

Assembly of Zn(II) Coordination Polymers Based on Tetrachloroterephthalate and Dipyridyl-type Ligands

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2,3,5,6-Tetrachloroterephthalic acid (H₂BDC-Cl₄) has been selected for assembly with Zn^{II} ions in the presence of the co-ligands 2,2-bipyridine (bipy) or 1,10-phenanthroline (phen). Through pH regulation, two coordination compounds were obtained at ambient temperature with the formula [Zn₂(BDC-Cl₄)(bipy)₂(OAc)₂(H₂O)₂] (**1**) and {[Zn(BDC-Cl₄)(phen)₂](CH₃OH)(H₂O)}_n (**2**). Single-crystal X-ray analysis has indicated that complex **1** exhibits a binuclear coordination unit, while complex **2** is a wave-like polymeric chain. In both complexes, the anionic BDC-Cl₄ ligands show bis-monodentate bridging coordination in the *trans*-mode. Because of the introduction of the bipyridyl co-ligands, multiple hydrogen-bonding interactions and π - π interactions are formed in both complexes.

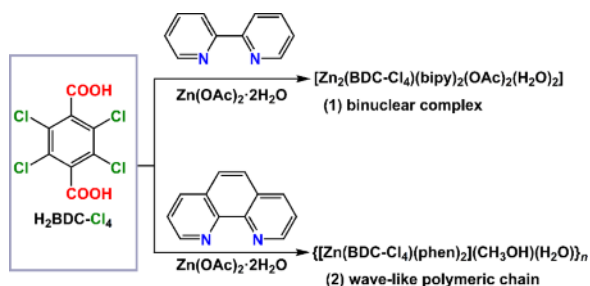
Key words: Tetrachloroterephthalic Acid, Zinc Coordination Compound, Crystal Structure

Introduction

Crystal engineering of metal complexes, especially coordination polymers (CPs) frequently termed as metal-organic frameworks, is currently of great interest due to their fascinating structures as well as potential performances in adsorption/separation, optics, magnetism, and catalysis [1–10]. However, to rationally and predictably prepare the desired crystalline products is still a challenge, as it depends, among others, on the structural characteristics of the ligands [11–13], the coordination geometry of metal ions, the pH, and the solvents [14–16]. For mixed-ligand CPs, polycarboxylate and bipyridine components represent the most reliable building blocks which can be readily applied to synthesize a wide range of coordination networks. To date, terephthalate (benzene-1,4-dicarboxylate, BDC) has been widely utilized to fabricate coordination polymers based on paddlewheel units with robust networks and attractive properties as porous materials [17–26]. Derivatives of BDC with selected substituents, such as bulky methyl or halogen groups, have also received considerable attention

in the design of porous materials with an efficient hydrogen-storage capacity and of nanoparticle materials for computer tomography (CT) contrast enhancement [27–39].

Recently, we have been engaged in studying the influence of solvents on the structures of a series of metal-BDC-Cl₄ polymers (including Mn^{II} [32], Cu^{II} [33], Co^{II} [34], and Pb^{II} [35]). For these solvent-induced systems, it has been primarily suggested that the coordination properties of the solvent molecules strongly affect the spacial arrays of the coordination frameworks. For the fluorine-substituted BDC, introduction of bipyridyl co-ligands produces porous perfluorinated MOFs [31]. In mixed-ligand CPs, the terephthalate anion has been utilized with chelating bipyridyl co-ligands, such as 2,2-bipyridine (bipy) and 1,10-phenanthroline (phen) to establish both coordination bonds and robust aromatic π - π stacking interactions [21–26]. These coordination arrays tend to be zigzag chains with few exceptions [25, 26]. Coordination frameworks with mixed ligands involving BDC-Cl₄ moieties have not been explored with the exception of monodentate pyridine as a solvent ligand [32].

Scheme 1. Synthesis of compounds **1** and **2**.

Bipy generally chelates metal ions through both of its nitrogen atoms and acts as a terminal or capping ligand. Hybrid structures containing bipy are typically of lower dimensionality and can furnish recognition sites for aromatic stacking to construct complicated supramolecular arrays with promising luminescence properties [40]. As a continuation of investigations on coordination assemblies with the BDC- Cl_4 ligand, herein, we present the syntheses and crystal structures of two Zn^{II} coordination polymers with BDC- Cl_4 and two dipyriddy ligands, $[\text{Zn}_2(\text{BDC-Cl}_4)(\text{bipy})_2(\text{OAc})_2(\text{H}_2\text{O})_2]$ (**1**) and $\{[\text{Zn}(\text{BDC-Cl}_4)(\text{phen})_2](\text{CH}_3\text{OH})(\text{H}_2\text{O})\}_n$ (**2**) (Scheme 1).

Results and Discussion

Synthesis and general characterization

Complexes **1** and **2** can be prepared in water and methanol solvent media with a 1 : 1 : 1 acidic ligand/co-ligand/metal molar ratio. The ratios 2 : 1 : 2 and 2 : 2 : 1 gave the same products. The pH was adjusted to 7~8 with triethylamine. The absence of intense infrared (IR) peaks at about 1720 cm^{-1} ($\nu_{\text{C=O}}$) indicates the complete deprotonation of the carboxyl groups. The characteristic carboxylate peaks at $1620/1335\text{ cm}^{-1}$ (**1**) and $1604/1326\text{ cm}^{-1}$ (**2**), can be attributed to the antisymmetric and symmetric carboxylate stretching vibrations.

Structure of $[\text{Zn}_2(\text{BDC-Cl}_4)(\text{bipy})_2(\text{OAc})_2(\text{H}_2\text{O})_2]$ (**1**)

Single-crystal X-ray analysis has revealed that compound **1** crystallizes in the orthorhombic system, space group $Pbca$. The asymmetric unit contains one Zn^{II} ion, half a centrosymmetrical BDC- Cl_4 ligand, one chelating bipy ligand and one acetate ion, as well as one

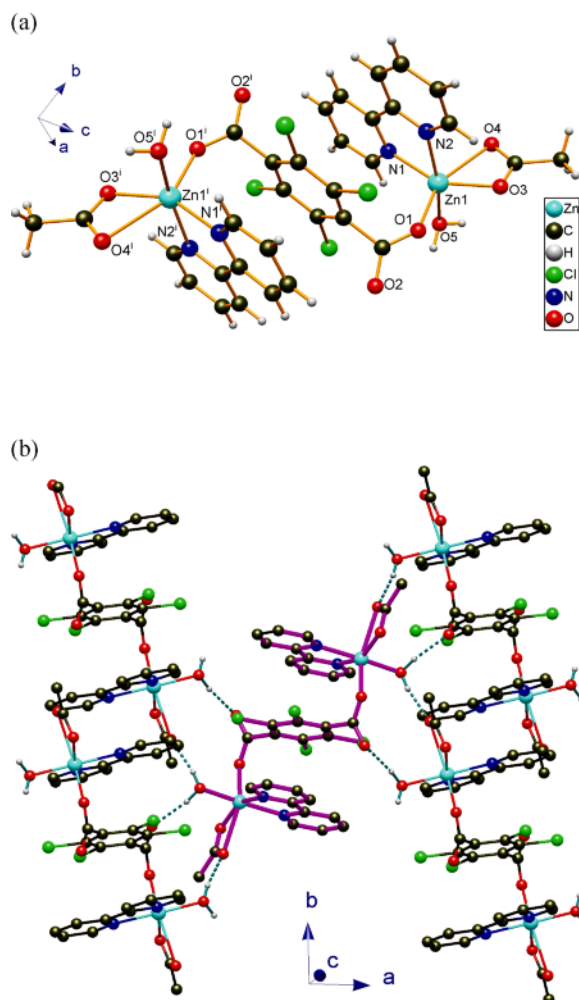


Fig. 1. (color online). (a) Molecular structure of **1** with atom labeling of the heteroatoms in the metal coordination sphere (symmetry code: $i = -x, -y + 1, -z$). (b) The hydrogen-bonding architecture in complex **1**, with green dashed lines indicating the hydrogen bonds, and blue dashed lines indicating the 4^4 topology.

coordinated water molecule. The Zn^{II} ion, which resides on an inversion center has a distorted octahedral coordination sphere, being surrounded by four oxygen donors from one carboxylate group of the BDC- Cl_4 ligand, one chelating acetate ion and one water molecule, and by two nitrogen donors from one bipy ligand, where O5 and N2 occupy the axial positions and the other donor atoms compose the equatorial plane (see Fig. 1a). The BDC- Cl_4 serves as a bis-monodentate bridge in *trans*-pattern linking

a pair of centrosymmetry-related Zn^{II} centers to generate a binuclear structure with the Zn···Zn separations of 8.621(1) Å. Within the BDC-Cl₄ ligand, the dihedral angle between the carboxylate group and the central phenyl plane is 77.99(2)°. The coordinated water molecule builds O5–H5A···O4 and O5–H5B···O2 interactions with the coordinated acetate anion and the uncoordinated carboxylate oxygen atom of BDC-Cl₄. In this way, each dinuclear entity is joined to four such units into a 2D hydrogen-bonding network (see Fig. 1b). There are significant π - π interactions between the bipyr moieties and the aromatic rings of the dicarboxylate ligands to further stabilize the resultant 2D supramolecular framework.

Structure of $\{[Zn(BDC-Cl_4)(phen)_2](CH_3OH)(H_2O)]_n$ (**2**)

The structure of **2** is a one-dimensional coordination assembly with the asymmetric unit containing one Zn^{II} ion, two phen ligands, a pair of centrosymmetrical BDC-Cl₄ ligands, one methanol and one water molecule. The Zn^{II} center adopts a distorted octahedral ZnN₄O₂ coordination sphere. As illustrated in Fig. 2a, the Zn^{II} ion is coordinated by three pyridyl N donors and a monodentate carboxylic O atom in the equatorial plane and by a carboxylic O atom from a BDC-Cl₄ and the other N atom of the phen entity occupying the axial positions. Within two crystallographically independent BDC-Cl₄ ligands, the carboxyl groups and the central phenyl planes are approximately perpendicular with dihedral angles of 76.51(2) and 87.16(2)°. As depicted in Fig. 2b, the Zn^{II} ions are linked by the BDC-Cl₄ ligands at the *trans*-position to form a zigzag chain with Zn···Zn separations of 9.797(3) and 11.362(3) Å. π - π Interactions between the phen moieties and the aromatic rings of BDC-Cl₄ are found to further stabilize the chain, which is similar to the interactions in the binuclear unit of **1**. Although the one-dimensional structure of **2** is somewhat similar to that of other Zn-phen terephthalate polymers [23, 24], it is, in fact, constructed in a significantly different fashion. The one-dimensional architecture of this zinc compound comprises a parallel aromatic stacking of phen and substituted benzene rings with Zn: phen = 1 : 2; in contrast, previously reported [23] one-dimensional Zn^{II} polymers with mixed terephthalate and phen ligands are mostly further extended by the zipper-like π - π intercalation of the lateral phen ligands, in which the Zn^{II}

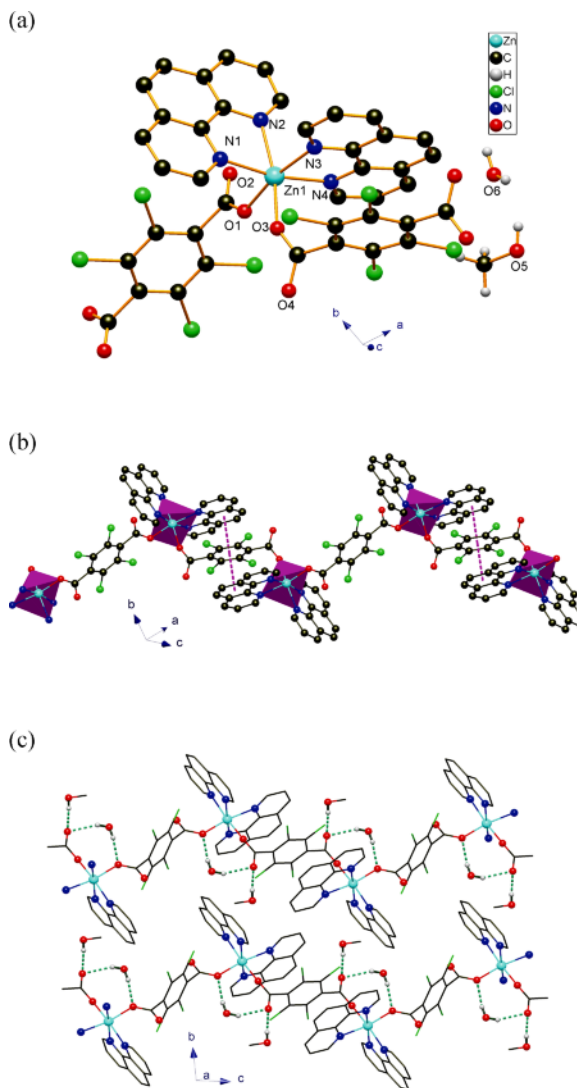


Fig. 2. (color online). (a) Asymmetric unit of **2** with atom labeling of heteroatoms in the metal coordination sphere. (b) View of the wave-like polymeric chain in **2** with the Zn^{II} atoms shown as polyhedra in **2**. (c) View of the hydrogen-bonding interactions between host and guest molecules in **2**.

centers are four-coordinated by two BDC anions and one chelating phen ligand.

Packing analyses have revealed that the chains run along the [001] direction (see Fig. 2c) and are arranged in a parallel fashion along the [010] direction. As calculated by PLATON [41] the effective free volume of **2** is 154.8 Å³ (9.8% of the unit cell volume) to accommodate solvents. Each coordination chain is anchored

by water and methanol molecules through multiple O–H···O interactions (O5–H5···O4, O6–H6A···O4 and O6–H6B···O1 bonds). Surprisingly, no further weak interactions are found to extend these decorated host-guest chains to a higher dimensional network.

Summary

In summary, 2,3,5,6-tetrachloroterephthalic acid (H₂BDC-Cl₄) has been employed to assemble with Zn^{II} ions in the presence of the co-ligands 2,2-bipyridine (bipy) or 1,10-phenanthroline (phen) to form a binuclear structure (**1**) and a zigzag chain structure (**2**), respectively. In both cases, the BDC-Cl₄ moiety accepts a bis-monodentate mode as the bridging ligand due to the stereochemical effects of the chlorine substituents and the co-ligands. This work has provided the first examples of tetrachloroterephthalate coordination assembly with chelating co-ligands. Further investigation on mixed ligand tetrachloroterephthalate complexes are underway.

Experimental Section

Tetrachloroterephthalic acid (H₂BDC-Cl₄) was prepared according to the procedures described in the literature [42]. All the other reagents were obtained from local commercial suppliers and used without further purification. ¹H spectra were recorded on a Bruker Advance III 500 spectrometer. Fourier transform (FT) infrared data were collected on an Avatar-370 (Nicolet) spectrometer by transmission through the sample deposited on a KBr pellet. Elemental analyses were performed on a CE-440 (Leemanlabs) analyzer.

Synthesis of [Zn₂(BDC-Cl₄)(bipy)₂(OAc)₂(H₂O)₂] (**1**)

Equimolar amounts of Zn(OAc)₂·2H₂O (22 mg, 0.1 mmol), H₂BDC-Cl₄ (31 mg, 0.1 mmol) and 2,2'-bipy (16 mg, 0.1 mmol) were mixed in a CH₃OH-H₂O (v:v = 1 : 2) solvent medium with stirring and slowly adding a mixed solvent of triethylamine and ethanol (v:v = 1 : 4) to adjust the pH to 7~8. After stirring for *ca.* 30 min, the reaction mixture was filtered and the filtrate was left to stand at room temperature. Colorless block-shaped single crystals suitable for X-ray analysis were obtained after several weeks. Yield: 22% (10 mg, based on bipy). – Anal. for C₃₂H₂₆Cl₄N₄O₁₀Zn₂: calcd. C 42.74, H 2.91, N 6.23; found C 42.62, H 2.94, N 6.30%. –FT-IR (KBr pellet, cm⁻¹): ν = 3333b, 1620vs, 1542vs, 1444s, 1403s, 1335vs, 1118w, 1054m, 1022m, 937w, 845m, 771s, 736m, 683m, 652w, 631w, 615w.

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

	1	2
Empirical formula	C ₃₂ H ₂₆ Cl ₄ N ₄ O ₁₀ Zn ₂	C ₃₃ H ₂₂ Cl ₄ N ₄ O ₆ Zn
<i>M_r</i>	899.15	777.74
Crystal size, mm ³	0.32 × 0.30 × 0.30	0.30 × 0.28 × 0.28
Crystal system	orthorhombic	triclinic
Space group	<i>Pbca</i>	<i>P</i> $\bar{1}$
<i>a</i> , Å	17.3083(14)	9.443(3)
<i>b</i> , Å	10.4556(9)	10.445(4)
<i>c</i> , Å	18.2704(15)	16.707(6)
α, deg	90	93.956(4)
β, deg	90	92.250(4)
γ, deg	90	106.645(4)
<i>V</i> , Å ³	3306.4(5)	1572.1(9)
<i>Z</i>	4	2
μ(MoK α), cm ⁻¹	1.8	1.2
<i>F</i> (000), e	1816	788
<i>D</i> _{calcd.} , g cm ⁻³	1.81	1.64
Refl. measured	27412	12094
Refl. unique	3851	6070
Param. refined	236	435
<i>R</i> _{int}	0.0468	0.0397
<i>R</i> ¹ / <i>wR</i> ² ^b	0.0251 / 0.0548	0.0415 / 0.1292
GOF (<i>F</i> ²) ^c	1.039	1.063
Δρ _{fin} (max/min), e Å ⁻³	0.37 / -0.30	0.58 / -0.74

^a *R*1 = Σ||*F*_o| - |*F*_c||/Σ|*F*_o|; ^b *wR*2 = [Σ*w*(*F*_o² - *F*_c²)²/Σ*w*(*F*_o²)²]^{1/2}; *w* = [σ²(*F*_o²) + (*AP*)² + *BP*]⁻¹, where *P* = (Max(*F*_o², 0) + 2*F*_c²)/3; ^c GoF = [Σ*w*(*F*_o² - *F*_c²)²/(*n*_{obs} - *n*_{param})]^{1/2}.

Synthesis of {[Zn(BDC-Cl₄)(phen)₂](CH₃OH)(H₂O)}_n (**2**)

Complex **2** was synthesized in a similar way to that for **1**, except that bipy was replaced by phen (18 mg, 0.1 mmol). Yield: 51% (20 mg, based on phen). – Anal. for C₃₃H₂₂Cl₄N₄O₆Zn: calcd. C 50.96, H 2.85, N 7.20; found C 50.92, H 2.90, N 7.27%. – FT-IR (KBr pellet, cm⁻¹): ν = 3464b, 1604s, 1518vs, 1429s, 1393s, 1326vs, 1228m, 1111m, 1030m, 866m, 854m, 728s, 640m, 629w, 615m.

X-Ray crystallography

Single-crystal X-ray diffraction data for complexes **1** and **2** were collected on a Bruker Apex II CCD diffractometer equipped with graphite-monochromatized MoK α radiation (λ = 0.71073 Å) at room temperature. There was no evidence of crystal decay during data collection. The program APEX II was used for collecting frames of data, indexing reflections and determination of lattice parameters. A semiempirical absorption correction was applied using SADABS, and the program SAINT was used for integration of the diffraction profiles [43]. All structures were solved by Direct Methods with SHELXS and refined by full-matrix least-squares calculation on *F*² with the SHELXL pro-

Compound	1		2	
	Distances		Distances	
	Zn1–O3	2.0251 (15)	Zn1–O1	2.087 (2)
	Zn1–O1	2.0277 (14)	Zn1–N4	2.116 (3)
	Zn1–O5	2.1000 (14)	Zn1–O3	2.129 (2)
	Zn1–N1	2.1204 (17)	Zn1–N1	2.133 (3)
	Zn1–N2	2.1550 (16)	Zn1–N3	2.208 (3)
			Zn1–N2	2.210 (3)
	Angles		Angles	
	O3–Zn1–O1	97.73 (6)	O1–Zn1–N4	95.12 (10)
	O3–Zn1–O5	95.44 (6)	O1–Zn1–O3	85.71 (9)
	O1–Zn1–O5	88.39 (6)	N4–Zn1–O3	97.84 (10)
	O3–Zn1–N1	149.71 (6)	O1–Zn1–N1	91.99 (10)
	O1–Zn1–N1	111.88 (6)	N4–Zn1–N1	168.99 (10)
	O5–Zn1–N1	91.79 (6)	O3–Zn1–N1	91.05 (10)
	O3–Zn1–N2	94.36 (6)	O1–Zn1–N3	170.27 (9)
	O1–Zn1–N2	96.89 (6)	N4–Zn1–N3	77.63 (11)
	O5–Zn1–N2	168.14 (6)	O3–Zn1–N3	88.83 (9)
	N1–Zn1–N2	76.40 (6)	N1–Zn1–N3	96.17 (10)
			O1–Zn1–N2	94.87 (9)
			N4–Zn1–N2	93.66 (11)
			O3–Zn1–N2	168.39 (10)
			N1–Zn1–N2	77.35 (11)
			N3–Zn1–N2	92.10 (10)

Table 2. Selected bond lengths (Å) and angles (deg) for **1** and **2** with estimated standard deviations in parentheses.

Compound	D—H···A	H···A (Å)	D···A (Å)	D—H···A (deg)	Symmetry code A
1	O5–H5A···O4	1.87	2.708(2)	169	$1/2 - x, -1/2 + y, z$
	O5–H5B···O2	1.94	2.780(2)	169	$1/2 - x, 1/2 + y, z$
	C6–H6A···O1	2.34	3.214(3)	152	$1/2 - x, 1/2 + y, z$
	C8–H8···O2	2.43	3.286(3)	153	$-x, 1/2 + y, 1/2 - z$
	C16–H16···O5	2.52	3.103(3)	121	
2	O5–H5···O4	1.97	2.782(4)	173	$x + 1, y, z$
	O6–H6A···O4	2.13	2.904(4)	156	$x + 1, y, z$
	O6–H6B···O1	2.11	2.918(3)	166	$x + 1, y, z$
	C6–H6···O6	2.57	3.425(5)	153	$x - 1, y + 1, z$
	C7–H7···O2	2.47	3.299(4)	149	$-x, 2 - y, 1 - z$
	C10–H10···O2	2.58	3.378(5)	144	$-x, 2 - y, 1 - z$
	C15–H15···O5	2.55	3.414(5)	154	$1 - x, 1 - y, 2 - z$
	C19–H19···O4	2.54	3.466(5)	173	$x + 1, y, z$
	C22–H22···O6	2.46	3.370(5)	166	

Table 3. Hydrogen-bonding geometries in the crystal structures of **1** and **2**.

gram of the SHELXTL package [44, 45]. Hydrogen atoms bonded to carbon atoms were assigned to idealized positions with isotropic displacement parameters fixed at 1.2 times that of the attached atoms. *N*- and *O*-bound hydrogen atoms were localized in the difference Fourier maps and refined in subsequent refinement cycles. The isotropic displacement parameters for hydrogen atoms bonded to nitrogen and oxygen atoms were kept at a factor of 1.5. Crystallographic data and structural refinement parameters are summarized in Table 1. Selected bond lengths and angles are listed in Table 2, and hydrogen-bonding geometries are given in Table 3.

CCDC 961381 and 961382 contain the supplementary crystallographic data for this paper. These data can be ob-

tained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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