Synthesis, Structural Characterization and Thermal Stability of [Mn(3-bpd)₂(NCS)₂(H₂O)₂]₂·2H₂O (**1**) and {[Mn(bpe)(NCS)₂(H₂O)₂]₂·(3-bpd)·(bpe)·H₂O}_n (**2**) from One-Pot Crystallization

Chuan-Yien Liu^a (劉娟瑛), Gene-Hsiang Lee^{b*} (李錦祥) and Hsin-Ta Wang^{a*} (王賢達)

^aDepartment of Molecular Science and Engineering & Institute of Organic and Polymeric Materials,
National Taipei University of Technology, Taipei, Taiwan, R.O.C.

^bInstrumentation Center, National Taiwan University, Taipei, Taiwan, R.O.C.

Two supramolecular architectures, [Mn(3-bpd)₂(NCS)₂(H₂O)₂]₂·2H₂O (**1**) and {[Mn(bpe)(NCS)₂(H₂O)₂]₂·(3-bpd)·(bpe)·H₂O}_n (**2**) [bpe = 1,2-bis(4-pyridyl)ethylene and 3-bpd = 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene] have been synthesized and characterized by spectroscopic, elemental and single crystal X-ray diffraction analyses. Compound **1** crystallizes in the monoclinic system, space group *P*2₁/*c*, with chemical formula C₂₆H₂₈MnN₁₀O₄S₂, *a* = 9.1360(6), *b* = 9.7490(6), *c* = 17.776(1) Å, β = 93.212(1)°, and *Z* = 2 while compound **2** crystallizes in the orthorhombic system, space group *P*2₁2₁2₁, with chemical formula C₃₈H₃₆Mn₁N₁₀O₃S₂, *a* = 14.1902(6), *b* = 15.4569(7), *c* = 18.2838(8) Å, α = β = γ = 90°, and *Z* = 4. Structural determination reveals that the coordination geometry at Mn(II) in compound **1** or **2** is a distorted octahedral which consists of two nitrogen donors of two NCS[−] ligands, two oxygen donors of two water molecules, and two nitrogen donors of two 3-bpd ligands for **1** and two dpe ligands for **2**, respectively. The two 3-bpd ligands in **1** adopt a monodentate binding mode and the dpe in **2** adopts a bimonodentate bridging mode to connect the Mn(II) ions forming a 1D chain-like coordination polymer. Both the π-π stacking interactions between the coordinated and the free pyridyl-based ligands and intermolecular hydrogen bonds among the coordinated and the crystallized water molecules and the free pyridyl-based ligands play an important role in construction of these 3D supramolecular architectures.

Keywords: Coordination polymer; Metal-organic framework; bpe; 3-bpd.

INTRODUCTION

In the past decade, the design and preparation of coordination polymers with metal-organic frameworks (MOFs) or well-regulated networks have attracted great interest for the sake of the potential applications in catalysis, gas absorption, nonlinear optics, ion-exchange, luminescence and magnetism.¹⁻³ In principle, the MOFs with desired structural topologies and/or physicochemical properties greatly depend on the binding sites, directionality of the organic ligands (spacers), the coordination number, and geometry of metal ions (nodes). Based on this concept, utilizing suitable organic spacers with functional groups that are capable of bridging metal centers to construct the well-defined crystalline materials has shown to be a fast developing research in connection with crystal engineering, coordination chemistry, supramolecular chemistry, and material science.⁴⁻⁷ The majority of metal-based supramolecular architectures have been reported with bipyridyl-based lig-

ands.⁸⁻¹⁰ Recently, two Schiff-base ligands, 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (4-bpd) and 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene (3-bpd), are found to act an important role in design of the multi-dimensional MOFs.^{11,12} These ligands show the zigzag conformation of the spacer moiety (−CR=N−N=CR−) between the two pyridyl groups resulting in coordination polymers with novel networks.¹¹ In this contribution, we report the syntheses, structure characterization, and thermal stability of two supramolecular architectures, [Mn(3-bpd)₂(NCS)₂(H₂O)₂]₂·2H₂O (**1**) and {[Mn(bpe)(NCS)₂(H₂O)₂]₂·(3-bpd)·(bpe)·H₂O}_n (**2**).

EXPERIMENTAL SECTION

Materials and Physical Techniques

All chemicals were reagent grade and were used without further purification. The infrared (IR) spectra were measured on a Fourier Transform IR spectrometer (Nicolet MAGNA-IR 500) in the range of 500-4000 cm^{−1} using the

KBr disc technique. Thermogravimetric analyses (TGA) were performed on a computer-controlled Perkin-Elmer 7 Series/UNIX TGA7 analyzer under a nitrogen atmosphere with a heating rate of 5 °C/min from room temperature to 800 °C. The elemental analyses were determined with a Perkin-Elmer Model 2400 Series II Analyzer.

Synthesis of Compounds **1** and **2**

An ethanol/H₂O solution (1:1 4 mL) of 3-bpd (41.5 mg, 0.2 mmol) and an ethanol/H₂O solution (1:1 4 mL) of bpe (18.1 mg, 0.1 mmol) were added to an aqueous solution (4 mL) containing MnCl₂·4H₂O (19.5 mg, 0.1 mmol) and KSCN (19.1 mg, 0.2 mmol) at room temperature. The light-yellow plate shaped crystals of complex **1** were obtained along with some colorless block crystals of complex **2** after the above solution was left and undisturbed for over one week. The crystals were separated by hand picking, washed with an ethanol/H₂O (1:1) solution and dried. Yield: **1**, 0.0276 g (43%) and **2**, 0.0065 g (14%). Anal. Calcd for **1**, C₂₆H₂₈MnN₁₀O₄S₂: C, 47.06; H, 4.25; N, 21.10. Found: C, 47.65; H, 3.58; N, 20.79. IR (KBr pellet): ν = 3047 (m), 2073 (vs), 1633 (s), 1603 (s), 1475 (m), 1419 (m), 1319 (m), 1188 (m), 1030 (m), 969 (m), 873 (m), 808 (m), 696 (s), 641 (m), 534 (m) cm⁻¹. Anal. Calcd for **2**, C₃₈H₃₆MnN₁₀O₃S₂: C, 57.04; H, 4.54; N, 17.50. Found: C, 57.68; H, 4.56; N, 17.68. IR (KBr pellet): ν = 3054 (m), 2074 (vs), 1605 (s), 1553 (m), 1421 (m), 1341 (m), 1227 (m), 1072 (m), 1006 (m), 950 (m), 887 (m), 815 (s), 706 (s), 636 (m), 534 (m) cm⁻¹.

Crystallographic Data Collection and Refinement

Single-crystal data of **1** and **2** were collected on a Bruker SMART diffractometer with a ApexCCD detector and Mo radiation (λ = 0.71073 Å) at room temperature. A preliminary orientation matrix and unit cell parameters were determined from the 3 runs of the 20 frames, each frame corresponding to a 0.4° ω scan in 10 s, following by spot integration and least-squares refinement. For each structure, data were measured using an ω scan of 0.3° per frame for 10 s until three complete hemisphere data had been collected. Cell parameters were retrieved using SMART¹³ software and refined with SAINT.¹³ Data reduction was performed with the SAINT¹⁴ software and Lorentz and polarization effects were also corrected. Absorption corrections were applied with the program SADABS.¹⁵ Direct phase determination and subsequent difference Fourier map synthesis yielded the positions of all non-hydrogen atoms which were refined anisotropically. For compounds **1** and **2**, all hydrogen atoms were constrained geometrically

(C–H = 0.93 Å) with the exception of the hydrogen atoms of the coordinated and solvated water molecules, which were located in the difference Fourier map with the corresponding positions. The final full-matrix, least-squares refinement on F^2 was applied for all observed reflections [$I > 2\sigma(I)$]. All calculations were performed using the SHELXTL V 6.10 software package.¹⁶ Crystallographic and experimental data for compounds **1** and **2** data are listed in Table 1.

CCDC-730580 and 730579 for **1** and **2** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internet.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

RESULTS AND DISCUSSION

Synthesis and IR Spectra

The light-yellow crystals, compound **1** and the colorless crystals, compound **2** were obtained in a one-pot crystallization *via* mixing of MnCl₂·4H₂O, 3-bpd, bpe and KSCN in ethanol/aqueous solution and standing for a period of several days. These crystals were distinctly different in color and morphology. They are very stable in air and at ambient temperature and insoluble in common solvents such as water, alcohol, and acetonitrile. The reproducibility of the synthesis is very nice. The most relevant IR feature is that associated with the SCN⁻ ligands. The IR spectra of **1** and **2** show the sharp band at 2073 and 2074 cm⁻¹ for **1** and **2**, respectively, indicating the C≡N stretching mode of the monodentate SCN⁻ ligands. This feature is consistent with possession of thiocyanate-N coordination in these complexes.

Structural Description of **1**

A perspective view of **1** with the atom numbering scheme is shown in Fig. 1. The selected bond lengths and angles with their estimated standard deviations around the Mn(II) center are listed in Table 2. The asymmetric unit of **1** consists of a half [Mn(3-bpd)₂(NCS)₂(H₂O)₂] and a water molecule. The Mn(II) ion is located at the inversion center of (0.5, 0.5, 1.0) and coordinated to four nitrogen donors of two 3-bpd and two NCS⁻ ligands with the Mn–N bond lengths of 2.321(2) and 2.177(2) Å, respectively, and coordinated to two oxygen donors of water molecules with the

Table 1. Crystallographic and experimental data for compounds **1** and **2**

	1	2
chemical formula	C ₂₆ H ₂₈ MnN ₁₀ O ₄ S ₂	C ₃₈ H ₃₆ MnN ₁₀ O ₃ S ₂
formula mass	663.64	799.83
crystal syst	Monoclinic	Orthorhombic
space group	<i>P</i> 2 ₁ /c	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	9.1360(6)	14.1902(6)
<i>b</i> (Å)	9.7490(6)	15.4569(7)
<i>c</i> (Å)	17.776(1)	18.2838(8)
α (deg)	90.0	90.0
β (deg)	93.212(1)	90.0
γ (deg)	90.0	90.0
<i>V</i> (Å ³)	1580.7(2)	4010.3(3)
<i>Z</i>	2	4
μ (mm ⁻¹)	0.598	0.482
θ range (deg)	2.23–27.50	1.73–27.50
total no. of data collected	11966	31236
independent reflection	3630 (<i>R</i> _{int} = 3.57%)	9213 (<i>R</i> _{int} = 4.21%)
no. of obsd data (<i>I</i> > 2 σ (<i>I</i>))	2927	7197
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>))	0.0521, 0.1205	0.0569, 0.1396
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0671, 0.1279	0.0748, 0.1504
GOF	1.107	1.040
no. of variable	196	487

$$R_F = \Sigma ||F_o - F_c|| / \Sigma |F_o|; R_w(F^2) = [\Sigma w|F_o^2 - F_c^2|^2 / \Sigma w(F_o^4)]^{1/2}.$$

Table 2. Selected bond lengths (Å) and angles (°) for **1**^a

Mn(1)–O(1)	2.159(2)	Mn(1)–O(1) ⁱ	2.159(2)
Mn(1)–N(1)	2.321(2)	Mn(1)–N(1) ⁱ	2.321(2)
Mn(1)–N(5)	2.177(2)	Mn(1)–N(5) ⁱ	2.177(2)
O(1)–Mn(1)–O(1) _i	180.0	N(1)–Mn(1)–N(1) ⁱ	180.0
O(1)–Mn(1)–N(1)	89.48(7)	O(1)–Mn(1)–N(1) ⁱ	90.52(7)
O(1)–Mn(1)–N(5)	89.50(8)	O(1)–Mn(1)–N(5) ⁱ	90.50(8)
N(5)–Mn(1)–N(1)	91.52(8)	N(5)–Mn(1)–N(1) ⁱ	88.48(8)
N(5)–Mn(1)–N(5) ⁱ	180.0		

^a Symmetry transformations used to generate equivalent atoms: *i* = –*x*+1, –*y*+1, –*z*+2

Mn–O bond lengths of 2.159(2) Å. It is interesting to note that the construction of the 3D supramolecular architecture (Figs. 2(a) and (b)) of **1** is a subtle combination of $\pi \cdots \pi$ stacking and hydrogen-bonding interactions. Firstly, the occurrence of the $\pi \cdots \pi$ stacking interactions between neighboring 3-bpd ligands of **1** leads to a 1D chain-like structure (shown in Fig. 2(c)). The distance between the ring centroids of the 3-bpd ligands is 3.783 Å in **1** (Table 3), falling in the general range of $\pi \cdots \pi$ stacking interaction.¹⁷ The hydrogen bonds are the second factor for the construction of

Fig. 1. Perspective view with atom labeling scheme of **1** (ORTEP drawing, 30% thermal ellipsoids).

Table 3. The π - π interactions (face-to-face) of pyridyl rings of 3-bpd ligands in **1**^a

Ring(i) $\rightarrow$ Ring(j)	Slip angle ^b (i,j)/°	Interplanar (i,j) distance ^c /Å	Horizontal shift between the (i,j) ring centroids ^d /Å	Distance between the (i,j) ring centroids/Å
R(1) $\rightarrow$ R(2) ⁱ	23.33	3.432	1.591	3.783
R(2) $\rightarrow$ R(1) ⁱ	20.73	3.538	1.339	3.783

^a Symmetry code: (i) = $-x, +5/2-y, +5/2-z$. R(i)/R(j) denotes the centroids of i-th/j-th of croconate/croconate; R(1) = N(1)–C(1)–C(2)–C(3)–C(4)–C(5); R(2) = N(4)–C(8)–C(9)–C(10)–C(11)–C(12).

^b Slip angle: the angle formed between the ring-centroid vector (CC) and the ring normal to one of the croconate planes.

^c Interplanar distance: the perpendicular distance between two parallel pyridyl rings.

^d Horizontal shift between the ring centroids: a shift from the face-to-face alignment.

the 3D packing of **1**. The hydrogen bond geometries for **1** are listed in Table 4. It is important to note that the O–H...N hydrogen bonds are formed through the coordinated water molecules interacting with the uncoordinated terminal N(4) atoms of 3-bpd ligands with the N...O distance of 2.755 Å (Fig. 2(b)). These hydrogen bonds let these 1D chain-like arrays be mutually interlinked and extended into 3D supramolecular network. The overall 3D architecture is further reinforced by O(1)–H(1A)...O(2) (coordinated and solvated H₂O) and O(2)–H(2A)...N(3) (solvated H₂O and 3-bpd) hydrogen bonds with the O...O and O...N distances of 2.807 and 2.934 Å, respectively.

Structural Description of **2**

Fig. 3 represents the molecular structure consisting of the repeating unit of **2** and part of the symmetry-related independent molecules of **2** in the asymmetric unit. Selected bond lengths and angles are reported in Table 5. The Mn(II) centers in a distorted octahedral coordinating two nitrogen donors (N(1) and N(2)) of the bridging bpe ligands with Mn(1)–N(1) and Mn(1)–N(2) of 2.393(2) and 2.344(2) Å, respectively, connecting two nitrogen donors (N(3) and N(4)) of the NCS[−] ligands with Mn(1)–N(3) and Mn(1)–N(4) of 2.171(3) and 2.176(3) Å, and linking two water molecules (O(1) and O(2)) with Mn(1)–O(1) of 2.173(2) and Mn(1)–O(2) of 2.173(2) Å. The bpe ligands bridge Mn(II) ions forming an 1D chain with an intrachain distance of 14.190 Å (Mn...Mn).

The most remarkable and interesting features on construction of the 3D supramolecular architecture of compound **2** is that the subtle combination of π ... π stacking and hydrogen-bonding interactions of N-based ligands building 1D coordination linear chains and free N-based ligands (bpe and 3-bpd) into a 3D array (Fig. 4(c)). Firstly, the N–H...O hydrogen bonds for the free 3-bpd ligands (N(7)

Table 4. Hydrogen bonds geometries (Å, °) for **1**^a

D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	$\angle$ D–H...A (°)
O(1)–H(1A)...O(2) ⁱ	0.74	2.07	2.807	176
O(2)–H(2A)...N(3)	0.97	2.01	2.938	159
O(1)–H(1B)...N(4) ⁱⁱ	0.78	1.98	2.755	177

^a Symmetry code: (i) = $1+x, -1+y, z$; (ii) = $1+x, 3/2-y, 1/2+z$.

Table 5. Selected bond lengths (Å) and angles (°) for **2**

Mn(1)–O(1)	2.173(2)	Mn(1)–O(2)	2.173(2)
Mn(1)–N(1)	2.393(2)	Mn(1)–N(2)	2.344(2)
Mn(1)–N(3)	2.171(3)	Mn(1)–N(4)	2.176(3)
O(1)–Mn(1)–N(1)	90.14(8)	O(1)–Mn(1)–N(2)	90.51(9)
O(1)–Mn(1)–N(4)	87.2(1)	O(2)–Mn(1)–O(1)	177.71(8)
O(2)–Mn(1)–N(1)	89.47(8)	O(2)–Mn(1)–N(2)	89.92(9)
O(2)–Mn(1)–N(4)	90.5(1)	N(2)–Mn(1)–N(1)	178.72(9)
N(3)–Mn(1)–O(1)	93.1(1)	N(3)–Mn(1)–O(2)	89.2(1)
N(3)–Mn(1)–N(1)	89.40(9)	N(3)–Mn(1)–N(2)	89.46(9)
N(3)–Mn(1)–N(4)	179.6(1)	N(4)–Mn(1)–N(1)	90.41(9)
N(4)–Mn(1)–N(2)	90.72(9)		

Table 6. Hydrogen bonds geometries (Å, °) for **2**^a

D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	$\angle$ D–H...A (°)
O(1)–H(1B)...N(10) ⁱ	0.76	2.01	2.769	174
O(2)–H(2A)...N(7)	0.71	2.07	2.776	171
O(1)–H(1A)...O(3) ⁱⁱ	0.85	1.99	2.784	155
O(2)–H(2B)...O(3) ⁱⁱⁱ	0.82	1.98	2.734	153
O(3)–H(3A)...N(5) ^{iv}	0.77	2.02	2.766	157
O(3)–H(3B)...N(6)	0.72	2.04	2.740	168

^a Symmetry code: (i) = $1-x, 1/2+y, 3/2-z$; (ii) = $1+x, y, z$; (iii) = $1-x, -1/2+y, 3/2-z$; (iv) = $-1+x, y, z$.

and N(10)) and coordinated water molecules (O(2) and O(1)) with the N(7)...O(2) and N(10)...O(1) distances of 2.769 and 2.776 Å, respectively, extend 1D coordination chains into 2D layer-like network as shown in Fig. 4(a).

The hydrogen bond geometries are listed in Table 6. Meanwhile, the $\pi\cdots\pi$ stacking interactions between one coordinated bpe and two free 3-bpd ligands (Fig. 4(a)) are the second factor for the construction of the 2D layer-like network. The distances between the ring centroids of the pyridyl rings of 3-bpd and bpe ligands are 3.638 and 3.733 Å (Table 7), falling in the general range of $\pi\cdots\pi$ stacking in-

teraction.¹⁷ Furthermore, these 2D layered networks are extended to 3D supramolecular architecture by the $\pi\cdots\pi$ stacking interactions between free bpe and 3-bpd ligands (shown in Fig. 4(b)), which the distances between the ring centroids of ligands are 3.745 and 3.928 Å (Table 7). The overall 3D architecture is further reinforced by O–H $\cdots$ O and O–H $\cdots$ N hydrogen bonds among the solvated H₂O, the

Fig. 2. 3D Packing diagrams of **1** viewing along (a) the *a* axis and (b) the *b* axis. (c) 1D chain-like structure via π - π interaction of neighboring 3-bpd ligands of **1**.

Fig. 3. Perspective view with atom labeling scheme of **2** (ORTEP drawing, 30% thermal ellipsoids).

coordinated H₂O, and the free bpe (N(5) and N(6)) ligands with the O...O and O...N lengths in the range of 2.734–2.784 Å. The related hydrogen bond lengths and angles are listed in Table 6.

Thermal Stability of **1** and **2**

The TGA thermograms (Fig. 5(a) and (b)) show that compounds **1** and **2** are stable in the temperature range of approximate 35–90 °C. Weights of **1** and **2** are decreased at

approximate 90–141 °C and 90–105 °C with losses of 10.90% (calc 10.84%) and 6.16% (calc 6.75%), respectively, corresponding to the loss of coordinated and crystallized water molecules. Other ligands in their 3D supramolecular architectures are stable up to 220 and 186 °C. Both compounds are decomposed at temperatures higher than these.

CONCLUSIONS

In this paper, the synthesis, crystal structure and ther-

Table 7. The π - π interactions (face-to-face) of pyridyl rings of free 3-bpe, coordinated and free bpe ligands in **2**^a

Ring(i) $\rightarrow$ Ring(j)	Slip angle ^b (i,j)/°	Interplanar (i,j) distance ^c /Å	Horizontal shift between the (i,j) ring centroids ^d /Å	Distance between the (i,j) ring centroids/Å
R(1) $\rightarrow$ R(2) ⁱ	12.04	3.558	0.758	3.638
R(2) ⁱ $\rightarrow$ R(1)	12.84	3.547	0.809	3.638
R(2) ⁱ $\rightarrow$ R(3) ⁱⁱ	16.68	3.576	1.071	3.733
R(3) ⁱⁱ $\rightarrow$ R(2) ⁱ	19.90	3.510	1.271	3.733
R(1) $\rightarrow$ R(4) ⁱⁱⁱ	18.23	3.557	1.172	3.745
R(4) ⁱⁱⁱ $\rightarrow$ R(1)	19.92	3.521	1.276	3.745
R(3) $\rightarrow$ R(5) ^{iv}	19.66	3.699	1.322	3.928
R(5) ^{iv} $\rightarrow$ R(3)	24.58	3.572	1.634	3.928

^a Symmetry code: (i) = $-1+x, y, z$; (ii) = $1-x, 1/2+y, 3/2-z$; (iii) = $-1/2+x, 3/2-y, 2-z$; (iv) = $+1/2+x, 3/2-y, 2-z$. R(i)/R(j) denotes the centroids of i-th/j-th of croconate/croconate; R(1) = N(10)–C(34)–C(35)–C(36)–C(37)–C(38); R(2) = N(2)–C(8)–C(9)–C(10)–C(11)–C(12); R(3) = N(7)–C(27)–C(28)–C(29)–C(30)–C(31); R(4) = N(5)–C(15)–C(16)–C(17)–C(18)–C(19); R(5) = N(6)–C(22)–C(23)–C(24)–C(25)–C(26).

^b Slip angle: the angle formed between the ring-centroid vector (CC) and the ring normal to one of the croconate planes.

^c Interplanar distance: the perpendicular distance between two parallel croconate rings.

^d Horizontal shift between the ring centroids: a shift from the face-to-face alignment.

Fig. 4. (a) 2D layer-like network composed of the 1D chains of $[\text{Mn}(\text{bpe})(\text{NCS})_2(\text{H}_2\text{O})_2]$ and free 3-bpd ligands via hydrogen bonding and π - π interaction. (b) The π - π interaction between the free 3-bpd and bpe ligands. (c) 3D Packing diagram of **2** viewing along the b axis.

Fig. 5. TGA thermograms of (a) compound **1** and (b) compound **2**.

mal stability of compound **1** and **2** have been presented. Compounds **1** and **2** formed in one-pot crystallization. Compound **1** contains coordinated ligands with the solvated water molecules, whereas compound **2** contains coordinated ligands with the free ligands and the solvated water molecules. Their 3D supramolecular architectures are constructed by a subtle combination of intermolecular $\pi\cdots\pi$ stacking interactions between pyridyl-based ligands (3-bpd and bpe) and intermolecular hydrogen bonds among the coordinated and the crystallized water molecules and pyridyl-based ligands.

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