Hydrothermal Synthesis and Crystal Structure of a Nickel(II) Coordination Polymer with 1,1′-Biphenyl-2,2′-dicarboxylato-6,6′-dicarboxylic Acid and 2,2′:6,2″-Terpyridine Ligands

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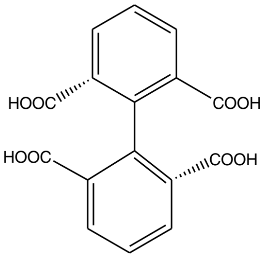
A new metal-organic framework $\{[\mathrm{Ni(H_2BPTC)(tpy)(H_2O)}]\cdot(\mathrm{H_2O})_3\}_n$ (**1**) ($\mathrm{H_4BPTC}$ = 1,1′-biphenyl-2,2′,6,6′-tetracarboxylic acid, tby = 2,2′:6,2″-terpyridine) has been synthesized and characterized by single-crystal X-ray diffraction and IR spectroscopy. The one-dimensional metal-organic chains of the title complex, namely $\{\mathrm{Ni(H_2BPTC)(tpy)(H_2O)}\}_n$, are connected through weak $\pi\cdots\pi$ and C–H$\cdots\pi$ interactions to form layers, which are further held together by rich O-H$\cdots$O hydrogen bonding to give a three-dimensional supramolecular network. The thermal stability of the title complex was studied by thermal gravimetric (TG) and differential thermal analyses (DTA).

Key words: Nickel(II), 1,1′-Biphenyl-2,2′,6,6′-tetracarboxylic Acid, 2,2′:6,2″-Terpyridine, Coordination Polymer, Thermal Analysis

Introduction

In recent years, more and more attention has been focused on the construction of polymeric frameworks due to their intriguing structures and interesting properties [1, 2]. The self-assembly of mixed multidentate organic ligands and metal ions has resulted in many coordination polymer frameworks, whose structures are influenced by the subtle interplay of many factors such as geometric preference of metal ions, sizes and shapes of the organic building blocks, *etc.* In particular, the selection or design of suitable ligands containing certain features like flexibility or versatile binding modes is crucial for the construction of metal-organic coordination polymers. Aromatic multicarboxylate ligands with rigid or flexible configurations have been proven to be good candidates for the construction of a rich variety of coordination polymers with high-dimensional networks and interesting properties because of their diverse coordination modes and high structural stability [3 – 8]. On the other hand, dipyridine and its analogs are neutral linkers or chelating ligands widely used as excellent auxiliary spacers in the construction of novel supramolecular compounds [5 – 7]. In addition supramolecular contacts (hydrogen bonding, $\pi\cdots\pi$ stacking, *etc.*) may occur in these coordination polymers [5 – 8].

Recently a series of multidimensional metal-organic supramolecular complexes constructed using 1,1′-biphenyl-2,2′,3,3′-tetracarboxylic acid ($\mathrm{H_4bptc}$) [6] and 1,1′-biphenyl-2,3′,3,4′-tetracarboxylic acid (m-$\mathrm{H_4bptc}$) [7, 8] have been reported. However, to the best of our knowledge, only a few metal-organic compounds have been obtained from the related ligand 1,1′-biphenyl-2,2′,6,6′-tetracarboxylic acid ($\mathrm{H_4BPTC}$) [9, 10]. With the aim of further understanding the coordination chemistry of $\mathrm{H_4BPTC}$ ligands with various metal ions in the presence of different “secondary” ligands and preparing new materials with interesting structural topologies, we have become engaged in the research of coordination polymers based on the $\mathrm{H_4BPTC}$ ligand (Scheme 1). As a part of our continuing investigations, herein we report the synthesis and crystal structure of a new coordination polymer $\{[\mathrm{Ni(H_2BPTC)(tpy)(H_2O)}]\cdot(\mathrm{H_2O})_3\}_n$ (**1**).



Scheme 1. 1,1′-Biphenyl-2,2′,6,6′-tetracarboxylic acid ($\mathrm{H_4BPTC}$).

Experimental Section

Materials and physical measurements

All chemicals and solvents used in the synthesis were of reagent grade and were used without further purifi-

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Table 1. Crystallographic data for complex **1**.

Empirical formula	$C_{31}H_{27}N_3NiO_{12}$
Formula weight	692.27
Color, habit	blue, block
Crystal size, mm^3	$0.25 \times 0.20 \times 0.18$
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	10.858(2)
b, Å	20.659(4)
c, Å	14.283(3)
β, deg	109.94(3)
Volume, Å^3	3011.8(10)
Z	4
Density (calcd.), g cm^{-3}	1.53
Absorption coeff., mm^{-1}	0.7
Temperature, K	296(2)
$F(000)$, e	1432
Range of h,k,l	± 12, ± 24, ± 16
Refl. collected / independent / R_{int}	30210 / 5298 / 0.06
Reflections with $I \geq 2\sigma(I)$	4790
Parameters refined	434
Final $R1$ / $wR2$ [$I \geq 2\sigma(I)$]	0.059 / 0.134
$R1$ / $wR2$ (all data)	0.068 / 0.141
Goodness of fit (GoF)	0.918
$\Delta\rho_{\text{fin}}$ (max / min), e Å^{-3}	$+0.25$ / -0.34

cation. H_4BPTC (1,1′-biphenyl-2,2′,6,6′-tetracarboxyl acid) was prepared according to the methods previously reported [11]. Elemental analyses were carried out on an Elementar Vario EL III analyzer. The infrared spectra were recorded from KBr pellets in the range $4000 \sim 400$ cm^{-1} on a Bruker model Vector22 FT-IR spectrometer. Thermogravimetric measurements were carried out from r. t. to 700 °C on crystalline samples in a nitrogen stream using a TA Instruments SBT Q600 apparatus at a heating rate of 10 °C min^{-1}.

*Synthesis of complex **1***

A mixture of $Ni(NO_3)_2 \cdot 6H_2O$ (14.6 mg, 0.05 mmol), H_4BPTC (16.5 mg, 0.05 mmol), terpyridine (11.8 mg, 0.05 mmol) and NaOH (4 mg, 0.1 mmol) in 6 mL water was sealed in a 25-mL Teflon-lined stainless-steel autoclave, heated to 120 °C for 72 h and then slowly cooled to r. t. over 24 h. Blue block-shaped crystals of **1** were collected, washed with deionized water and dried in air. Yield: *ca.* 60 %. – Elemental analysis for $NiC_{31}H_{27}N_3O_{12}$ (692.27): calcd. C 5378, H 3.93, N 607; found C 5385, H 3.89, N 610. – IR (KBr, cm^{-1}): ν = 3346 (s), 1700 (vs), 1562 (s), 1465 (w), 1420 (s), 1319 (w), 1151 (w), 776 (s), 707 (m), 643 (w), 583 (w), 426 (w).

Crystallography data collection and structure determination

Single-crystal X-ray diffraction analysis of complex **1** was carried out on a Bruker SMART APEX II CCD diffractometer using graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) at r. t. Data collection was done with the ω-scan technique, Lorentz, polarization and absorption corrections were applied. The structure was solved by Direct Methods and refined with full-matrix least-squares methods using SHELXS-97 and SHELXL-97 [12]. Anisotropic displacement parameters were assigned to all non-hydrogen atoms. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. The hydrogen atoms were assigned common isotropic displacement factors and included in the final refinement by use of geometrical restraints. Crystal data, data collection parameters and details of the structure refinement are summarized in Table 1, selected bond lengths and angles are listed in Table 2.

Table 2. Selected bond lengths (Å) and angles (deg) for complex **1**.[a]

Ni(1)–N(1)	2.097(3)	Ni(1)–N(2)	1.994(3)
Ni(1)–N(3)	2.096(3)	Ni(1)–O(1)	2.075(3)
Ni(1)–O(3)$^{\#1}$	2.079(2)	Ni(1)–O(4W)	2.037(3)
O(1)–Ni(1)–O(3)$^{\#1}$	167.21(11)	O(1)–Ni(1)–N(3)	98.45(12)
O(1)–Ni(1)–N(1)	85.89(11)	O(3)$^{\#1}$–Ni(1)–N(3)	92.97(12)
O(3)$^{\#1}$–Ni(1)–N(1)	85.85(11)	O(4W)–Ni(1)–N(3)	102.43(13)
O(4W)–Ni(1)–N(1)	100.66(12)	O(4W)–Ni(1)–O(3)$^{\#1}$	88.47(11)
O(4W)–Ni(1)–O(1)	83.48(11)	N(2)–Ni(1)–N(3)	78.69(13)
N(2)–Ni(1)–N(1)	78.19(12)	N(2)–Ni(1)–O(4W)	178.50(12)
N(2)–Ni(1)–O(1)	97.37(11)	N(2)–Ni(1)–O(3)$^{\#1}$	90.48(11)
N(3)–Ni(1)–N(1)	156.84(12)		

[a] Symmetry code: $^{\#1}$ $x-1, y, z$.

CCDC 806235 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

*Crystal structure of $\{[Ni(H_2BPTC)(tpy)(H_2O)] \cdot (H_2O)_3\}_n$ (**1**)*

Single-crystal X-ray diffraction analysis has revealed that the asymmetric unit of compound **1** contains one Ni(II) cation, one bridging H_2BPTC^{2-} anion, one chelating tpy molecule, one coordinated and three solvent water molecules (Fig. 1a). The Ni atom displays a distorted N_3O_3 octahedral geometry. Three nitrogen atoms of a tpy ligand and one oxygen atom of a coordinated water molecule comprise the equatorial plane, while two carboxylate oxygen atoms of two H_2BPTC^{2-} anions occupy the axial positions with 167.21° for the angle O(1)–Ni(1)–O(3)$^{\#1}$. All bond lengths are normal, with the Ni–N bonds ranging from 1.994(3) to 2.097(3) Å and the Ni–O bonds from 2.037(3) to 2.079(2) Å.

As to the H_2BPTC^{2-} ligand, the two phenyl rings are twisted and almost perpendicular to each other (dihedral angle 85.3°). The four carboxyl groups in 2,2′-

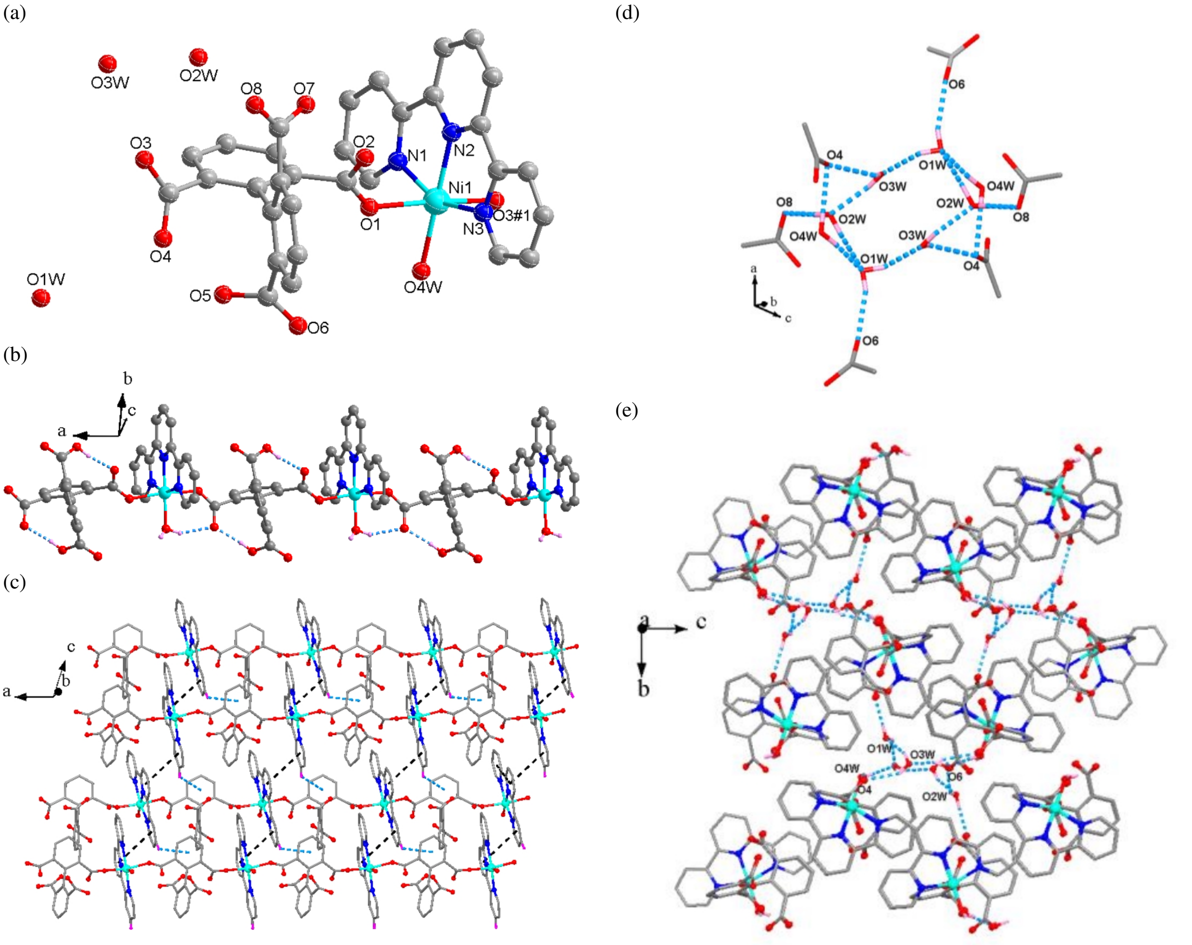

Fig. 1. (a) The connectivity pattern in the asymmetric unit of complex **1** (all hydrogen atoms are omitted for clarity); (b) the chain of complex **1** along the *a* axis showing hydrogen bonds; (c) the layer structure parallel to the *ac* plane showing the $\pi\cdots\pi$ and C–H$\cdots\pi$ interactions; (d) representation of the cyclic water hexamers connected by hydrogen bonds present between the layers; (e) the 3D metal-organic framework formed.

COO$^-$ and 6,6′-COOH have dihedral angles of 61.2°, 57.5°, 65.2°, and 52.0° with the planes of the corresponding phenyl rings. Three pyridine rings of a tpy ligand and the equatorial plane of [NiN_3O_3] are approximately coplanar. It is worth noting that each H_2BPTC^{2-} anion acts as bis-monodentate ligand for two Ni(II) cations along the *a* axis to form a chain with strong O–H$\cdots$O interactions (H$\cdots$O distances from 1.72 to 1.97 Å) between a carboxylate O atom of the H_2BPTC^{2-} anion and the coordinated water molecule thus making the chain more stable (Fig. 1b). The chains are held together *via* weak $\pi\cdots\pi$ interactions (centroid-centroid distance 4.151 Å) between the middle pyridine ring of one tpy ligand and an outside pyridine ring of another tpy from a neighboring parallel chain to form layers, in which there are also the C–H$\cdots\pi$ interactions (H$\cdots$centroid distance 3.245 Å) between C29–H29 of the tpy ligand and the benzene ring of the H_2BPTC^{2-} anion from an adjacent chain to stabilize the layer (Fig. 1c). In addition, the solvate water molecules in the complex form a symmetrical cyclic water hexamer $(H_2O)_6$ (Fig. 1d) which fills the space between adjacent layers through substantial O–H$\cdots$O interactions. Rich hydrogen bonding exists not only in the $(H_2O)_6$ cluster but also between the $(H_2O)_6$ cluster and the coordinated water molecule and carboxylate oxygen atoms to form a 3D metal-organic framework, as shown in Fig. 1e. The hydrogen bond lengths and angles are listed in Table 3.

Table 3. Hydrogen bond lengths (Å) and angles (deg) for complex **1**.[a]

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O(7)–H(7)···O(2)	0.82	1.72	2.532	170.7
O(5)–H(5)···O(4)	0.82	1.76	2.573	174.0
O(4W)–H(4WA)···O(4)$^{\#1}$	0.82	1.97	2.723	152.8
O(4W)–H(4WB)···O(1W)$^{\#1}$	0.85	1.89	2.736	174
O(1W)–H(1WB)···O(6)$^{\#2}$	0.85	2.03	2.815	153.9
O(1W)–H(1WA)···O(3W)$^{\#3}$	0.85	1.96	2.735	150.2
O(3W)–H(3WB)···O(2W)	0.85	1.93	2.735	157.6
O(3W)–H(3WA)···O(4)$^{\#4}$	0.86	2.44	3.162	142.1
O(2W)–H(2WA)···O(8)$^{\#5}$	0.85	1.93	2.775	177.7
O(2W)–H(2WB)···O(1W)$^{\#4}$	0.85	2.33	3.003	135.7

[a] Symmetry codes: $^{\#1}$ $x-1, y, z$; $^{\#2}$ $x+1, y, z$; $^{\#3}$ $x, y, z-1$; $^{\#4}$ $-x+1, y, -z+1$; $^{\#5}$ $x, -y+1/2, z+1/2$.

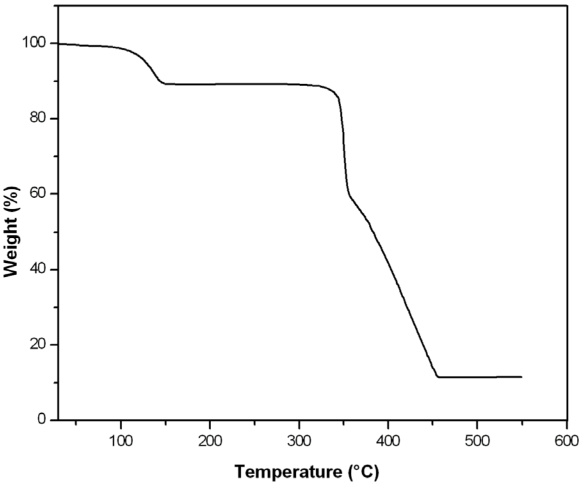

Fig. 2. Thermogravimetric analysis (TGA) curve for **1**.

Thermogravimetric analysis of complex 1

The thermogravimetric analysis (TGA) was conducted to determine the thermal stability of the title complex, which is an important aspect for a metal-organic framework. TGA was performed on crystalline samples of **1** in the range of 25 ~ 700 °C, as depicted in Fig. 2. The results indicate that the first weight loss of 10.9 % (calcd. 10.40 %) below 139 °C corresponds to the loss of three solvate and one coordinated water molecules per formula unit, followed by a continuous two step weight loss of 77.8 % from 344 to 500 °C (calcd. 81.0 %) corresponding to the loss of the H_2BPTC^{2-} and tpy ligands.

Conclusion

In summary, we have presented a new Ni(II) coordination polymer constructed from H_4BPTC. The results have revealed that the partially protonated H_2BPTC^{2-} anion adopts a bis-monodentate μ_2-bridging mode between the Ni(II) cations to generate a chain. The steric hindrance of the tpy molecule may contribute to this simple coordination mode of the H_2BPTC^{2-} ligand indicating that the secondary ligand can play an important role in determining the structural diversity of MOFs. The H_4BPTC ligand could thus be used as a versatile ligand to construct novel MOFs by an appropriate choice of coligands and metal-centers. Subsequent work will be focused on the construction of new interesting coordination polymers by reacting H_4BPTC and other auxiliary *N*-donor ligands with suitable metal ions.

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