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First 3D Pr(III)–Ni(II)–Na(I) Polymer and A 3D Pr(III) Open Network Based on Pyridine-2,4,6-tricarboxylic Acid

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The self-assembly of pyridine-2,4,6-tricarboxylic acid (H_3ptc) with metal salts under hydrothermal conditions gave two novel coordination polymers, $\{[Pr(\mu_5\text{-ptc})(H_2O)_2]\cdot 1.5H_2O\}_n$ (**1**) and $\{Na_2NiPr(\mu_4\text{-}ClO_4)(\mu_2\text{-}HOCH_2CH_2OH)(\mu_4\text{-ptc})_2(H_2O)_8\}\cdot 4.5H_2O\}_n$ (**2**). **1** is a 3D open network with five ptc ligands coordinating with one metal center and carboxylate groups linking metal centers to form a (4,6) net. **2** is the first Pr/Ni/Na heterotrimetallic complex, a unique 3D framework containing four different bridged ligands in the system.

The construction of 3D coordination polymers has been a field of rapid growth in supramolecular and material chemistry because of the formation of fascinating structures and their potentially useful ion-exchange, adsorption, catalytic, fluorescence, and magnetic properties.[1] Consequently, a variety of 3D metal−organic frameworks (MOFs) have been prepared through taking certain factors into account, such as the coordination nature of the metal ion and the shape, functionality, flexibility, and symmetry of the organic ligand,[2] of which many are derived from multicarboxylate ligands because of their rich coordination modes.[3] For example, Williams reported a Cu(II) MOF with nanocavities based on benzene-1,3,5-tricarboxylate (H_3btc).[4] Pyridinylcarboxylic acids are good choices for constructing MOFs due to the existence of both N and O atoms in the ligands, which can link 3d, 4f, and 3d−4f metal ions. In our previous studies, pyridine-2,6-dicarboxylic acid (H_2PDA) was employed to synthesize a 3d−4f 3D MOF.[5] Pyridine-2,4,6-tricarboxylic acid (H_3ptc) unites the coordination geometry of H_2PDA and H_3btc and potentially exhibits a strong and typical property of acting as a multidentate ligand.[6] To continue our research of 3d−4f MOFs, H_3ptc was employed in the self-assembly.

Herein, we isolated two 3D polymers, $\{[Pr(\mu_5\text{-ptc})(H_2O)_2]\cdot 1.5H_2O\}_n$ (**1**) and $\{Na_2NiPr(\mu_4\text{-}ClO_4)(\mu_2\text{-}HOCH_2CH_2OH)(\mu_4\text{-ptc})_2(H_2O)_8\}\cdot 4.5H_2O\}_n$ (**2**), under hydrothermal conditions,[7] which were structurally characterized by X-ray single-crystal diffraction.[8] We report the first Pr/Ni/Na heterotrimetallic complex, two (4,6) nets for Pr atoms linked by

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(7) Preparation of $\{[Pr(\mu_5\text{-ptc})(H_2O)_2]\cdot 1.5H_2O\}_n$ (**1**): a mixture of H_3ptc (0.5 mmol, 0.1055 g), $Pr(ClO_4)_3\cdot 6H_2O$ (0.5 mmol, 0.2736 g), NaOH (1.5 mmol, 0.060 g), H_2O (12.0 mL), and $(CH_2OH)_2$ (3.0 mL) was put in a 25 mL acid digestion bomb and heated at 180 °C for 3 days. The green products were collected after washing with H_2O (2 × 5 mL) and diethyl ether (2 × 5 mL). Yield, 61% (based on Pr(III) salts). Elemental analysis (%) calcd for **1**: C 23.32, H 2.20, N 3.40; found: C 23.58, H 1.95, N 3.31. Preparation of $\{Na_2NiPr(\mu_4\text{-}ClO_4)(\mu_2\text{-}HOCH_2CH_2OH)(\mu_4\text{-ptc})_2(H_2O)_8\}\cdot 4.5H_2O\}_n$ (**2**): a mixture of H_3ptc (0.5 mmol, 0.1055 g), $Pr(ClO_4)_3\cdot 6H_2O$ (0.5 mmol, 0.2736 g), $Ni(ClO_4)_2\cdot 6H_2O$ (0.5 mmol, 0.1828 g), NaOH (1.5 mmol, 0.060 g), H_2O (12.0 mL), and $(CH_2OH)_2$ (3.0 mL) was put in a 25 mL acid digestion bomb and heated at 180 °C for 3 days. The green products were collected after washing with H_2O (2 × 5 mL) and diethyl ether (2 × 5 mL). Yield, 65% (based on Pr(III) salts). Elemental analysis (%) calcd for **2**: C 21.17, H 2.82, N 2.91; found: C 21.39, H 2.55, N 2.67.

(8) Crystal data: for **1**, $C_8H_9NO_{9.5}Pr$, $M = 412.07$, Monoclinic, $P2(1)/n$, $a = 6.7981(12)$ Å, $b = 11.978(2)$ Å, $c = 13.515(3)$ Å, $\beta = 100.174(2)°$, $V = 1083.1(3)$ Å^3, $Z = 4$, $T = 293(2)$ K, $F_{(000)} = 796$, GOF = 1.017, R1 = 0.0266, wR2 = 0.0676; for **2**, $C_{17}H_{27}ClN_2Na_2NiO_{26.5}Pr$, $M = 964.46$, Orthorhombic, *Pccn*, $a = 21.288(4)$ Å, $b = 6.4991(13)$ Å, $c = 21.651(4)$ Å, $V = 2995.5(10)$ Å^3, $Z = 4$, $T = 293(2)$ K, $F_{(000)} = 1924$, GOF = 1.189, R1 = 0.0755, wR2 = 0.1731; direct methods with SHELXS-97 and refinement on F^2 using SHELXL-97.

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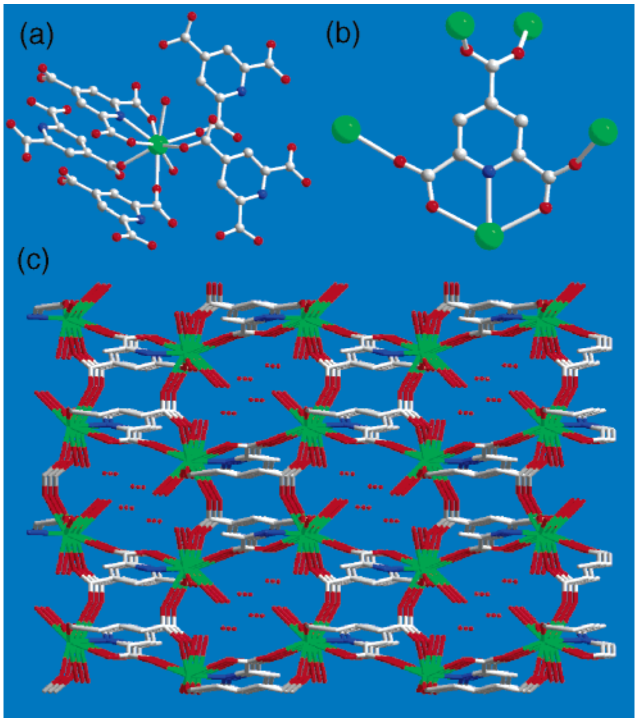

Figure 1. The coordination environment of Pr(III) (a); the coordination environment of ptc (b); and the 3D coordinated networks along the *a* direction (c) in **1**. Green, Pr; red, O; gray, C; blue, N; H atoms are omitted.

carboxylic groups in **1** and the connection between Pr and Ni atoms in **2**, and the coordination mode of ptc found in 3d, 4f, and 3d−4f complexes.

The single-crystal analysis reveals that **1** is a 3D open MOF constructed via ptc and Pr(III). As shown in Figure 1, each Pr(III) center coordinates with one tridentate ptc and four monodentate ptc ligands together with two water molecules to complete the coordination sphere of the Pr atom, which conforms most closely to a tricapped trigonal prism. This is a very rare example for five multicarboxylate ligands coordinating with one metal center. The Pr−O and Pr−N bond lengths are in the normal range of bond lengths for Pr(III) ion.[9] Each ptc ligand links five Pr(III) centers and all nitrogen and oxygen atoms in ptc coordinate with metal ions. Four carboxylate groups from different ptc ligands linked four Pr(III) centers as subunits, which are further assembled into a 3D open network (Figure 1c). The open channels possess approximate dimensionalities of 10.3 Å × 6.8 Å along the crystallographic *a* axis, and guest water molecules occupy the channels. The connection between carboxylate groups and Pr centers can be represented as a (4,6) net.

While Ni(II) salts were added in the reaction system of **1**, Na(I) ions and $(CH_2OH)_2$ involved in the self-assembly process and an unexpected heterotrimetallic complex **2** was isolated. **2** is a quite unique 3D structure constructed from three kinds of metal ions and three kinds of bridged ligands. As shown in Figure 2, each Pr atom shows a 10-coordinated environment. Two ptc's act as tridentate ligands (ONO) chelated to the Pr center, and two ClO_4^- anions as bidentate

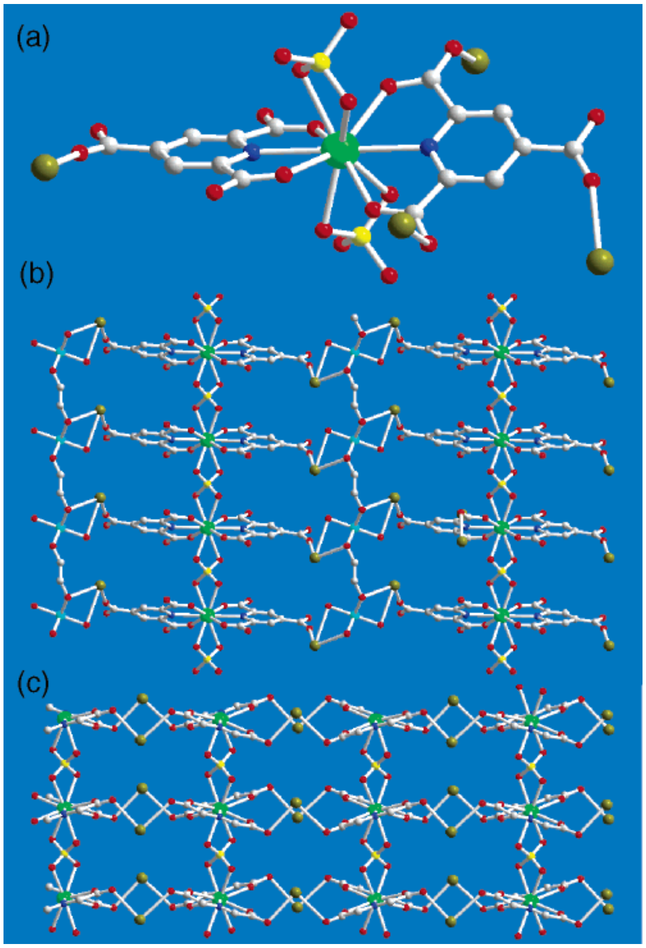

Figure 2. The coordination environment of Pr(III) and ptc (a) and the 2D coordination layers along the *c* direction (b) and *a* direction (c) in the 3D network of **2**. Green, Pr; red, O; gray, C; blue, N; yellow, Cl; cyan, Ni; brown, Na.

ligands (OClO) occupy four coordination sites. The dihedral angle between pyridine rings of ptc connected to the Pr center is 35.2°, with a deviation from the coplanar case. Actually, from the stereochemical effect point of view, without coordination of ClO_4^- anions, the closer the dihedral angle is to 90°, the more stable the configuration of **2**. The ClO_4^- anions chelated to the Pr center from both the upper and lower directions result in the formation of a kind of $[Pr(ClO_4)]_n$ chains, while $(CH_2OH)_2$ molecules and Ni(II) ions construct another 1D $[Ni(CH_2OH)_2]_n$ chain in the same direction. The two kinds of parallel chains alternately array and are linked by Na(I) ions with 4-carboxylate groups of ptc to construct an unusual 2D grid along the *c* direction (Figure 2b). Na(I) ions also coordinate with 2,6-carboxylate groups of ptc to link the $[Pr(ClO_4)]_n$ chains to form a 2D layer along the *a* direction (Figure 2c). Therefore, a 3D MOF is formed and the connection between Pr and Ni centers can be represented as a (4,6) net (Figure 3).

Four coordination modes of ptc have been found (Scheme 1). The full coordination mode A and six-coordinated mode B exist for f and s metal centers, while the coordinated modes C and D with relatively lower coordinated numbers are found for d metal centers (mode C for Co(II),[6b] Fe(II);[6b] mode D for Cu(II),[6b] Zn(II)[6a]). The ptc ligand coordinated with large

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[9] Zhao, B.; Yi, L.; Dai, Y.; Chen, X.-Y.; Cheng, P.; Liao, D.-Z.; Yan, S.-P.; Jiang, Z.-H. *Inorg. Chem.* **2005**, *44*, 911.

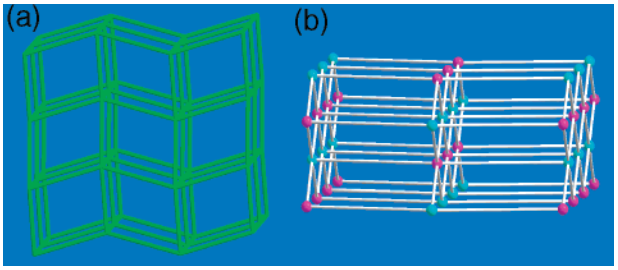
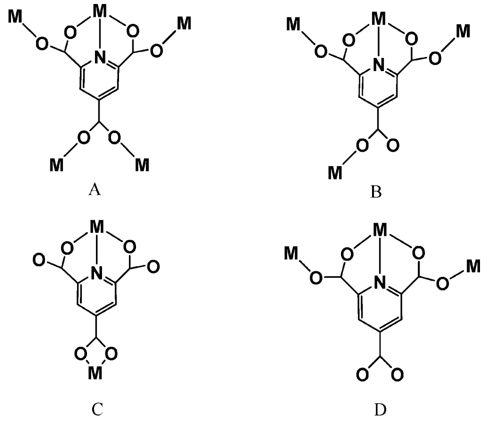


Figure 3. Schemic draw representing two (4,6) nets of Pr atoms linked by carboxylic groups in **1** (a) and the connection between Pr and Ni atoms in **2** (b). Purple, Pr; cyan, Ni.

Scheme 1. Coordination Mode for ptc



radius f and s metal ions gives higher coordination numbers. What is more, the higher the coordination numbers is, the higher is the structural dimensionality of the complex (C, 1D; D, 2D; A, 3D).

Thermogravimetric analysis (TGA) of the polycrystalline samples of **1** and **2** were performed in the temperature range 25−600 °C. From 100 to 315 °C, 14.87% of the weight of **1** was lost due to uncoordinated and coordinated water molecules (calcd 15.29%). Compounds **1** gradually decompose above this temperature. TGA of **2** shows four regions of weight loss. The first, a mass loss of 23.57% from room temperature to 270 °C, corresponds to the loss of 8 coordinated and 4.5 uncoordinated water molecules (calcd 21.14%). Then, the weight losses from 326 to 420 °C and from 420 to 470 °C correspond to the loss of a ClO_4^- and a $(CH_2OH)_2$, respectively. Above this temperature, ptc ligands begin to decompose. Phase purity of the bulk materials of **1** and **2** was confirmed by comparison of its powder diffraction pattern with that calculated from the single-crystal study.

Informative magnetic susceptibility measurements of **1** and **2** have been performed on a Quantum Design MPMS-5S superconducting quantum interference device (SQUID) magnetometer in the 2−300 K temperature range. The diamagnetic correction was evaluated by using Pascal's constants. The $\chi_M T$ values are equal to 1.61 cm^3 K mol^{-1} at room temperature, which are slightly lower than those expected, 1.60 cm^3 K mol^{-1} per insulated Pr ion in the $^3H_4$ ground state ($g = 4/5$). Although the $\chi_M T$ values for **1** smoothly decrease with decreasing temperature, antiferromagnetic coupling between adjacent Pr ions could not be explicitly deduced due to the existence of strong spin−orbit coupling for lanthanide atoms. The decrease in $\chi_M T$ possibly originates in the thermal depopulation of the highest Stark components deriving from the splitting of the free-ion ground state, $^3H_4$, by the crystal field.[9] Accordingly, any weak exchange interaction within the structure is masked by the crystal field.

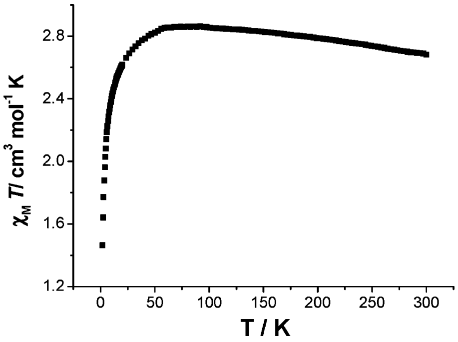


Figure 4. Thermal dependence of the $\chi_M T$ (■) curves for 2.

As shown in Figure 4, the observed $\chi_M T$ value for **2** at 300 K is 2.68 cm^3 mol^{-1} K, slightly higher than the calculated value of 2.60 cm^3 mol^{-1} K for the uncorrelated magnetic moments of one Pr(III) and one Ni(II) ion. Upon cooling, the $\chi_M T$ of **2** increases continuously from 300 to 60 K to reach a maximum of 2.86 cm^3 mol^{-1} K and then decreases rapidly to reach 1.46 cm^3 mol^{-1} K at 2 K. The decrease of $\chi_M T$ from 60 to 2 K might be due to zero-field splitting of Ni(II) ions and the existence of strong spin−orbit coupling for Pr(III) ions.

In summary, we have isolated two novel 3D MOFs based on H_3ptc under hydrothermal conditions. **1** is a 3D open network containing five multicarboxylate ptc ligands coordinating with one metal center and carboxyl groups linking metal centers to form a (4,6) net. **2** is the first Pr/Ni/Na heterotrimetallic complex, a 3D framework containing three different bridged ligands. The ptc exhibits a full coordination mode in **1** and a six-coordinated mode in **2**, which implies that it has a greatly potential possibility to design novel MOFs and heteromultimetallic complexes in coordination chemistry.

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Supporting Information Available: X-ray crystallographic files in CIF format for **1**−**3**; and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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