An Unusual Linear Trinuclear Ni^{II}-based MOF with an Unprecedented μ_4 - κ^2 N1,N5: κ^1 N2: κ^1 N6 Binding Mode by 5-(Pyrazinyl)tetrazolate Ligand

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Abstract. A photofluorescent linear trinuclear Ni^{II}-based three-dimensional (3D) metal-organic framework (MOF) with tfz-d topology, $\{[Ni_3(H_2O)_4(ptz)_2(btec)]\cdot 4H_2O\}_n$ (1) (ptz⁻ = 5-(pyrazinyl)tetrazolate, btec⁴⁻ = 1,2,4,5-benzenetetracarboxylate), was achieved by in situ hydrothermal reaction of 2-cyanopyrazine with NaN₃ in the presence of

Introduction

Since *Xiong* and co-workers borrowed Sharpless' idea [1] and prepared a series of tetrazole-based coordination polymers by in situ tetrazole synthesis from various nitriles and azides [2, 3], the design and construction of metal-organic frameworks (MOFs) with tetrazolyl ligands are of great interest because of the effectiveness, simplicity, and environmental friendliness of the in situ synthetic route as well as the potential applications of crystalline MOFs in gas storage [4], second order nonlinear optics [5], luminescence [5–7], and magnetism [7-8]. To date, lots of functional MOFs with pyridyl- [2], phenyl- [9], pyrazinyl- [10-12], pyrimidyl- [6b], aliphatic- [3], ditetrazolate ligands [13–15], as well as Zn^{II} [5], Cd^{II} [5, 10], Cu^{I/II} [10, 11, 16], Mn^{II} [17], Ag^I [9, 16], Co^{II} [11], Ni^{II} [18], Fe^{II} [19], and $Pt^{I\bar{I}}$ [20] ions, have been successfully generated by in situ reactions with special interest on the tuning of the organic nitrile and Lewis acid combinations. However, to the best of our knowledge, little investigation has been performed on the roles of the functional secondary ligands in the in situ reaction by far. It is well known that the co-coordination of the auxiliary ligands can significantly dominate the overall architectures and functions of the target MOFs. Therefore, to explore the intrinsic co-coordination of the aromatic polycarboxylate co-ligand on the resulting MOF herein, the in situ hydrothermal reaction of 2-cyanopyrazine with sodium azide in the presence of Ni²⁺ as Lewis acid and 1,2,4,5-benzenetetracarboxylic acid (H₄btec) as auxiliary ligand was performed.

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 Ni^{2+} as Lewis acid and aromatic H₄btec as coligand. Interestingly, the ptz⁻ ligand in **1** represents an unprecedented tetradentate $\mu_{4-}\kappa^2N1,N5:\kappa^1N2:\kappa^1N6$ chelating-bridging mode and contributes to the extension of the 1D ribbons into a 3D framework.

Unexpectedly, the first Ni^{II}-ptz⁻-based three-dimensional (3D) MOF with an unusual linear trinuclear motif, $\{[Ni_3(H_2O)_4(ptz)_2(btec)]\cdot 4H_2O\}_n$ (1) (ptz⁻ = 5-(pyrazinyl)tetrazolate), was successfully isolated, which exhibits a (3,8)-connected tfz-d topological structure and strong fluorescent emission. More importantly, the ptz⁻ ligand in 1 presents an unprecedented tetradentate μ_4 - κ^2 N1,N5: κ^1 N2: κ^1 N6 chelating-bridging mode, which essentially contributes to the extension of the high-dimensional framework of 1.

Experimental Section

Reagents and Instruments

2-Cyanopyrazine was purchased from TCI and other analytical-grade starting materials were obtained commercially and used as received without further purification. Doubly deionized water was employed for the conventional synthesis. The IR spectrum was performed in the range 4000–400 cm⁻¹ with a Nicolet IR-200 spectrometer as KBr pellets. Elemental analyses for C, H and N were determined with a Perkin–Elmer 2400C elemental analyzer. The TG-DTA measurement was carried out with a Shimadzu simultaneous DTG-60A thermal analysis instrument with a heating rate of 8 °C·min⁻¹ from room temperature to 800 °C under nitrogen (flow rate 10 mL·min⁻¹). Fluorescence spectra of the polycrystalline samples were performed with a Cary Eclipse fluorescence spectrophotometer (Varian) equipped with a xenon lamp and quartz carrier at room temperature.

Synthesis

{[Ni₃(H₂O)₄(ptz)₂(btec)]·4H₂O}_n (1): NiCl₂·6H₂O (47.5 mg, 0.2 mmol), H₄btec (25.4 mg, 0.1 mmol), 2-cyanopyrazine (10.5 mg, 0.1 mmol), and NaN₃ (13.0 mg, 0.2 mmol) were dissolved in water (10 mL) and stirred for 10 minutes. Afterwards, the resulting mixture was transferred into a parr Teflon-lined stainless steel vessel (23 mL) and heated to 160 °C for 96 h under autogenous pressure. Green block-shaped crystals suitable for X-ray analysis were obtained directly, washed with ethanol, and dried in air. Yield: 56 % based on 2-cyanopyrazine. C₁₀H₁₂N₆Ni_{1.5}O₈ (%): C, 27.78; H, 2.80; N, 19.44. Found (%):



C, 27.64 H, 2.62; N, 19.65. IR (KBr): $\tilde{\nu} = 3431$ br, 3104 m, 1595 s, 1567 vs, 1486 m, 1418 s, 1373 vs, 1320 w, 1279 w, 1172 m, 1150 m, 1075 w, 1049 m, 939 w, 872 m, 809 m, 769 m, 581 ms, 545 ms, 441 ms cm⁻¹.

X-ray Crystallography

Diffraction intensity for 1 was collected on a computer controlled Bruker APEX-II CCD diffractometer equipped with graphite-monochromated Mo- K_a radiation with radiation wavelength 0.71073 Å by using ω - φ scan technique. The program SAINT [21] was used for integration of the diffraction profiles. Semi-empirical absorption corrections were applied using SADABS [22] program. The structure was solved by direct methods and refined with the full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs [23]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically. The starting positions of hydrogen attached to oxygen atom were located in difference Fourier syntheses and then fixed geometrically as riding atoms. One lattice water molecule (O8) was found disordered over three positions and refined with the sum of the occupation factors restrained to one (0.20, 0.30 and 0.50 for O(8), O(8'), and O(8") respectively). The crystallographic data and experimental details for structural analyses are summarized in Table 1. Selected bond lengths and angles for 1 are listed in Table 2. CCDC-717632 contains the supplementary crystallographic data for 1. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: +44-1223-336033; or E-Mail: deposit@ccdc.cam.ac.uk).

Table 1.	Crystal	data	and	structure	refinement	for	1
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Empirical formula	C ₁₀ H ₁₂ Ni _{1.50} N ₆ O ₈
Formula weight	432.32
Crystal size /mm	$0.14 \times 0.13 \times 0.12$
Temperature /K	296(2)
Crystal system	triclinic
Space group	$P\overline{1}$
μ / mm^{-1}	1.859
$D_c / \text{g} \cdot \text{cm}^{-3}$	1.815
a /Å	8.1933(3)
b /Å	8.8646(3)
c /Å	12.2028(5)
α /°	110.0570(10)
$\beta/^{\circ}$	92.8970(10)
γ /°	105.7410(10)
$V/Å^3$	791.15(5)
Z	2
θ /deg	1.80 to 25.01
h/k/l	-9, 8 / -10, 10 / -14, 13
F(000)	440
Reflections collected / unique	4099 / 2789
R _{int}	0.0109
Completeness to $\theta = 25.01$	99.6 %
Data/restraints/parameters	2789 / 0 / 239
$R_1, wR_2[I > 2\sigma (I)]^{a}$	0.0296 / 0.0790
R_1, wR_2 (all data) ^{a)}	0.0331 / 0.0815
Max. and min. transmission	0.8077 / 0.7808
GOF on F^2	1.048
$\Delta ho_{\rm max}, \Delta ho_{\rm min}$ /e·Å ⁻³	0.613 and -0.661

a) $R_1 = \Sigma(||F_0| - |F_C||) / \Sigma |F_0|; \ w R_2 = [\Sigma w(|F_0|^2 - |F_C|^2)^2 / \Sigma w(F_0^2)]^{1/2}.$

Table 2. Selected bond	lengths /Å	and angles /°	for 1 ^{a)} .
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Ni(1)-O(3)	2.0161(18)	Ni(1)–N(6)	2.145(2)		
Ni(1)–O(2)	2.0318(19)	$Ni(2) - N(2)^{\#2}$	2.064(2)		
Ni(2)–O(6)	2.059(2)	$Ni(2)-N(1)^{\#3}$	2.087(2)		
Ni(2)–O(1)	2.0448(19)	$Ni(2) - N(5)^{\#3}$	2.135(2)		
Ni(2)–O(5)	2.054(2)				
$O(3)-Ni(1)-O(3)^{\#1}$	180.0	$O(5)-Ni(2)-N(2)^{\#2}$	89.93(10)		
$O(2)-Ni(1)-O(2)^{\#1}$	180.0	$O(6)-Ni(2)-N(2)^{\#2}$	90.33(10)		
$O(3)^{\#1}$ -Ni(1)-O(2) ^{#1}	92.20(8)	$O(1)-Ni(2)-N(1)^{\#3}$	172.17(9)		
$O(3)-Ni(1)-N(6)^{\#1}$	92.14(8)	$O(5)-Ni(2)-N(1)^{\#3}$	86.46(9)		
O(3)–Ni(1)–N(6)	87.86(8)	$O(6)-Ni(2)-N(1)^{\#3}$	89.28(9)		
O(2)-Ni(1)-N(6)	88.83(8)	$N(2)^{#2}-Ni(2)-N(1)^{#3}$	95.48(9)		
$O(2)-Ni(1)-N(6)^{\#1}$	91.17(8)	$O(1)-Ni(2)-N(5)^{\#3}$	95.02(8)		
$N(6)^{\#1} - Ni(1) - N(6)$	180.0	$O(5)-Ni(2)-N(5)^{\#3}$	87.39(10)		
$O(3)-Ni(1)-O(2)^{\#1}$	87.80(8)	$O(6)-Ni(2)-N(5)^{\#3}$	91.91(10)		
O(1)–Ni(2)–O(6)	86.48(9)	$N(2)^{#2} - Ni(2) - N(5)^{#3}$	173.58(9)		
O(5)–Ni(2)–O(6)	175.73(9)	$N(1)^{#3} - Ni(2) - N(5)^{#3}$	78.53(9)		
$O(1)-Ni(2)-N(2)^{#2}$	91.13(8)	O(1)-Ni(2)-O(5)	97.77(8)		
a) Symmetry Codes: $\#1 - x + 1, -y + 1, -z + 1; \#2 x, y + 1, z + 1;$					

#3 - x + 2, -y + 1, -z + 1.

Supporting Information (see footnote on the first page of this article): Local coordination environments of Ni^{II} atoms and X-ray powder diffraction patterns for **1**.

Results and Discussion

Synthesis and FT-IR Spectra

In situ [2+3] cycloaddition reaction of 2-cyanopyrazine and NaN₃ with a molar ratio of 1:2 in the presence of NiCl₂·6H₂O as Lewis acid catalyst and H4btec as coligand under hydrothermal conditions directly gave green block-shaped crystals, $\{[Ni_3(H_2O)_4(ptz)_2(btec)]\cdot 4H_2O\}_n$ (1). In the IR spectrum of 1, the strong and broad adsorption band at ca. 3431 cm⁻¹ represents the characteristic vibration of hydroxyl group, which confirms the existence of lattice water molecules. The absence of the band for stretching vibrations of the cvano group at 2200 cm^{-1} and the appearance of bands at 1567 and 1486 cm⁻¹ for the stretching vibrations of a tetrazole group [9, 20] suggest the formation of the ptz⁻ ligand. The absence of the band at ca. 1700 cm⁻¹ suggests the deprotonation of H₄btec in **1**. In addition, the differences ($\Delta \tilde{v}$) in $\tilde{v}(COO^{-})$ and $\tilde{v}(COO^{-})$ in 1 $(81 \text{ and } 177 \text{ cm}^{-1})$ indicate that the carboxylate groups adopt the chelating bidentate and monodentate coordination mode [24], which are also in agreement with the single-crystal X-ray diffraction data.

Structural Description of 1

Single crystal X-ray diffraction analysis reveals that $\{[Ni_3(H_2O)_4(ptz)_2(btc)]\cdot 4H_2O\}_n$ (1) crystallizes in the triclinic space group $P\overline{1}$, displaying a robust 3D MOF with unusual linear trinuclear $[Ni_3(H_2O)_4(btc)]^{2+}$ cation as a core subunit and a pair of ptz⁻ anions as linkers. As shown in Figure 1, the core subunit of 1 consists of three Ni^{II} atoms with Ni1 located at the crystallographic symmetry center, one fully deprotonated btec⁴⁻ anion at another inversion center, and two pairs of coor-



dinated water molecules. Both crystallographically independent Ni^{II} atoms reside in distorted octahedrons, in which Ni1 is surrounded by four carboxylate oxygen atoms from two different btec^{4–} ligands, which occupy an equatorial plane and two pyrazinyl nitrogen atoms from two separate ptz[–] anions located at the axial positions. Instead, Ni2 is coordinated by three nitrogen atoms from two ptz[–] ligands (one tetrazolyl N2 atom from one ptz[–] molecule and chelated pyrazinyl N5 and tetrazolyl N1 donors from the other ptz[–] molecule), one carboxylate oxygen donor of the btec^{4–} anion and two coordinated water molecules, respectively (see Supporting Information Figure S1). The Ni–O bond lengths [2.0161(18) – 2.059(2) Å] are generally shorter than those of Ni–N [2.064(2) – 2.145(2) Å, see Table 2], although they are similar to previously reported values [18, 25].



Figure 1. The trinuclear Ni^{II} unit of **1** (the centrosymmetric btec^{4–} ligands are shaded differently, and hydrogen atoms are omitted for clarity; Symmetric codes: A = 1-x, 1-y, 1-z; B = 1-x, 2-y, 1-z).

Ni2A is related to Ni2 by the symmetry-generated code (A: 1-x, 1-y, 1-z). Ni1, Ni2, and Ni2A are doubly held together by two carboxylate groups of the btec⁴⁻ anions in bidentate

bridging and monodentate modes to generate a linear trinuclear $[Ni_3(H_2O)_4(btec)]^{2+}$ subunit with coordinated water molecules as terminal ligands (Figure 1). The Ni···Ni separation within the trinuclear subunit is 5.0464(1) Å, and the bond angle of Ni2–Ni1–Ni2A is 180 °. Previously, some analogous trinuclear motifs constructed from metal ions and carboxylate groups of aromatic ring, M₃(COO)_n, have also been observed (M = Zn^{II}, Cd^{II}, Co^{II}, La^{III} [13, 26, 27], Mn^{II} [28], Mg^{II} [29], Zn^{II}/Co^{II}, Zn^{II}/Ni^{II} and Zn^{II}/Cd^{II} [30]), although the source of the carboxylate groups is different from each other. Herein, the first Ni₃(COO)₄ subunit was obtained by introducing the btec^{4–} anion in the in situ reactions, suggesting that M₃(COO)_n can be considered as a fundamental subunit upon the controlled construction of the MOFs with variable dimensions.

Owing to the presence of centrosymmetric btec⁴⁻ anions, the trinuclear subunits are infinitely extended to generate a 1D ribbon along the crystallographic *b* direction (Figure 2). A pair of head-to-tail arranged ptz⁻ ligands doubly link the paralleled ribbons in a tridentate μ_3 - κ^2 N1,N5: κ^1 N2 chelating-bridging



Figure 2. 2D layer structure of 1.



Figure 3. (a) 3D framework of 1. (b) The (3,8)-connected tfz-d network of 1 ($[Ni_3(H_2O)_4(COO)_4]^{2+}$ and ptz^- nods are shown in light grey and white balls, respectively).



Figure 4. Coordination modes of 5-(pyrazinyl)tetrazolate ligand.

mode, which leads to the formation of a 2D layer (Figure 2). These layers are then covalently stacked together by the coordination bonds of the pyrazinyl N6 of ptz⁻ and Ni1 to produce a robust 3D MOF (Figure 3a). Thus, the ptz⁻ anion in 1 adopts a tetradentate $\mu_4 - \kappa^2 N1, N5: \kappa^1 N2: \kappa^1 N6$ chelating-bridging mode, which significantly contributes to the extension of the 1D ribbons to 3D MOF. More interestingly, the tetradentate binding mode presented by the ptz⁻ ion is unprecedented, although six different kinds of coordination modes (μ_2 - κ^2 N1,N5, $\mu_2 - \kappa^1 \text{N1} : \kappa^1 \text{N3},$ $\mu_3 - \kappa^2 N1, N5: \kappa^1 N2,$ $\mu_3 - \kappa^2 N1, N5: \kappa^1 N6,$ $\mu_4 - \kappa^2 N1, N5: \kappa^1 N3: \kappa^1 N6$ and $\mu_4 - \kappa^1 N1: \kappa^1 N2: \kappa^1 N3: \kappa^1 N6$, see Figure 4) were observed in previous reports [10-12, 31]. If the $[Ni_3(H_2O)_4(COO)_4]^{2+}$ and ptz⁻ ions are considered as two topologically different nodes, 1 can be simplified as a (3,8)connected net with the $(4^3)_2(4^6 \cdot 6^{18} \cdot 8^4)$ topology symbol. And the topological structure is in agreement with the tfz-d net [27]. On the other hand, the (3,8)-connected framework is microporous with 200 $Å^3$ cavity volume when removing the lattice and coordinated water molecules [32]. The resulting solvent-accessible cavities were estimated to be 25.3 % of the unit cell volume.

Thermal Stability and Luminescent Properties

Although the 3D framework of 1 can be considered as trinuclear [Ni₃(H₂O)₄(btec)]²⁺ cations linked by ptz⁻ anions, the thermogravimetric measurements (see Figure 5) indicate that there are no direct connections between the two subunits $([Ni_3(H_2O)_4(btec)]^{2+}$ cation and ptz⁻ anion). Compound 1 loses its lattice and coordinated water molecules from room temperature to 258 °C (expt. 16.0 %, calcd. 17.5 %), accompanying an obviously endothermic effect. And the mixed organic ligands, ptz⁻ and btec⁴⁻ anions, are removed between 367 °C and 463 °C, accompanying the collapse of the 3D framework of 1. The final residue is calculated to be NiO (expt. 27.1 %, calcd. 25.9 %). To investigate the stability of the framework, compound 1 was heated at 270 °C for four hours and afterwards the powder X-ray diffraction experiments were carried out (see Supporting Information Figure S2). The results indicate that the framework of complex 1 does not collapse after the loss of the water molecules. At room temperature, solid 1 exhibits a

considerably intense luminescence emission at 421 nm upon excitation at 370 nm (see Figure 6), which is similar to the intraligand charge transfer of the ptz^{-} ligand [10, 31c].



Figure 5. TG-DTA curves for 1.



Figure 6. Solid excitation/emission spectra of 1 at room temperature.

Conclusions

In conclusion, the first mixed-ligand 3D MOF with unusual linear trinuclear Ni^{II} as core subunit, {[Ni₃(H₂O)₄-



 $(\text{ptz})_2(\text{btec})]\cdot 4H_2O\}_n$, was successfully obtained by introducing H₄btec as co-ligands into the traditionally hydrothermal in situ synthesis of tetrazolyl ligands. Unexpectedly, the ptz⁻ ligand in 1 adopts an unique μ_4 - κ^2 N1,N5: κ^1 N2: κ^1 N6 binding mode and significantly contributes to the 3D periodic extension of the high-dimensional framework.

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