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1D slide-fastener-like coordination polymers of Mn(II) derived from pyrazine-2,3,5,6-tetracarboxylic acid

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ABSTRACT

Two new 1D slide-fastener-like coordination polymers $\{[Mn_2(pztc)(phen)_2(H_2O)_2]\cdot 4H_2O\}_n$ (**1**) and $\{[Mn_2(pztc)(bpy)_2(H_2O)_2]\cdot 2H_2O\}_n$ (**2**) have been synthesized by the reactions of pyrazine-2,3,5,6-tetracarboxylic acid ($pztcH_4$) and $Mn(OAc)_2\cdot 4H_2O$ in the presence of 1,10-phenanthroline (phen) or 2,2′-bipyridine (bpy) under hydrothermal conditions and characterized by elemental analyses, FT-IR, TGA and X-ray diffraction. In complex **1** and **2**, metal ions are bridged by pyrazine-2,3,5,6-tetracarboxylate, coordinating in a hexadentate manner, so forming 1D polymeric chains. The remaining coordination sites of the metal ions are occupied by one O atom of water molecule and two N atoms of the terminal ligand (phen or bpy). IR spectra and thermal analysis data are in agreement with the crystal structure.

1. Introduction

Metal–organic frameworks (MOFs) have attracted great interest in recent years because of their potential applications in magnetism, electrical conductivity, catalysis, separation, gas storage, ion exchange, and nonlinear optical materials [1–3]. The connection of metal–organic coordination polymers based on transition metals and multifunctional bridging ligands has proven to be a promising field. Polycarboxylic acid and their transition metal complexes have been extensively investigated on coordination and/or covalent crystal engineering [4,5]. The structures and the optical or magnetic properties of metal–organic compounds with pyrazinyl-carboxylic acids have proven to be of great interest in many fields, such as solid chemistry and material chemistry. Pyrazine-2,3,5,6-tetracarboxylic acid ($pztcH_4$), a preferred multifunctional nitrogen and oxygen-donor connector with diverse chelating and bridging mode for constructing coordination complex, has been utilized to generate MOFs. There are a few researches of complexes with pyrazine-2,3,5,6-tetracarboxylic acid have achieved in the last years [6–8]. However, its coordination chemistry remains largely unexplored compared with those of benzene polycarboxylate ligands. To the best of our knowledge, there is no report about 1D coordination polymers containing pyrazine-2,3,5,6-tetracaboxylic acid and 1,10-phenanthroline or 2,2′-bipyridine as ligands. In this contribution, pyrazine-2,3,5,6-tetracarboxylic acid ($pztcH_4$) and 1,10-phenanthroline (phen) or 2,2′-bipyridine (bpy) were employed to synthesize two novel 1D complexes, namely $\{[Mn_2(pztc)(phen)_2(H_2O)_2]\cdot 4H_2O\}_n$ (**1**) and $\{[Mn_2(pztc)(bpy)_2(H_2O)_2]\cdot 2H_2O\}_n$ (**2**).

2. Experimental

2.1. General

All reagents were purchased commercially and used without further purification. Deionized water was used for the conventional synthesis. Elemental analyses of carbon, hydrogen and nitrogen were carried out with a Perkin-Elmer 240 analyzer. The infrared spectra of the complexes in KBr pellets were obtained on a BIO-RAD FTS 3000 instrument in the range of 4000–400 cm^{-1}. Thermal analysis curves (TG) were obtained from a NETZSCH TG 209 thermal analyzer in a static air atmosphere using a sample size of 5–10 mg with a heating rate of 10 °C min^{-1}.

2.2. Syntheses of pyrazine-2,3,5,6-tetracarboxylic acid ($pztcH_4$) and the complexes

Pyrazine-2,3,5,6-tetracarboxylic acid was synthesized in 59% yield by oxidation of 2,3,5,6-tetramethylpyrazine by aqueous $KMnO_4$.

The mixtures of $pztcH_4$ (0.1 mmol, 0.0260 g), $Mn(OAc)_2\cdot 4H_2O$ (0.2 mmol, 0.0492 g), 1,10-phenanthroline (phen) (0.2 mmol, 0.0360 g) and 15.0 mL water were sealed in a 25 mL stainless steel reactor with teflon liner and heated to 150 °C and kept at this temperature for 72 h, and then slowly cooled to 30 °C at a rate of 1.4 °C/h. The yellow crystals of **1** suitable for X-ray analysis were obtained in 43% yield (based on $pztcH_4$).

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Table 1
Crystal data and structure refinement for compounds **1 – 2**

Compound	$C_{32}H_{28}Mn_2N_6O_{14}$ **1**	$C_{28}H_{24}Mn_2N_6O_{12}$ **2**
Formula weight (g mol^{-1})	830.48	746.41
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2(1)/c$
a (Å)	7.763(3)	9.2560(15)
b (Å)	8.931(3)	20.212(3)
c (Å)	12.717(4)	7.8527(13)
α (°)	67.952(7)	90
β (°)	82.638(14)	100.834(3)
γ (°)	84.101(13)	90
V (Å^3)	809.1(5)	1442.9(4)
Z	1	2
Calculated density (g cm^{-3})	1.704	1.718
Absorption coefficient (mm^{-1})	0.865	0.954
$F(000)$	424	760
Crystal size (mm^3)	0.12 × 0.10 × 0.06	0.22 × 0.20 × 0.12
θ range for data collection (°)	1.74–27.85	2.02–26.42
Index ranges	$-9 \leqslant h \leqslant 10$	$-11 \leqslant h \leqslant 11$
	$-11 \leqslant k \leqslant 11$	$-25 \leqslant k \leqslant 11$
	$-16 \leqslant l \leqslant 16$	$-9 \leqslant l \leqslant 9$
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Independent reflections	3752 [R(int) = 0.0258]	2959 [R(int) = 0 .0341]
Goodness-of-fit on F^2	1.091	1.061
Final R_1 and wR_2 [$I > 2\sigma(I)$]	0.0301, 0.0714	0.0333, 0.0811
R_1 and wR_2 [all data]	0.0400, 0.0754	0.0489, 0.0875
Largest diff. Peak and hole (e Å^{-3})	0.364 and −0.262	0.370 and −0.361

Table 2
Selected bond lengths [Å] and angles [°] for **1–2**

1		**2**	
Mn(1)–O(1)	2.1129(13)	Mn(1)–O(3)#1	2.1261(10)
Mn(1)–O(5)	2.1313(15)	Mn(1)–O(1)	2.1697(11)
Mn(1)–O(3)#1	2.1539(13)	Mn(1)–O(5)	2.1996(13)
Mn(1)–N(2)	2.2423(15)	Mn(1)–N(2)	2.2262(14)
Mn(1)–N(3)	2.2668(15)	Mn(1)–N(3)	2.2811(14)
Mn(1)–N(1)#1	2.3709(14)	Mn(1)–N(1)	2.3316(13)
N(1)–Mn(1)#1	2.3709(14)	O(3)–Mn(1)#1	2.1261(10)
O(3)–Mn(1)#1	2.1539(13)		
O(1)–Mn(1)–O(5)	86.11(6)	O(3)#1–Mn(1)–O(1)	169.89(4)
O(1)–Mn(1)–O(3)#1	164.36(4)	O(3)#1–Mn(1)–O(5)	86.93(4)
O(5)–Mn(1)–O(3)#1	82.28(6)	O(1)–Mn(1)–O(5)	83.04(4)
O(1)–Mn(1)–N(2)	102.86(5)	O(3)#1–Mn(1)–N(2)	95.95(5)
O(5)–Mn(1)–N(2)	98.31(7)	O(1)–Mn(1)–N(2)	87.85(5)
O(3)#1–Mn(1)–N(2)	89.20(5)	O(5)–Mn(1)–N(2)	104.87(5)
O(1)–Mn(1)–N(3)	100.83(5)	O(3)#1–Mn(1)–N(3)	98.76(4)
O(5)–Mn(1)–N(3)	170.38(6)	O(1)–Mn(1)–N(3)	91.31(4)
O(3)#1–Mn(1)–N(3)	92.01(5)	O(5)–Mn(1)–N(3)	174.00(4)
N(2)–Mn(1)–N(3)	73.77(6)	N(2)–Mn(1)–N(3)	72.79(5)
O(1)–Mn(1)–N(1)#1	98.12(5)	O(3)#1–Mn(1)–N(1)	105.10(4)
O(5)–Mn(1)–N(1)#1	97.03(7)	O(1)–Mn(1)–N(1)	73.37(4)
O(3)#1–Mn(1)–N(1)#1	73.09(5)	O(5)–Mn(1)–N(1)	87.81(5)
N(2)–Mn(1)–N(1)#1	154.72(5)	N(2)–Mn(1)–N(1)	156.04(5)
N(3)–Mn(1)–N(1)#1	88.64(5)	N(3)–Mn(1)–N(1)	92.50(5)

Symmetry transformations used to generate equivalent atoms for compound **1**: # 1x, y, z + 1; for **2**: #1 −x, −y + 1, −z.

Compound **2** was prepared by similar methods to **1** only using the 2,2′-bipyridine (bpy) instead of 1,10-phenanthroline (phen) at 160°C. The well blocked-shaped yellow crystals of **2** suitable for X-ray analysis were obtained in 45% yield (based on pztcH$_4$).

Anal. Found: C, 46.22; H, 3.43; N, 10.17% for **1** and C, 45.11; H, 3.27; N, 11.23% for **2**. Calc. for $C_{32}H_{28}Mn_2N_6O_{14}$ (**1**): C, 46.28; H, 3.40; N, 10.12%; $C_{28}H_{24}Zn_2N_6O_{12}$ (**2**): C, 45.06; H, 3.24; N, 11.26%.

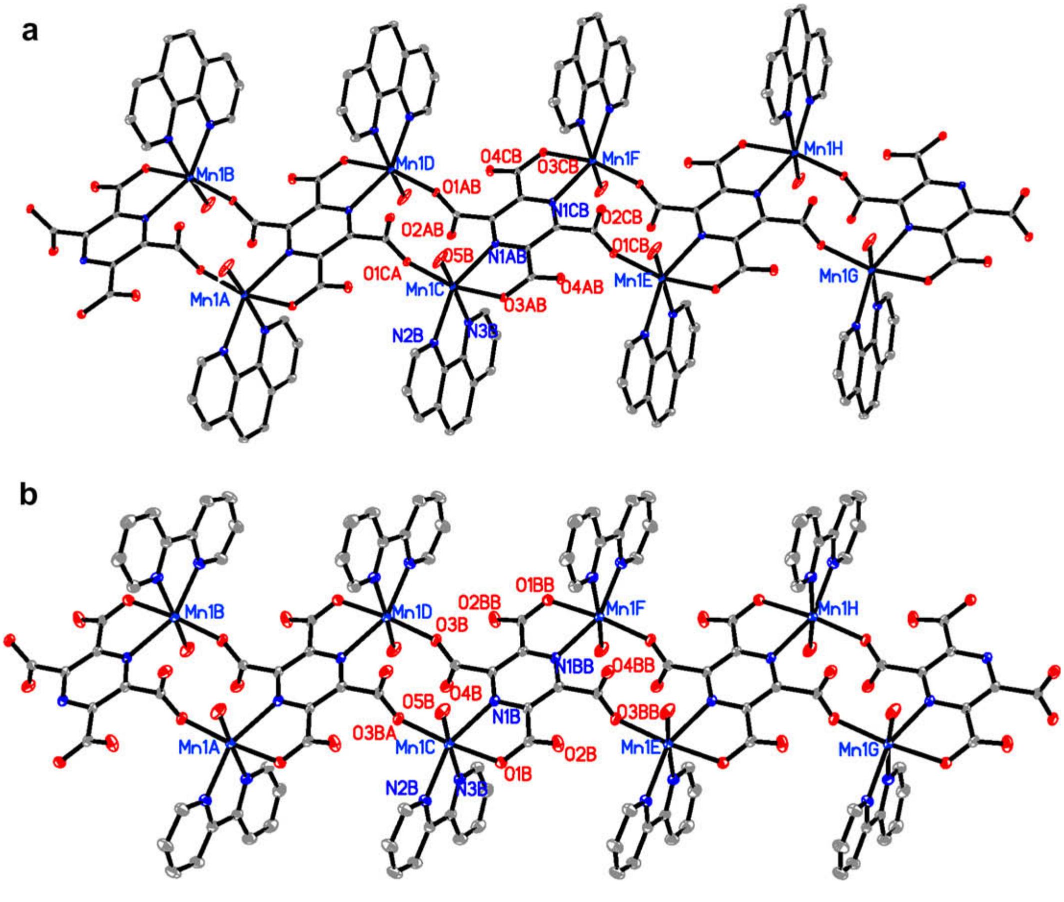

Fig. 1. The 1D slide-fastener-like chain of complex **1**(a) and **2**(b), H atoms and uncoordinated water molecules are omitted.

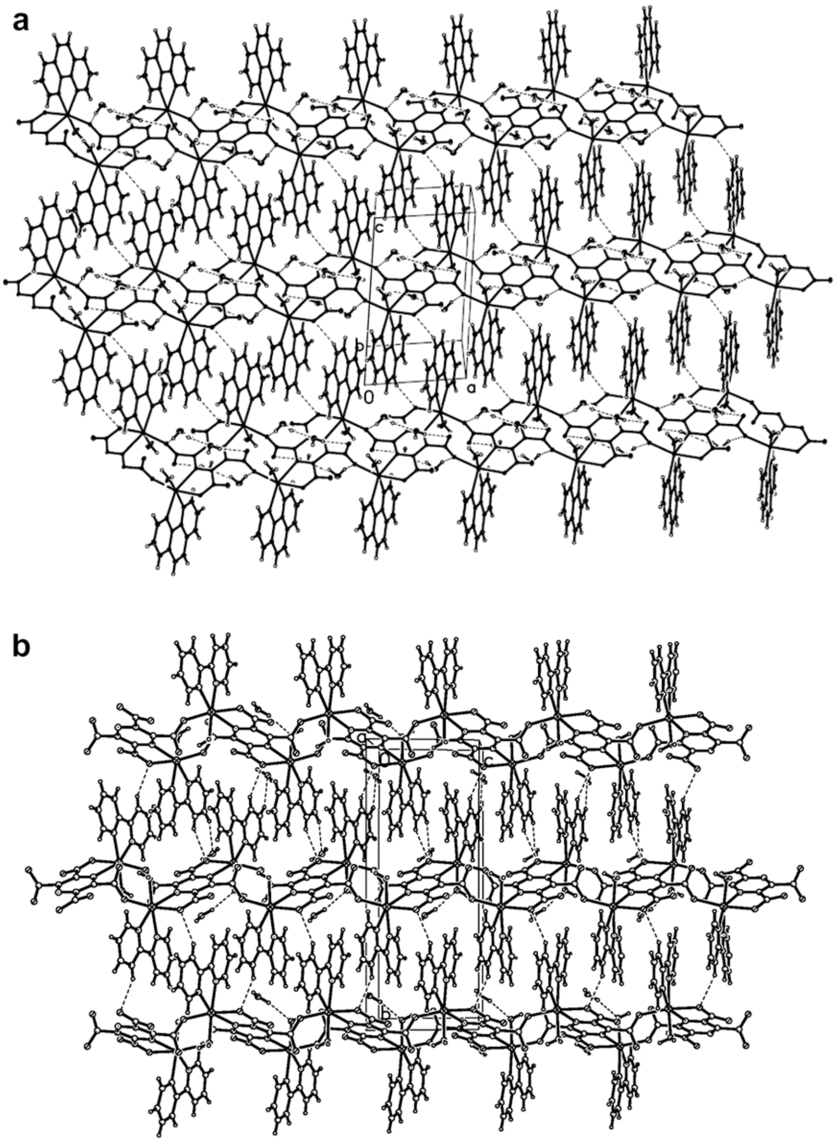

Fig. 2. 2D structure of the complex **1**(a) and **2**(b) connected by hydrogen bonds.

2.3. X-ray crystallography

Structure measurements of complexes were performed on a computer controlled Bruker SMART 1000 CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation with radiation wavelength 0.71073 Å by using the ω-scan technique. The structures were solved by direct methods and refined with the full-matrix least-squares technique using the SHELX-97 and SHELXL-97 programs [9,10]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically; the hydrogen atoms of the water molecules were located from difference maps and refined with isotropic temperature factors. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [11]. The crystallographic data and selected bond lengths and angles are listed in Table 1 and Table 2, respectively. CCDC-648149 **1** and CCDC-648148 **2** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

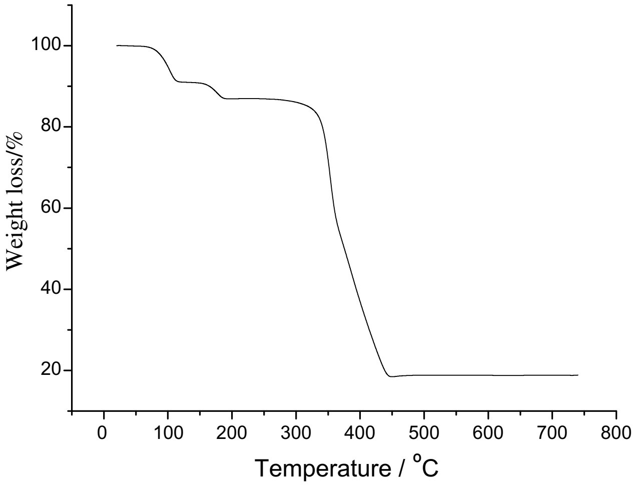

Fig. 3. TGA curves of **1**.

3. Results and discussion

3.1. Structure description

All the compounds once isolated, are air-stable and can retain their structural integrity at room temperature for a considerable length of time. Complex **1** crystallizes in the triclinic space group $P\bar{1}$. The molecular structure and coordination environments of metal centers in **1** are shown in Fig. 1.The single-crystal X-ray diffraction analysis reveals that the symmetric unit of **1** consists of two Mn(II) ions, one pztc^{4-}, two phen molecules, two coordinated water molecules and four uncoordinated water molecules. The Mn(II) ion is hexacoordinated and exhibits a distorted octahedron geometrical coordination environment. The equatorial coordination to Mn(II) ion is provided by one N atom of pztc^{4-}, two N atoms of phen and a water molecule. The two axial sites of the metal center are occupied by one carboxylate O atom of the coordinated of pztc^{4-} and a carboxylate O atom from the neighboring pztc^{4-}ligand (Fig. 1(a)).

Complex **2** crystallize in the monoclinic space group $P2_1/c$. The structures of the two complexes are very similar, except that 1,10-phenanthroline in **1** were replaced by 2,2′-bipyridine in **2**. The coordination environment of metal centers in **2** is shown in Fig. 1(b).

The coordination numbers of metal ion in **2** were also six. Among them two oxygen atoms (O1, O3) were from two carboxyl groups of different pztc^{4-} molecules and one oxygen atom (O5) was from a terminal water. The other three nitrogen atoms (N1, N2, and N3) were from the pyrazinyl and pyridyl rings. The average bond lengths of Mn–O and Mn–N were 2.1657 and 2.2796 Å for complex **2** and the two corresponding values of compound **1** are 2.1327 and 2.2933 Å, respectively. The selected bond lengths and angles are listed in Table 2.

For compounds **1** and **2**, the pyrazinyl rings of pztc^{4-} are completely parallel to each other. The planes of phen or bpy are completely parallel to each other, too. Each pztc^{4-} ligand can be described as hexadenate ligands linking four metal centers through its four carboxylate groups and two N atoms, to afford 1D slide-fastener-like chain (Fig. 1). The distances between Mn1E and Mn1F in complex **1** and **2** are 5.694 and 5.601 Å, while the Mn1E–Mn1D distance are 7.492 and 7.407 Å, respectively. The coordination mode of the all four carboxylate groups is monodentate (Fig. 1). The distances of adjacent phen or bpy rings between the two neighboring chains are both 3.427 Å in **1** and **2**.That means there are intermolecular π–π stacking interactions between the phen or bpy planes. These 1D slide-fastener-like chains are further assembled via π–π interactions and hydrogen bonds (between H atoms of phen or bpy and O atoms of pztc^{4-} or water molecule) to give rise to 2D layer supramolecular structure (Fig. 2).

The crystal structure of complex **1** and **2** are quite different from the reported compounds [12] and the decarboxylation of pyrazine-2,3,5,6-tetracarboxylic acid do not occur[13], either. It may be due to the existence of phen/bpy, π–π interactions and hydrogen bonds.

3.2. IR result

The FT-IR spectra have been employed to distinguish the coordination modes of carboxylate groups in **1**–**2**. The FT-IR spectra of **1** and **2** are almost identical and show strong characteristic bands of carboxyl group at 1633 cm^{-1} for the antisymmetric stretching and at 1406 cm^{-1} for symmetric stretching, respectively. The separations (Δ) between $\nu_{\mathrm{asym}}(\mathrm{CO_2})$ and $\nu_{\mathrm{sym}}(\mathrm{CO_2})$ of 227 cm^{-1} indicates the presence of the monodendate mode in **1** and **2**, respectively [14]. The broad absorption peak at 3390 cm^{-1} is assigned to $\nu_{\mathrm{O-H}}$ of water molecules. The absence of the characteristic bands at around 1700 cm^{-1} in **1** indicates the complete deprotonation of the ligand upon reaction with the central metal ions [15]. The IR spectra of compounds **1** and **2** are consistent with the crystal structure of them, respectively.

3.3. Thermal analysis

The molecular structures of **1** and **2** are very similar, therefore only the TGA of **1** is operated. The thermal behaviors of complex **1** were examined by TGA under the atmosphere of air. Thermal curves of **1** are illustrated in Fig. 3. The TGA curve in Fig. 3 shows that **1** begins to decompose at 100 °C displaying three stages of mass loss. The first mass loss of 8.62% from 100 to 120 °C is due to the loss of the four lattice water molecules (calculated value 8.69%). The second weight loss of 4.42% between 145 and 189 °C is consistent with the mass loss of the two coordinated water molecules. The degradation of the phen and pztc occurs in the third step in the temperature range of 294–354 °C. The remaining mass of 20.10% is presumably MnO_2 that is in agreement with the calculated value of 20.92%.

4. Conclusions

The ligand pyrazine-2,3,5,6-teracarboxylic acid was an extremely flexible ligand in coordination chemistry with 3d metals. We have synthesized two new 1D slide-fastener-like complexes by reaction of Mn(II) with pyrazine-2,3,5,6-tetracarboxylic acid and 1,10-phenanthroline(phen) or 2,2′-bipyridine(bpy) under hydrothermal conditions at 150 °C and 160 °C, respectively. The packing structures of **1** and **2** form two-dimensional supramolecular structures with the aid of intermolecular π–π interactions and hydrogen bonds. They are the first two 1D coordination polymers using both pyrazine-2,3,5,6-tetracaboxylic acid and 1,10-phenanthroline or 2,2′-bipyridine as organic linkers. Efforts to further investigate other luminescent chelating compounds and decarboxylation mechanism of pyrazine-2,3,5,6-tetracaboxylic acid in coordination polymers are underway in our laboratory.

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