. The two kinds of cba^{2-} ligands link the Zn sites into right-handed (P-) and left-handed (M-) helices along the c-axis, respectively (Fig. 1b). These helical chains with opposite chirality are united alternately together through two kinds of bmimx ligands to make the final 3D structure (Fig. 1c). Both kinds of ligands bmimx present *trans* conformations. From a topological perspective, the whole framework is identified as the 4-connected *dmp* net with the symbol $(6^5 \cdot 8)_3$ by reducing each Zn site as the 4-connected node. The large cavities within the structure allow interpenetration of two other identical nets to form the final 3-fold interpenetrated architecture (Fig. 1d). Furthermore, hydrogen bonding interactions between lattice water molecules and carboxylate oxygen atoms ($O3 \cdots O11 = 2.933$ Å and $O6 \cdots O11 = 2.809$ Å) presumably help to further reinforce the 3D framework.

The results of crystallographic analysis revealed that the asymmetric unit of complex **2** contains one Zn(II) atom, two halves of bmimx ligands, two halve of suc^{2-} ligands and two lattice water molecules. As shown in Fig. 2a, each Zn(II) atom is also in the distorted tetrahedral geometry with ZnO_2N_2 coordination environment finished by two nitrogen atoms from two bmimx ligands, and two carboxylate oxygen atoms from two suc^{2-} ligands. The distances of Zn–O/N bonds range from 1.938(2)–2.053(2) Å, which are similar to those of **1**. Both kinds of suc^{2-} ligands also adopt the bis-monodentate coordination mode. The Zn(II) atom is connected by the two kinds of suc^{2-} ligands to generate a 1D chain structure. Then these 1D chains are pillared by two kinds of bmimx ligands to form the 3D framework as depicted in Fig. 2b. The two kinds of ligands bmimx also present *trans* conformations. Topological analysis of this compound reveals that it is a 4-connected *dia* net with point symbol 6^6, if the Zn(II) atoms are simplified as nodes, and bmimx and suc^{2-} ligands are defined as linkers, respectively (Fig. 2b). The typical adamantanoid cage possesses the maximum dimensions of 30.57 × 26.95 × 26.95 Å corresponding to the longest intracage $Zn \cdots Zn$ distances (Fig. 2c). The potential voids are filled via mutual interpenetration of the other three independent equivalent diamondoid frameworks giving rise to a 4-fold interpenetrated architecture (Fig. 2d). The crystal structure of complex **2** is further strengthened through hydrogen bonding interactions between lattice water molecules and carboxylate oxygen atoms ($O1 \cdots O3w = 2.893$ Å, $O1 \cdots O4w = 2.856$ Å and $O4 \cdots O1w = 2.714$ Å), as well as between lattice water molecules ($O1w \cdots O2w = 2.904$ Å).

The long flexible ligands H_2cba and H_2suc are introduced into the Zn/bmimx system to form a 4-connected *dmp* net with 3-fold interpenetration and a *dia* topology with 4-fold interpenetration, respectively. Obviously, the different interpenetrating networks of the two complexes should be attributed to the different spacers of the dicarboxylate ligands. The two carboxylate groups of H_2cba are located in 4,4′-positions of two phenyl rings linked by a C=O group, so the two phenyl rings of H_2cba can freely twist around the C=O group, which manifests as a V-shaped bridging ligand. Consequently, the employment of V-shaped bridging ligand H_2cba affords a 4-connected *dmp* net with 3-fold interpenetration. H_2suc, as a fatty acid ligand, possesses flexibility owing to the presence of the $-CH_2-$ spacers, which allows the two carboxylate groups to bridge the metals from different directions. As a result, complex **2** exhibits a *dia* topology with 4-fold interpenetration. It is notable that the right- and left-handed helical chains exist in complex **1**. This is because that the employment of V-shaped bridging ligand

Fig. 1. (a) Coordination environment around the Zn(II) center in **1**. Hydrogen atoms and solvent molecules are omitted for clarity. Symmetry code: A = −0.5 − x, −0.5 + y, 1 − z; B = −0.5 + x, 0.5 − y, −2 − z; C = −x, 1 − y, z; D = 1 − x, 1 − y, z. (b) View of the left-handed and right-handed helices constructed by Zn(II) atoms with cba^{2-} ligands along the *c* axis. (c) The 3D architecture along the *bc* plane. (d) Schematic representation of the *dmp* topology (left); schematic of the 3-fold interpenetration (right).