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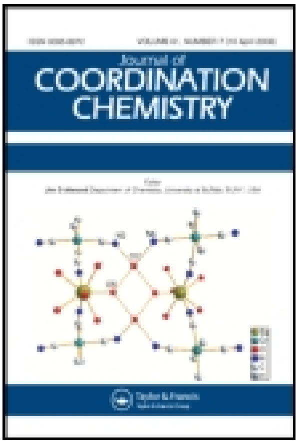

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Syntheses and crystal structures of two complexes based on 2-amino-4,6-bis(4-pyridyl)-1,3,5-triazine

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Syntheses and crystal structures of two complexes based on 2-amino-4,6-*bis*(4-pyridyl)-1,3,5-triazine

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Two compounds based on 2-amino-4,6-*bis*(4-pyridyl)-1,3,5-triazine (4-HABPT), [Co(4-HABPT)$_2$(H$_2$O)$_4$](CH$_3$COO)$_2$ (**1**), and Zn(4-HABPT)$_2$Cl$_2$ (**2**) were obtained at room temperature. Single-crystal X-ray diffraction analyses indicate that **1** crystallizes in the triclinic $P\bar{1}$ with cobalt(II) coordinated by two 4-HABPT and four waters, two acetates are counter ions. The complex cations and acetates are linked to a 3-D framework by hydrogen bonds. Compound **2** crystallizes in the orthorhombic *Pnc*2 with zinc(II) coordinated by two 4-HABPT and two chlorides in a tetrahedral geometry; the complex also forms a 3-D framework by hydrogen bonds and $\pi \cdots \pi$ interactions.

Keywords: Coordination compound; 1,3,5-Triazine; Hydrogen bonding

1. Introduction

Many complexes based on polypyridyl ligands have been reported [1], especially rigid multidentate polypyridyl ligands containing a triazine ring as a bridge have attracted attention due to their coordination diversity [2, 3]. Although coordination chemistry of symmetrical ligands containing a triazine ring like tri(2-pyridyl)-1,3,5-triazine (TPT), tri(4-pyridyl)-1,3,5-triazine (4-TPT), and tri(3-pyridyl)-1,3,5-triazine (3-TPT) has been explored well [4–9], asymmetric ligands containing triazine rings are rare [10].

Recently, we designed and synthesized a family of rigid, asymmetric ligands on the basis of replacement of a pyridyl group from TPT by hydroxyl, amino, and sulphydryl groups. In our initial studies, using 4,6-*bis*(2-pyridyl)-1,3,5-triazin-2-ol (2-HOBPT) and 2-amino-4,6-*bis*(2-pyridyl)-1,3,5-triazine (2-HABPT) (scheme 1), we assembled two hydrophobic, cubic, nanosize cations $[\mathrm{Co(H_2O)_6} \subset \mathrm{Co_8(2\text{-}OBPT)_{12}}]^{6+}$, and $[\mathrm{Co(H_2O)_6} \subset \mathrm{Co_8(2\text{-}ABPT)_{12}}]^{6+}$ using $[\mathrm{Co(H_2O)_6}]^{2+}$ as the template; the deprotonated ligands offer rare, *bis*-bipyridine-like binding with the capability of bridging two

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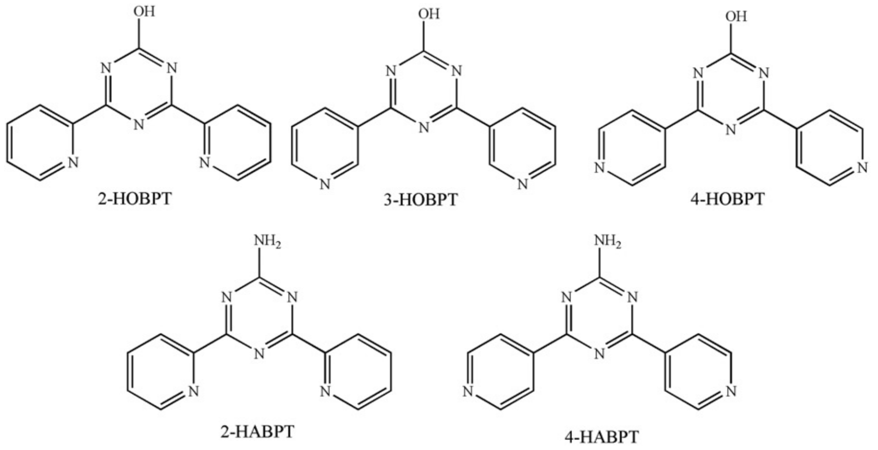

Scheme 1. Related ligands.

cobalt(II) ions in a chelating manner [11]. With 4,6-*bis*(4-pyridyl)-1,3,5-triazin-2-ol (4-HOBPT) and 4,6-*bis*(3-pyridyl)-1,3,5-triazin-2-ol (3-HOBPT), we have also obtained several complexes with different coordination modes [12].

As part of our ongoing study, we extend to the analogous ligand 2-amino-4,6-*bis*(4-pyridyl)-1,3,5-triazine (4-HABPT) (scheme 1) that has hydrogen bonding and coordination modes. Though the ligand was synthesized as early as 1959 [13], the coordination chemistry has not yet been explored. Herein, we report the single-crystal structures of two complexes, $[Co(4\text{-}HABPT)_2(H_2O)_4](CH_3COO)_2$ (**1**) and $Zn(4\text{-}HABPT)_2Cl_2$ (**2**); both are discrete structures linked to 3-D frameworks *via* hydrogen bonds and $\pi \cdots \pi$ interactions.

2. Experimental

2.1. *Materials and methods*

The reagents and solvents employed were commercially available and used as received. C, H, and N microanalyses were carried out with a Vario EL elemental analyzer. ^{1}H-NMR spectra were recorded on a Varian 300-MHz spectrometer at 25°C. Electron spray ionization (ESI) mass spectra were obtained on a LCQ DECA XP quadrupole ion trap mass spectrometer with methanol as the carrier solvent. FT-IR spectra were recorded as KBr pellets from 400 to 4000 cm^{-1} on a Bruker TENSOR 27 spectrometer. Thermogravimetric data were collected on a Netzsch TGS-2 analyzer in nitrogen at a heating rate of 10°C min^{-1}. Powder X-ray diffraction patterns were recorded on a D8 ADVANCE diffractometer with Cu-Kα radiation ($\lambda = 1.5409$ Å) at a scanning rate of 4 min^{-1} with 2θ ranging from 5° to 40°.

2.2. *Synthesis*

2.2.1. Synthesis of 4-HABPT. In this study, 4-HABPT was prepared according to previously reported procedures [13]. ESI–MS: $m^+/z = 251$. FT-IR (KBr, cm^{-1}): 3086(s), 2856(w), 2371(w), 1663(s), 1535(vs), 1376(s), 1256(m), 1188(w), 1128(w), 1049(w), 998(m), 950(w), 906(w), 786(s), 743(s), 632(m), and 481(w). ^{1}H-NMR data (DMSO-d$_6$, ppm): 8.29 (d, $J = 6.09$ Hz, 4 H), 8.80 (d, $J = 6.06$ Hz, 4 H).

2.2.2. Synthesis of [Co(4-HABPT)$_2$(H$_2$O)$_4$](CH$_3$COO)$_2$ (1). To a suspension of 4-HABPT (0.025 g, 0.1 mmol) in 7 mL of ethanol, a solution of $Co(CH_3COO)_2 \cdot 6H_2O$ (0.029 g, 0.1 mmol) in 7 mL distilled water was added. The resulting mixture was vibrated under ultrasonic conditions for 20 min and then filtered. The obtained red filtrate was allowed to stay at ambient temperature for 3 days, giving 0.015 g (40% yields based on the ligand) of red single crystals suitable for structural determination. Anal. Calcd for $C_{30}H_{34}CoN_{12}O_8$ (%): C, 48.07; H, 4.57; N, 22.42. Found (%): C, 47.94; H, 4.60; N, 22.34.

2.2.3. Synthesis of Zn(4-HABPT)$_2$Cl$_2$ (2). A mixture of 4-HABPT (0.025 g, 0.1 mmol) and $ZnCl_2$ (0.014 g, 0.1 mmol) in 7 mL distilled water and 7 mL methanol was stirred at room temperature for 2 h, and then filtered. The obtained colorless filtrate was allowed to stay at ambient temperature for 5 days, giving 0.018 g (56% yields based on the ligand) of colorless single crystals suitable for structure determinations. Anal. Calcd for $C_{26}H_{20}Cl_2N_{12}Zn$ (%): C, 49.04; H, 3.17; N, 26.39. Found (%): C, 48.97; H, 3.31; and N, 26.32.

2.3. *Structural characterizations*

Diffraction intensities for **1** and **2** were collected at 293 K on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Absorption corrections were applied using SADABS [14]. The structures were solved by direct methods and refined with full-matrix least-squares using SHELXS-97 and SHELXL-97 programs, respectively [15]. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The organic hydrogens were generated geometrically (C–H 0.96 Å and N–H 0.86 Å). Hydrogens of water were located from difference maps and refined with isotropic temperature factors. Crystal data, as well as details of data collection and refinement for the complexes, are summarized in table 1. Selected bond distances and angles are listed in table 2 and the hydrogen-bonding parameters are shown in table 3.

3. Results and discussion

3.1. *Synthesis and characterization*

4-HABPT was prepared by the reaction of 4-cyanopyridine and guanidine hydrochloride in an ethanol solution according to the previous report and recrystallized with methanol [13]. It is slightly soluble in common organic solvents, such as MeOH, CH_3CN, DMF, etc., but not soluble in water. Although the ligand was synthesized by Case in 1959, the coordination chemistry of this ligand has not yet been explored. Reaction of $Co(CH_3COO)_2 \cdot 6H_2O$ or $ZnCl_2$ with 4-HABPT in a water–alcohol solution

Table 1. Crystal data and structure refinement for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{30}H_{34}CoN_{12}O_8$	$C_{26}H_{20}C_{12}N_{12}Zn$
Formula weight	749.62	636.81
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$Pnc2$
Unit cell dimensions (Å, °)		
a	7.8883(7)	7.948(2)
b	8.1924(7)	27.184(8)
c	13.293(1)	6.249(2)
α	87.764(1)	
β	77.951(1)	
γ	77.407(2)	
Volume (Å^3), Z	819.9(1), 1	1350.1(7), 2
Calculated density (Mg m^{-3})	1.518	1.566
Absorption coefficient (mm^{-1})	0.594	1.150
$F(000)$	389	648
Crystal size (mm^3)	$0.18 \times 0.12 \times 0.09$	$0.26 \times 0.22 \times 0.18$
Range for data collection (°)	$2.55 < \theta < 25.99$	$1.50 < \theta < 26.00$
Reflections collected	5759	5751
Reflections unique	3164	2208
R_{int}	0.0206	0.0212
Completeness to $\theta = 26$ (%)	98.3	99.5
Goodness-of-fit on F^2	1.038	1.012
R_1[a]	0.0430	0.0245
wR_2[b]	0.1162	0.0849
$\Delta\rho_{\max}/\Delta\rho_{\min}$ (e Å^{-3})	0.351 and −0.296	0.257 and −0.215

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

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

1			
Co1–N1	2.164(2)	Co1–O1W	2.134(2)
Co1–O2W	2.075(2)	O1W–Co1–N1#1	88.08(7)
O2W–Co1–O2W#1	180	O2W–Co1–N1	89.59(7)
N1#1–Co1–N1	180	O2W–Co1–N1#1	90.41(7)
O1W#1–Co1–O1W	180.000(1)	O1W–Co1–N1	91.92(7)
O2W–Co1–O1W#1	87.66(7)	O2W–Co1–O1W	92.34(7)
2			
Zn1–N1	2.058(2)	Zn1–Cl1	2.2380(9)
N1–Zn1–Cl1	110.67(7)	N1–Zn1–Cl1#2	104.21(7)
Cl1–Zn1–Cl1#2	116.78(6)	N1–Zn1–N1#2	110.4(1)

Symmetry codes: #1: $-x+1$, $-y+1$, $-z+1$; #2: $-x+1$, $-y+1$, z.

at room temperature afforded red crystals of **1** or colorless crystals of **2**. Different from the structures formed by 2-HABPT we reported previously, in which the ligand is deprotonated and bridges two metal ions, 4-HABPT in **1** or **2** is neutral and monodentate with only one nitrogen of pyridine coordinated. Powder X-ray diffraction (XRD) was used to check the structural identity of the sample. The powder XRD patterns of the as-synthesized products closely match the simulated ones from the single-crystal data, indicating that they are pure (see figure S1 in ESI). Thermal gravimetric analyses (TGA) were carried out from 30 to 800°C to examine the

Table 3. Hydrogen bond parameters in **1** and **2**.

D–H···A	D–H/Å	H···A/Å	D···A/Å	∠D–H···A (°)
1				
O1W–H1WB···O2#1	0.89	1.89	2.763(3)	166.7
O1W–H1WA···O2#2	0.86	1.95	2.757(2)	155.3
O2W–H2WB···O1#3	0.87	1.88	2.716(2)	160.9
O2W–H2WA···O1	0.89	1.77	2.659(3)	173.6
N6–H6B···O1#4	0.82	2.15	2.968(3)	174.0
N6–H6A···N5#5	0.94	2.06	2.984(3)	168.0
2				
N6–H6B···N5#1	0.86	2.08	2.940(3)	174.1
N6–H6A···N4#2	0.86	2.66	3.476(3)	158.08
C1–H1A···Cl1#3	0.93	2.76	3.564(3)	145.03

Symmetry codes: **1**, #1: $-x+1, -y+1, -z+1$; #2: $x, y+1, z$; #3: $-x, -y+1, -z+1$; #4: $-x+1, -y+1, -z$; #5: $x+1, y-1, z$; **2**, #1: $x+1, y, z-1$; #2: $x, -y+3/2, z-1/2$; #3: $x, y, -1+z$.

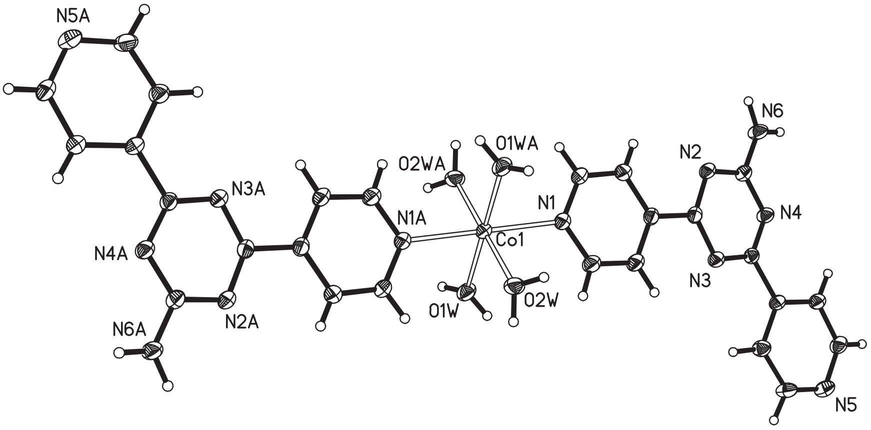

Figure 1. The coordination environment of Co(II) in **1** (symmetry code of A: $-x+1, -y+1, -z+1$).

coordinated waters and stability. For **1**, a weight loss of 9.72% from 30°C to 180°C (see figure S2 in ESI) corresponds to a loss of four coordinated waters (calculated 9.60%), indicating that the coordinated waters were completely removed at 180°C. Then, there is a plateau extending to 450°C, indicating that coordination frameworks are stable up to 450°C. For **2**, TGA study reveals that there is almost no loss from 25°C to 450°C (see figure S3 in ESI), indicating that there are no guest molecules in **2**, which is consistent with the result from single crystal analyses.

3.2. *Crystal structure of $[Co(4\text{-}HABPT)_2(H_2O)_4](CH_3COO)_2$ (1)*

Complex **1** crystallizes in a triclinic space group $P\bar{1}$. As shown in figure 1, Co(II) is on a symmetry inversion center and coordinated by two nitrogens from two ligands which are parallel (Co1−N1 = 2.164(2) Å) and four water molecules (Co−Ow = 2.075(1) Å and 2.134(1) Å) to furnish an octahedral geometry. In 4-HABPT, only pyridyl

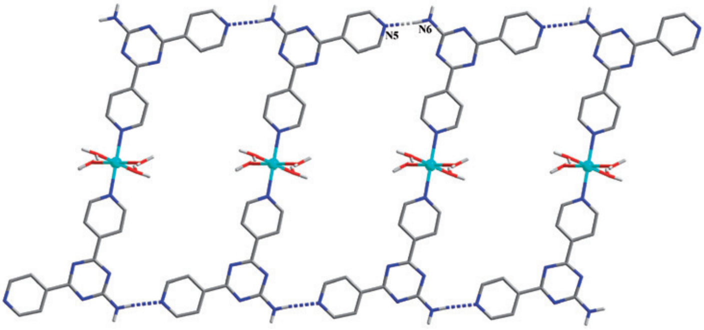

Figure 2. The 1-D ladder structure in **1** formed by N–H ··· N hydrogen bonds.

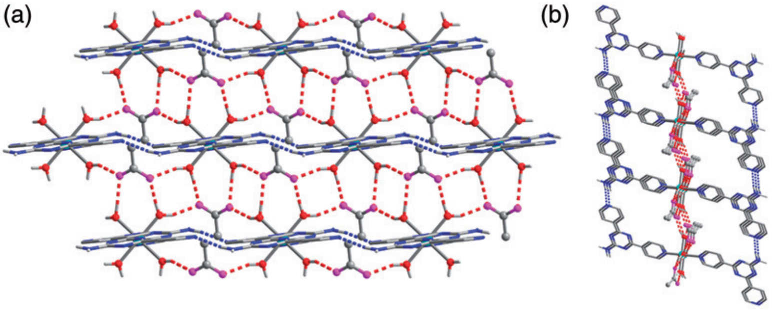

Figure 3. The 2-D framework in **1** linked by hydrogen bonds of coordinated waters (a, view along the *c* axis, oxygens of coordinated water are shown as red balls, the acetate oxygens are shown as purple balls; b, view along the *a* axis).

coordinates and the residual half is "free" and accepts hydrogen bonds from amino groups (N6−H6A ··· N5 = 2.984 Å) of another ligand to form a 1-D ladder structure, as shown in figure 2. Each ligand donates two hydrogen bonds from the amino and accepts one hydrogen bond with the uncoordinated pyridyl nitrogen. In the 1-D structure, the distance between the neighboring metal centers is 10.06 Å.

Two acetates are counter ions balancing the charge of Co(II). The coordinated waters (red balls in figure 3a) donate intermolecular hydrogen bonds to oxygens (purple balls in figure 3a) of acetate (OW ··· O = 2.659(3)–2.763(3) Å), resulting in a 2-D hydrogen-bonding structure in the *ab* plane (figure 3). For each cobalt coordinated by four waters, each water donates two hydrogen bonds, so each cobalt can be considered as the node in the 1-D ladder structure, donating eight hydrogen bonds to oxygens from acetates. The acetates further connect the 2-D hydrogen-bonding layers to 3-D framework *via* hydrogen bonds N6−H6B ··· O1 = 2.968(3) Å, which are formed between amino groups and acetate, as shown in figure 4.

3.3. *Crystal structure of Zn(4-HABPT)$_2$Cl$_2$ (2)*

When we react 4-HABPT with ZnCl$_2$ at room temperature, **2** was obtained, crystallizing in an orthorhombic *Pnc*2 space group with half of a Zn(II), one 4-HABPT and a

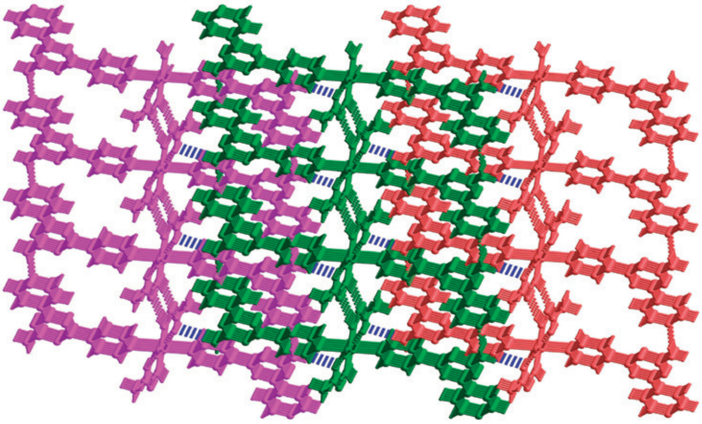

Figure 4. View of the 3-D hydrogen-bonding structure in **1**.

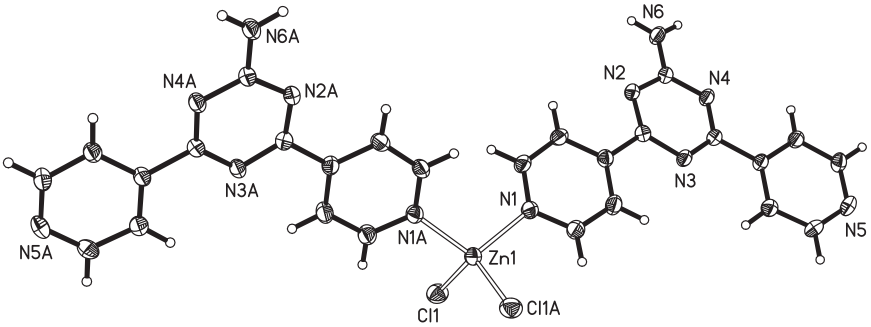

Figure 5. The coordination environment of Zn(II) in **2** (symmetry code of A: $-x+1$, $-y+1$, z).

coordinated chloride in an asymmetric unit. As shown in figure 5, each Zn(II) lies on an inversion center, coordinated by two pyridyl nitrogens (M–N = 2.058(2) Å) and two chlorides (M–Cl = 2.2380(9) Å) to furnish a distorted tetrahedral geometry. The average bond angle of X–M–X is about 110.5°, indicating that Zn(II) is sp^3 hybridized. Similar to **1**, 4-HABPT is N-monodentate with one pyridyl nitrogen uncoordinated. Different from **1**, the two ligands are not parallel but with a dihedral angle of 50.8°.

As shown in figure 6(a), the discrete complex forms helical 2-D (4,4) networks on the *ac* plane *via* hydrogen bond of $\mathrm{N6{-}H6B\cdots N5} = 2.940(3)$ Å, which is further connected to a 2-D interpenetrating double-layer through $\pi\cdots\pi$ interaction between pyridyl rings (the distance between two planes is 3.38 Å; figure 6b). Neighboring double layers are further linked to a 3-D framework *via* $\mathrm{N6{-}H6A\cdots N4}$ hydrogen bonds, shown as green dashed lines in figure 7.

4. Conclusions

We have synthesized two complexes based on 4-HABPT, which is monodentate with only one pyridyl coordinated. The uncoordinated pyridyl and amino form

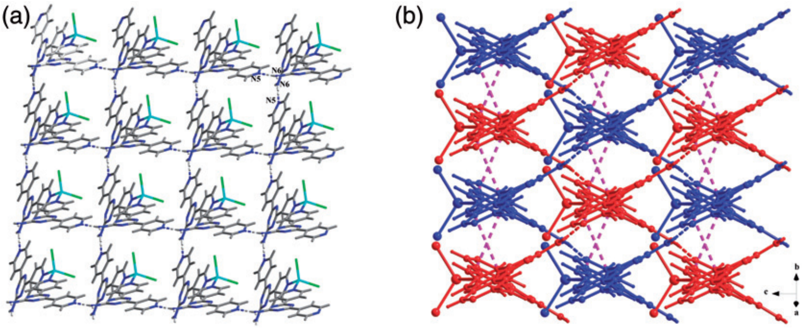

Figure 6. Views of (a) the 2-D (4,4) network in **2** linked by N6–H6B $\cdots$ N5 hydrogen bond; (b) the 2-D interpenetrating double-layer connected by $\pi\cdots\pi$ interactions (purple dashed lines).

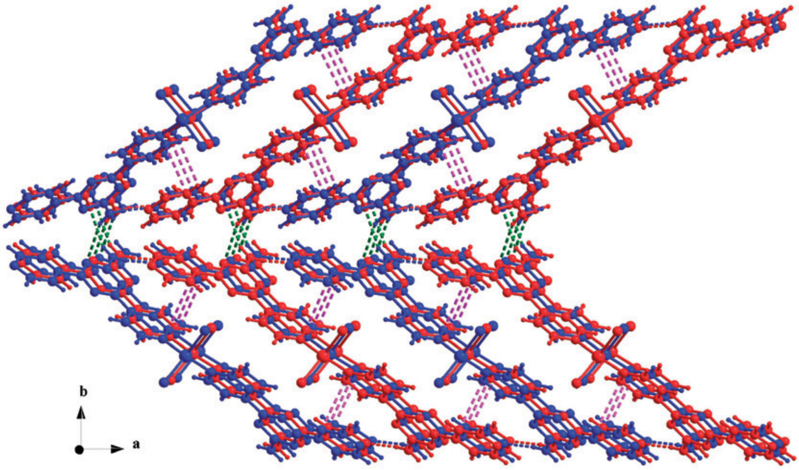

Figure 7. View of the 3-D framework formed from double-layers linked by a weak hydrogen bond of N6–H6A $\cdots$ N4 (green) in **2**.

hydrogen bonds. The discrete structures formed by coordination have matched hydrogen-bonding sites, which are linked to 3-D frameworks by hydrogen bonds and $\pi\cdots\pi$ interaction. TGA reveal that the compounds are stable to 450°C.

Supplementary material

Copies of X-ray crystallographic files in CIF format for the structural determination, the powder X-ray diffraction patterns and TGA plots may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk).

Acknowledgments

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