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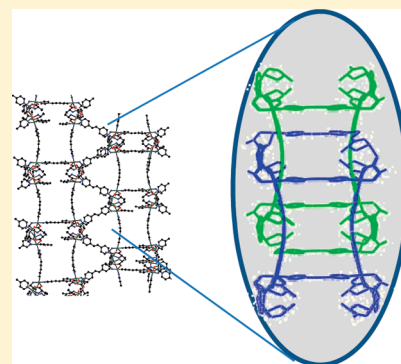
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Novel Twofold Interpenetrating Channel Framework Based on Metal Tetramer Subunits

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ABSTRACT: Tetrameric, metal-based subunits, $[\text{Ni}_4(\text{D-alala})_2(\text{L-alala})_2]$ (D-alala = D-alanine anion, L-alala = L-alanine anion), designed as nodes to construct coordination frameworks, allowed the synthesis of a new twofold interpenetrating channel architecture $\{[\text{Ni}_4(\text{D-alala})_2(\text{L-alala})_2(1,2\text{-bpe})_4] \cdot 17\text{H}_2\text{O}\}_n$ [1,2-bpe = 1,2-bis(4-pyridyl)ethylene]. Characterization included thermogravimetric analyses, IR spectroscopy, X-ray powder diffraction, and single crystal X-ray diffraction. Triangular and rectangular short circuits were formed by the tetrameric nodes and 1,2-bpe linkers that consisted of a triangular prism, and they were further assembled into a twofold interpenetrating parallelepiped motif. The hierarchical construction, based on tetramer nodes and the 1,2-bpe linkers in the channel framework, was investigated.



Over the past few years, rapid progress has been made in the design and construction of metal–organic frameworks (MOFs), owing to their intriguing structural topologies and wide potential applications as functional materials.¹ The porosity of MOFs shows size- and shape-selective adsorption properties and plays crucial roles in gas storage, separation processes, transport of organic substrates, ion-exchange, catalysis, etc.² An important aspect of MOFs chemistry is their ability to build structures with functionalized pores.³ It has been shown that metal cations and carboxylate ligands can form a range of multinuclear nodes with predefined geometries,⁴ for example, the binuclear paddle-wheel units $[\text{Zn}_2(\text{O}_2\text{CR})_4]$ ⁵ and $[\text{Cu}_2(\text{O}_2\text{CR})_4]$ (4-connected),⁶ the trinuclear units $[\text{Ni}_3\text{O}(\text{O}_2\text{CR})_6]$, $[\text{Fe}_3\text{O}(\text{O}_2\text{CR})_6]$,⁷ and $[\text{Cr}_3\text{O}(\text{O}_2\text{CR})_6]$ (6-connected),⁸ and the tetranuclear unit $[\text{Zn}_4\text{O}(\text{O}_2\text{CR})_6]$ (6-connected).⁹ Recent work has shown that amino acids are capable of binding to metals via two carboxylates and single amino functional groups to form extended open frameworks, which can be porous and display enantioselective sorption.¹⁰ Herein, we report the construction of tetrameric metal nodes $[\text{Ni}_4(\text{D-alala})_2(\text{L-alala})_2]$ (where D-alala = D-alanine anion, L-alala = L-alanine anion) bridged by D,L-alala and a novel, twofold interpenetrating channel framework, $\{[\text{Ni}_4(\text{D-alala})_2(\text{L-alala})_2(1,2\text{-bpe})_4] \cdot 17\text{H}_2\text{O}\}_n$ [1,2-bpe = 1,2-bis(4-pyridyl)ethylene], based nodes linked by 1,2-bpe.

Complex **1** possesses space group $P4n2$ with a $\text{Ni}_4(\text{D-alala})_2(\text{L-alala})_2(1,2\text{-bpe})_4$ subunit and seventeen free water molecules in the asymmetric unit.^{11,12} As shown in Figure 1, the Ni(II) center is in a distorted square pyramidal coordination geometry in

which the deprotonated D,L-alala chelates Ni(II) ion through an amino N atom and a carboxylic O atom. The remaining two sites in the basal plane are occupied by two N atoms from different 1,2-bpe ligands, and the apical position is occupied by a carboxylate O atom of another D,L-alala. Seventeen solvent water molecules form the guest, which interacts with the coordination host. The D,L-alala functions as a κ^3 -bridge between two Ni(II) ions and four Ni(II) ions linked by four D,L-alala anions forming a tetramer with S_4 symmetry (Figure 2). The tetramer subunits are neutral and can be envisioned as a node to construct functional coordination. Compared to a metal cation, this type of node has more abundant coordination numbers and predefined geometries. As depicted in Figure 2, the coordination number of the tetramer node is eight, but it is not a restricted regular polyhedron. Each tetrameric node is further bridged by eight 1,2-bpe linkers within the network.

Better insight into the structure of complex **1** can be achieved by the application of a topological approach, that is, reducing multi-dimensional structures to simple node-and-linker nets.¹³ According to the simplification principle, the tetramer is defined as an eight-connected node, while the 1,2-bpe serves as the linker. Therefore, on the basis of this chemical topology, there are two kinds of short circuits. One is a triangle, formed by three tetramer nodes and three 1,2-bpe linkers. The other is a rectangle, formed by four

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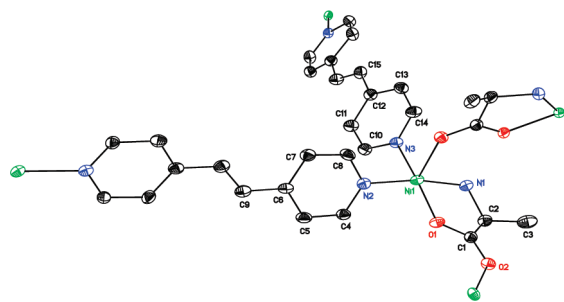


Figure 1. The coordination environment of Ni(II) ion in complex **1** with the atom numbering, showing displacement ellipsoids at the 30% probability level. H atoms and water molecules are omitted for clarity.

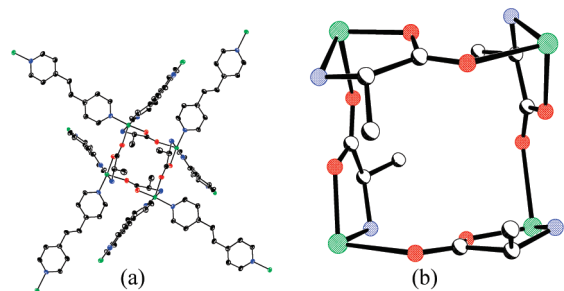


Figure 2. (a) The nickel tetramer in complex **1**. (b) The nickel tetramer bridged by the D,L-alanine in complex **1**. 1,2-bpe's are omitted for clarity.

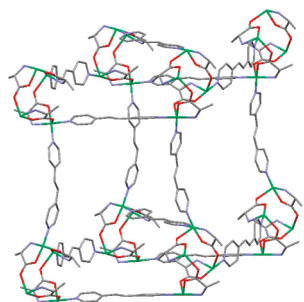


Figure 3. Perspective views of the parallelepiped motif.

tetramer nodes and four 1,2-bpe linkers; there are two types of rectangles. The triangle and two rectangles consist of a triangular prism individual motif, of which 1,2-bpe linkers form the length and height of the triangular prism. Aggregation of the triangular prism results in a novel parallelepiped motif (Figure 3). It is noteworthy that the parallelepiped motifs did not arrange in the same order; thus, the arrangement directions between two adjacent rows of parallelepiped motifs are vertical (Figure 4a). The aggregation of the parallelepiped motifs results in the 3D framework.

It is well-known that large networks tend to interpenetrate to fill the voids within a single network. Because 1,2-bpe is a long linker, and the parallelepiped motif is large enough to interpenetrate each other, it is observed (Figure 4b) that the two parallelepiped motifs are interlocked with each other, leading directly to the formation of a three-dimensional twofold interpenetrating network.¹⁴

Due to this interpenetration, all voids in the x , y , and z directions of the parallelepiped motifs are filled. Notably, there are still two channels between the x and z axes with the same size

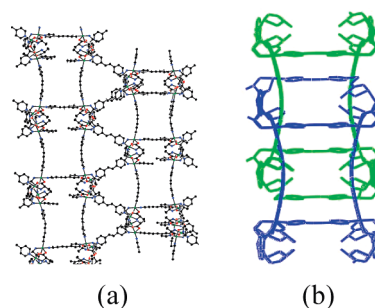


Figure 4. (a) Arrangement of parallelepiped motifs along with (b) the interpenetration mode for complex **1**.

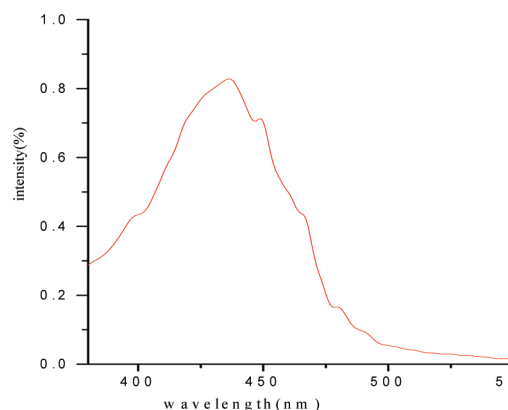


Figure 5. Fluorescence spectra of complex **1**.

and shape; thus, complex **1** is a type of channel framework. Although interpenetrated, complex **1** still has a large solvent accessible volume of *ca.* 1849 Å³ per unit cell (4827 Å³), amounting to 38.3% of the crystal lattice, and low density (1113 mg·cm⁻³). The charges of the tetramer can be changed at will, and we have designed a Cu(II) tetramer, bridged by four 2,3-pyrazinedicarboxylate trianions; this tetramer is a tetraanion, and we can place functional cations in the channel which act as functionalized sites¹⁵ for ion exchange or catalysis.

The IR spectrum of complex **1** was recorded in the range 4000–500 cm⁻¹ using KBr disks. This complex showed an asymmetric vibration band for the carboxylate at 1621 cm⁻¹ (ref 16) and the symmetric vibration band at 1393 cm⁻¹. A strong band at 1585 cm⁻¹ confirmed the presence of the 1,2-bpe ligand, which was consistent with the X-ray analysis. Because of interpenetration, complex **1** is more stable, and it expelled the uncoordinated water near 200 °C. The thermogravimetry analysis curve of complex **1** revealed a weight loss from 216 to 218 °C (3.3%), which could be attributed to this loss of water (2.5%). When heated above 218 °C, complex **1** began to slowly decompose. The XPRD powder diffraction pattern of complex **1** agrees with the XPRD patterns simulated for the single crystal structure, which indicated that the powder and single crystal were the same phase. The X-ray powder diffraction patterns of both complexes before and after removing water molecules were completely different, suggesting the host framework may be broken down due to dehydration. This showed that water guest molecules play an important role in stabilizing the channel structure of complex **1**.

It is interesting that we also obtained complex **2** starting with L-alanine, where it possessed the same structure as complex **1**, which

suggests that some L-ala converted into D-ala during the reaction; however, its crystal was not resolved as well as complex **1**. The same structure using copper(II) was also obtained, although its crystal was also not well resolved; the CIF file of the copper(II) structure is provided as Supporting Information.

The fluorescence excitation wavelength for compound **1** is 350 nm. As shown in Figure S, only a deep blue emission with a maximum at 435 nm was observed. The emission band was observed to shift to longer wavelength compared to the case of the 1,2-bpe ligand,¹⁶ and the red shift was considered to result from the metal–ligand charge transfer.

In summary, a novel twofold interpenetrating channel framework, $\{[\text{Ni}_4(\text{D-ala})_2(\text{L-ala})_2(1,2\text{-bpe})_4] \cdot 17\text{H}_2\text{O}\}_n$, was synthesized and characterized, based on well-designed metal tetramer subunits. The metal tetramer subunits have appropriate coordination numbers and angles and are well suited as framework design nodes. Furthermore, the charges of metal tetramer subunits can be designed and desired counterions can be placed in channel, which is envisioned as a functionalizable site for many properties.

■ ASSOCIATED CONTENT

S Supporting Information. X-ray crystallographic files in CIF format for the structure determination of complexes **1** and **2**, powder XRD pattern, TGA, and IR spectra of complex **1**, experimental procedures for **1**, **2**, and **3**, and a table of crystallographic data and parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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