Manipulation of Molecular and Supramolecular Structure in Cobalt(II) Complexes with Tetrachloroterephthalate through the Influence of Different Solvents

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Abstract. The reactions of cobalt acetates with tetrachloroterephthalic acid (H₂BDC-Cl₄) in different solvents gave two polymeric and one mononuclear Co^{II} complexes. X-ray single-crystal structural determination revealed that the ligand BDC-Cl₄ displays a reliable bridging tecton to construct diverse supramolecular architectures through coordinative bonds or secondary hydrogen-bonding interactions. The complexes $[Co(BDC-Cl_4)(DMF)_2(EtOH)_2]_n$ (1) and $\{[Co(BDC-Cl_4)(DMF)_2(DMF)_2(DMF)_n$ (2) demonstrate a one-dimensional (1D)

Introduction

The development of synthetic chemistry brought a great variety of new predesigned polyfunctional ligands in coordination chemistry and materials science with potential applications in optics, magnetism, adsorption, ion exchange and catalysis [1-6]. Equipped with robust and versatile coordination capability, aromatic dicarboxylate and polycarboxylate compounds attracted considerable attention in the preparation of coordination polymers and metallosupramolecular constructions with diverse topologies and permanent porosities [7-10]. Among them, benzene-1,4-dicarboxylic acid (H₂BDC) represents a popular module to build various open frameworks for solvents inclusion and/or gas sorption [11-15]. However, correlated ligands with unfavorable substituents on the phenyl group were investigated by only few documents, for instance the studies on H₂BDC analogues with bulky methyl or halogen groups [11, 14, 16] as well as polymeric supramolecular assemblies regulated by the solvent [16b]. The corresponding research is directed in the aspect of crystal engineering to enhance thermal and chemical stability of the resultant polymeric networks.

Recently, investigations on the solvent effects involved halogen substituted BDC molecules, such as tetrachloroterephthalic acid (H₂BDC-Cl₄) [16b, 17] and tetrabromoterephthalic acid (H₂BDC-Br₄) [18]. H₂BDC-Cl₄ was firstly investigated concerning its coordination chemistry and structural diversification about transition metal ions, such as Mn^{II} [16b], Cu^{II} [17a]

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coordination motif with infinite Co^{II} -tetrachloroterephthalate chains, which are tuned by different binding solvent systems of DMF/ethanol (EtOH) and DMF/methanol (MeOH). [Co(DMF)₂(H₂O)₄]·(BDC-Cl₄) (**3**) represents a two-dimensional (2D) metallosupramolecular network by hydrogen-bonded bridging between the aqua ligand of the mononuclear complex with the uncoordinated BDC-Cl₄ solvates. The spectroscopic, thermal, and fluorescent properties of **1**–**3** were also investigated.

and Co^{II} [17b] ions. Noticeable changes in the structures can arise from subtle differences in experimental conditions. The cobalt ion has a hexacoordinate octahedral arrangement and the combination of Co^{II} and tetrachloroterephthalate involving pyridine solvents is well explained in a recent report [17b]. Since a slightly change of the solvent media can significantly tune the hydrogen-bonding arrays as well as coordination environments, different architectures could be obtained by carrying out the reaction in different solvents. As an ongoing exploration of solvent effects, we consider tetrachloroterephthalate to form complexes with the classical octahedral cobalt(II) ion by employing the DMF entities as main solvent medium, because DMF has been proved to be a versatile guest ligand with variable binding modes and which is undoubtedly a good participant of hydrogen bonds.

In this context, we describe herein the solvent-regulating preparation, structural characterization, and thermal stabilities of three Co^{II} complexes with the ligand H₂BDC-Cl₄, [Co(BDC-Cl₄)(DMF)₂(EtOH)₂]_n (1), {[Co(BDC-Cl₄)(DMF)₂-(MeOH)₂]·2DMF}_n (2), and [Co(DMF)₂(H₂O)₄]·(BDC-Cl₄) (3). The luminescent properties of these complexes were also investigated.

Experimental Section

Materials and General Methods

All reagents and solvents for synthesis and analysis were commercially available and used without further purification, with the exception of the ligand H₂BDC-Cl₄, which was prepared according to the literature procedure [19]. Infrared spectra were recorded with a Nicolet ESP 460 FT-IR spectrometer on KBr pellets in the range of 4000–600 cm⁻¹. Carbon, hydrogen and nitrogen analyses were performed with a PE-



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2400II (Perkin–Elmer) elemental analyzer. Thermogravimetric (TGA) experiments were carried out on a SDT-Q600 (ThermoElectron) DSC-TGA analyzer from room temperature to 800 °C under nitrogen at a heating rate of 10 °C·min⁻¹. Luminescent spectra of **1–3** in the solid state were recorded with a Varian Cary Eclipse spectrometer.

Syntheses of the Co^{II} Complexes

[Co(BDC-Cl₄)(DMF)₂(EtOH)₂]_n (1): A mixture of H₂BDC-Cl₄ (30.4 mg, 0.10 mmol) and Co(OAc)₂·4H₂O (24.9 mg, 0.10 mmol) was dissolved in DMF/EtOH (10 mL, 1:1) whilst stirring for ca. 30 min. Afterwards, the resultant pink solution was filtered. Upon evaporation of the filtrate under ambient conditions, pink prismatic crystals were observed after one week in a yield of 72 % (43.1 mg, on the basis of Co^{II} acetate). Elemental analysis for C₁₈H₂₆Cl₄CoN₂O₈: calcd. C 36.08; H 4.37; N 4.68 %; found: C 36.21; H 4.23; N 4.60 %. **IR**: $\tilde{v} =$ 3527 s, 3131 b, 1650 vs, 1603 s, 1495 w, 1413 s, 1384 s, 1334 vs, 1113 m, 1064 w, 836 m, 798 m, 678 s, 620 s cm⁻¹.

{[Co(BDC-Cl₄)(DMF)₂(MeOH)₂]·2DMF}_n (2): The procedure was similar to that for 1 except that DMF/EtOH was replaced by DMF/MeOH (10 mL, 1:1). Pink block-shaped single crystals of 2 resulted after ten days in a 65 % yield (46.6 mg, on the basis of Co^{II} acetate). Elemental analysis for C₂₂H₃₆Cl₄CoN₄O₁₀: calcd. C 36.84; H 5.06; N 7.81 %; found: C 36.78; H 5.02; N 7.92 %. **IR**: $\tilde{\nu} = 3526$ s, 3125 b, 1650 vs, 1494 w, 1414 s, 1384 m, 1335 vs, 1251 w, 1114 m, 1063 w, 843 m, 798 m, 678 s, 619 s cm⁻¹.

[Co(DMF)₂(H₂O)₄]·(BDC-Cl₄) (3): The procedure was similar to that for **1** except that DMF/EtOH was replaced by DMF/H₂O (10 mL, 1:1), which afforded pink block crystals of **3** in a 48 % yield (27.8 mg, on the basis of Co^{II} acetate). Elemental analysis for C₁₄H₂₂Cl₄CoN₂O₁₀: calcd. C 29.04; H 3.83; N 4.84 %; found: C 29.12; H 3.83; N 4.82 %. **IR**: $\tilde{\nu} = 3527$ s, 3130 b, 1650 vs, 1604 s, 1495 w, 1413 s, 1384 m, 1334 vs, 1251 w, 1113 m, 1064 w, 836 m, 798 m, 678 s, 620 s cm⁻¹.

X-ray Crystallography

X-ray single crystal diffraction data collections for 1–3 were performed with a Bruker Apex II CCD diffractometer at room temperature with Mo- K_{α} radiation ($\lambda = 0.71073$ Å). A semiempirical absorption correction was applied (*SADABS*), and the program *SAINT* was used for integration of the diffraction profiles [20]. All structures were solved by direct methods using *SHELXS* and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares on F^2 with *SHELXL* [21]. In general, hydrogen atoms were located geometrically and allowed to ride during the subsequent refinement. Starting positions of the solvent hydrogen atoms were located in difference Fourier syntheses, and then fixed geometrically with isotropic temperature factors. Further crystallographic data and structural refinement parameters are listed in Table 1. Selected bond lengths and angles are given in Table 2.

Table 2. Selected bond lengths /Å and angles /° for complexes 13.

Bonds		Angles		
1				
Co1–O2	2.0824(11)	O2-Co1-O3	88.16(5)	
Co1–O3	2.1002(13)	O2-Co1-O4	87.75(5)	
Co1–O4	2.1242(12)	O3-Co1-O4	91.87(5)	
2				
Co1–O1	2.0773(11)	O1-Co1-O4	91.29(5)	
Co1–O4	2.0793(13)	O1-Co1-O3	91.65(5)	
Co1–O3	2.1267(12)	O4-Co1-O3	90.69(5)	
3				
Co1–O3	2.0257(12)	O3-Co1-O4	90.82(5)	
Co1–O4	2.1291(12)	O3-Co1-O5	88.45(5)	
Co1–O5	2.1480(12)	O4-Co1-O5	86.79(5)	

Crystallographic data (excluding structure factors) for the crystal structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center. Copies of the data can be obtained on

Table 1. Crystallographic data and structure refinement for complexes 1-3.

	1	2	3		
Formula	C ₁₈ H ₂₆ Cl ₄ CoN ₂ O ₈	C ₂₂ H ₃₆ Cl ₄ CoN ₄ O ₁₀	C ₁₄ H ₂₂ Cl ₄ CoN ₂ O ₁₀		
Mr	599.14	717.28	579.07		
Cryst system	Triclinic	Triclinic	Triclinic		
Space group	$P\overline{1}$	$P\overline{1}$	$P\bar{1}$		
Crystal size /mm	$0.22 \times 0.20 \times 0.16$	$0.24 \times 0.22 \times 0.18$	$0.25 \times 0.22 \times 0.17$		
a /Å	9.0573(11)	8.4499(14)	5.7811(15)		
b /Å	9.1021(11)	9.1077(15)	8.587(2)		
c /Å	9.9793(12)	11.4214(19)	12.087(3)		
α /°	64.2770(10)	90.705(2)	95.720(3)		
β /°	82.4490(10)	105.211(3)	102.039(3)		
γ /°	61.3530(10)	107.235(2)	98.720(3)		
$V/Å^3$	647.38(14)	806.2(2)	574.7(3)		
Z	1	1	1		
$D_{\rm calc} / \text{g-cm}^{-3}$	1.537	1.477	1.673		
μ / mm^{-1}	1.119	0.918	1.263		
<i>F</i> (000)	307	371	295		
Reflections, collected/unique	5074/2516	5825/2822	4995/2605		
Parameters	154	192	144		
R _{int}	0.0208	0.0191	0.0279		
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0268, wR_2 = 0.0801$	$R_1 = 0.0250, wR_2 = 0.0767$	$R_1 = 0.0273, wR_2 = 0.0794$		
Goodness-of-fit on F^2	1.101	1.049	1.083		
Max. res. peak and hole $/e \cdot Å^{-3}$	0.340 and -0.348	0.268 and -0.284	0.324 and -0.437		

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Results and Discussion

Synthesis and General Characterizations

DMF was proven to be a reliable binding guest molecule when coordinating to Mn^{II} and Cu^{II} ions [16b, 17]. Its coordination ability is better than that of MeOH. EtOH, and also the aqua ligand in mixed solvent media. In this work, we initiate the combination of cobalt(II) and tetrachloroterephthalate in three different solvent mixtures, namely DMF/EtOH, DMF/ MeOH, and DMF/H₂O (with each of the two components in equivalent amount). Three resultant Co^{II} complexes could be isolated through the same procedure by alternating the starting metal salts with Co(OAc)₂, Co(ClO₄)₂, Co(NO₃)₂, and CoCl₂ (confirmed by IR spectra and elemental analyses), which indicates that in these systems the final products are independent of the counteranions. In the IR spectra, the broad bands centered at ca. 3130 cm⁻¹ indicate the O-H stretching of solvents. The absence of characteristic absorption bands (at ca. 1720 cm⁻¹) of the carboxyl moiety in 1-3 suggests complete deprotonation. The difference between the $v_{as}(COO^{-})$ and $v_{sym}(COO^{-})$ indicates the monodentate coordination mode of each carboxylate group in 1 and 2.

Descriptions of Crystal Structures for Complexes 1-3

 $[Co(BDC-Cl_4)(DMF)_2(EtOH)_2]_n$ (1) and $\{[Co(BDC-Cl_4)(DMF)_2(MeOH)_2] \cdot 2DMF\}_n$ (2)

X-ray diffraction analysis revealed that both complexes 1 and 2 crystallize in the triclinic space group $P\bar{1}$ with analogous 1D polymeric coordination chain motifs (Figure 1 and Figure 2). The basic coordination frameworks of them are similar, except that the coordinated guest molecules are DMF/ethanol in complex 1 and DMF/methanol in complex 2. Different sizes and shapes of binding alcohol molecules lead to the fact that there are no free guests in 1 but lattice DMF molecules in 2.

In the asymmetric unit of 1, each Co^{II} atom is located at an inversion center [at (0, 1/2, 1/2)] and coordinated by six oxygen atoms coming from a pair of carboxylate groups of two centrosymmetric BDC-Cl₄ ligands, two DMF, and two ethanol guest molecules (Figure 1a). The coordination sphere around Co^{II} could be appropriately illustrated as a nearly ideal octahedron, with Co-O bond lengths in the range 2.0824(11) to 2.1242(12) Å. In each centrosymmetric BDC-Cl₄ molecule, the rotation angle (φ_{rot}) between the tetrachlorinated phenyl ring and the carboxylate group is $86.0(2)^\circ$; it adopts a nearly perpendicular fashion due to the steric effect, which is similar to the one of other carboxylate compounds with polychlorinated backbone [16b, 22]. As expected, the bond length of carboxylate C1–O2 [1.256(2) Å] is slightly longer than that of C1-O1 [1.233(2) Å] because of its monodentate coordination mode. As illustrated in Figure 1a, the Co^{II} ions are linked by



Figure 1. (a) Polymeric chain motif of **1** with the asymmetric unit and Co^{II} coordination environment labeled. Symmetry code: i, -x, -y+1, -z+1. (b) Polymeric chain motif of **2** with the asymmetric unit and Co^{II} coordination environment labeled. Symmetry code: i, -x+1, -y+2, -z+2. (c) Perspective view of the host/guest system in **2** with DMF guest molecules highlighted in dark grey.

the bis-monodentate BDC-Cl₄ spacer into a linear chain running along the $[1\overline{1}1]$ direction with adjacent Co···Co separation of 11.416(1) Å. Intramolecular hydrogen-bonding interaction was formed between the uncoordinated carboxylate atom O1 and the ligated EtOH molecule (O4–H4···O1ⁱ, H4···O1ⁱ, and O4···O1ⁱ distances of 1.81 and 2.626(2) Å, respectively; angle of 161°; symmetry code: i = -x, -y+1, -z+1, see Table 3). Additionally, no further hydrogen-bonding interactions were found in the crystal packing of 1.

As for compound **2**, the asymmetric unit contains one Co^{II} ion lying on an inversion center [at (1/2,1,1)], one centrosymmetric BDC-Cl₄ ligand, one coordinated DMF molecule and one coordinated methanol molecule, as well as one DMF guest molecule. A similar hexacoordinate arrangement of the Co^{II} atom also revealed nearly ideal octahedral coordination. Within the BDC-Cl₄ ligand, the carboxylate groups deviate from the Cl₄-substituted phenyl ring with a dihedral angle of 82.7(5)°,



Figure 2. (a) Molecular structure of **3** with the asymmetric unit and Co^{II} coordination environment labeled. Symmetry code: i, -x + 1, -y + 1, -z + 2. (b) Hydrogen-bonding layer of **3** along the *ac* plane.

Table 3. Possible hydrogen-bonding arrangements in the crystal structures of 1-3.

D–H•••A	D····A /Å	H•••A /Å	D−H•••A /°	Symmetry code
04–H4•••O1	2.626(2)	1.81	161	-x, -y+1, -z+1
O3–H3A…O2	2.615(2)	1.81	167	
С5-Н5•••О5	3.404(2)	2.55	153	
С6-Н6А•••О5	3.427(3)	2.52	157	
O3–H3A…O2	2.602(2)	1.79	173	-x+1, -y+1, -z+2
O3-H3B···O1	2.710(2)	1.90	170	-x+2, -y+1, -z+2
04–H4A…01	2.675(2)	1.87	167	-
O4–H4B•••O5	3.007(2)	2.33	140	- <i>x</i> +2, - <i>y</i> +1, - <i>z</i> +2

because of the steric effect that affords monodentate coordination modes. The final 1D coordination motif joined by bismonodentate BDC-Cl₄ spacers runs along the crystallographic [001] direction with the adjoining Co···Co distance of 11.422(2) Å (Figure 1b). Intramolecular O3–H3A···O2 (Table 3) interaction was found between the uncoordinated carboxylate atom and the ligated MeOH molecule to stabilize the resultant coordination structure, as the O4–H4···O1 bond in the complex 1. These coordination chains align parallel along *a* axis, leaving 251.1 Å³ interchain space (31.1 % of the unit cell volume) to accommodate DMF guest molecules (Figure 1c) [23] Notably, the DMF guest moieties are anchored to the coordination chain through hydrogen-bonding to the coordinated DMF molecules through C5–H5···O5 and C6–H6A···O5 bonds (Table 3).

$[Co(DMF)_2(H_2O)_4] \cdot (BDC-Cl_4)$ (3)

The molecular structure of 3, which is shown in Figure 2a, is made up of a discrete $[Co(DMF)_2(H_2O)_4]^{2+}$ cationic unit and a BDC-Cl₄ anion. Two DMF and four agua molecules surround the Co^{II} ion to form a nearly ideal octahedron with the metal ion lying on an inversion center at (1/2, 1/2, 1) and the Co–O bond lengths are in the range 2.0257(12)-2.1480(12) Å. In this case, the uncomplexed tetrachloroterephthalate with the inversion center at (1,1/2,1/2) is fully deprotonated for charge balance. Additionally, it acts as a secondary acceptor to the cationic complex unit with participation in multiple O-H···O interactions, which lead to an extended 2D supramolecular array. As indicated in Figure 2b, each $[Co(DMF)_2(H_2O)_4]^{2+}$ moiety generates a pair of Owater-H···Ocarboxylate contacting with two neighboring tetrachloroterephthalate anions to afford a 1D hydrogen-bond tape, including a $R_2^2(8)$ hydrogen-bonding pattern $[O4-H4A\cdots O1 \text{ and } O3-H3A\cdots O2^{i}]$, (symmetry code: i = -x + 1, -y + 1, -z + 2] [24]. As a result, adjacent Co--Co separation within each 1D supramolecular array is 14.421(2) Å, which is significantly longer that the values in complexes 1 and 2. Another two hydrogen-bonded interactions $(O3-H3B\cdots O1^{ii})$ and $O4-H4B\cdots O5^{ii}$, symmetry code: ii = -x + i2, -y + 1, -z + 2), forming a hydrogen-bonding model of $R_3^3(8)$ graphic set by the combination of O4-H4A···O1 bond [24], join the neighboring 1D motif into a (4,4) topologic supramolecular net if the cationic units are considered as nodes and the anionic units are considered as linkers. No significant evident shows there are other weak interactions, such as hydrogenbonding and aromatic interactions, between adjacent layers.

Structural Comparison of the Supramolecular Networks on the Basis of Different Coordinated Guests

In virtue of solvent-tuning strategy, three Co^{II} complexes with different binding guest molecules were synthesized and crystallographically characterized. Complexes 1 and 2 adopt a 1D linear coordination motif, whereas complex 3 is a mononuclear complex and represents furthermore, a metallosupramolecular assembly with 2D hydrogen-bonding network through the recognition between anionic acids and discrete Co^{II} solvates is formed. As for previously reported manganese(II) coordination polymers, the ligand H₂BDC-Cl₄ ligand exhibits different binding modes and allows further engineering of the dimensionality of the coordination networks with variable auxiliary solvent co-ligands. In the cases of copper(II) coordination polymers, the arrangement of the Cu^{II} atom with varying coordination mode (from four to six) because of Jahn-Teller effect, is responsible for the structural diversification besides the influence of binding-guests. In this work, the Co^{II} coordination modes always represent a typical octahedron. The solvent systems vary from DMF/EtOH (in 1), DMF/MeOH (in 2) to DMF/H₂O (in 3), and each participating solvent can work as a binding guest molecule. The BDC-Cl₄ anion forms two coordination polymers, 1 and 2, respectively, with nearly similar recognition patterns by only varying the alcohol solvent factor. Different sizes of the alcohol molecules cause no free guests in 1 but the inclusion of DMF molecules in 2. Unlikely, the assemblies of 1 and 2 are totally dissimilar compared with a previous reported Co^{II} polymer Co(BDC)(DMF) (BDC = terephthalate) [25], which was also obtained from a mixed DMF/ EtOH solvent system. The complex mentioned above has a doubly bridging oxygen bound DMF ligand and a bis-bidentate BDC ligand, thus the final 3D net of the structure has **sra** topology. In the case of complex **3**, the BDC-Cl₄ anion does not coordinate to Co^{II} ions but gives a metallosupramolecular aggregate. The reaction of the unsubstituted BDC ligand and Co^{II} ions in DMF/H₂O yielded a similar 1D polymeric chain like those found in compounds **1** and **2** [26].

Thermal Stability

To investigate thermal stabilities of complexes 1-3, Thermogravimetric measurements were carried out from room temperature to 800 °C. The corresponding curves are depicted in Figure 3. The TG curve of 1 shows that the first two weight losses from 80 to 200 °C were assigned to be the removal of coordinated DMF molecules (calcd. 24.4 %; found 25.6 %) at 86 and 101 °C. The following weight loss in the temperature range of 144 to 360 °C indicates the decomposition of vague components with a peak at 338 °C. Afterwards, slow pyrolysis of the residual fragment continued from 360 °C and did not end even when heated to 800 °C. For the TG plot of 2, the weight loss of 20.7 %, which occurred from 60 to 200 °C with a peak at 82 °C, clearly corresponds to the release of DMF solvents (calcd. 20.4 %). Afterwards, a sharp weight loss was observed in the temperature range of 250–375 °C with a peak at 344 °C, which indicates collapse of the remaining framework. Similar sluggish weight loss as that of 1 took place from 360 °C and did not end at 800 °C.



Figure 3. TG curves of 1–3.

Surprisingly, in the case of complex **3**, the release of coordinated DMF subunits happened earlier than the loss of uncoordinated BDC-Cl₄ molecules, probably because of the robust hydrogen bonds between coordinated water molecules and BDC-Cl₄ moieties. The corresponding weight loss of DMF (calcd. 25.2 %; found 25.3 %) occurred in the temperature



range 90 to 220 °C with a peak at 123 °C, which was followed by a series of weight losses of uncoordinated BDC-Cl₄ moieties and coordinated water ligands that did not end until heating to 800 °C.

Luminescent Properties

Hybrid inorganic-organic frameworks have received attention as materials capable of excellent photoluminescent properties since the complexation of organic ligands and metal ions may induce the enhancement, shift, and quench of the photoluminescence compared to those exhibited by the free organic ligands. In this work, the luminescent properties of complexes 1-3 in the solid state were investigated at room temperature. The emission spectra of complexes 1 and 2, as well as the sodium salt of H₂BDC-Cl₄, under excitation of ca. 340 nm are shown in Figure 4. For complex 3, the initial luminescence of Na₂BDC-Cl₄ was guenched after metal complexation as result of multiple water ligands and vigorous hydrogen-bonding interaction between water and aromatic molecules. One strong and one weak emission peak at 478 and 517 nm, respectively, were observed in the emission spectrum of Na2BDC-Cl4 in the solid state. Significantly, complexes 1 and 2 have similar emission maxima of 489 and 500 nm, respectively. The emission spectra show little red-shift and shape-dissimilar compared with that of free BDC-Cl₄ ligand, but they are in agreement with those of the previously reported Cu^{II}-BDC-Cl₄ polymers [17a].



Figure 4. Solid-state emission and excitation (inset) spectra of 1 and 2 at room temperature.

Conclusions

We designed and characterized three novel cobalt coordination compounds based on the deliberate choice of BDC-Cl₄ ligand and diverse solvents. All complexes have an octahedral arrangement at the Co^{II} atom. The BDC-Cl₄ molecule serves as a bis-monodentate ligand to bridge adjacent metal atoms into one-dimensional infinite chains, as found in either 1 or 2 with the binding solvents DMF/EtOH or DMF/MeOH. In the case of 3, binding DMF/H₂O solvent molecules afford the combination of the mononuclear Co^{II} complex with uncoordinated BDC-Cl₄ counterions. Different types of coordination linkages by carboxylate groups with the variation of coordinated solvent molecules lead to the creation of different supramolecular aggregations in complexes 1–3. The shapes of the binding solvents are reduced from 1 to 2, in agreement with the increase in void volume for solvent guest molecules (none for 1, and DMF for 2). This result gives a new challenge in the rational design of solvent-regulated polymeric complexes.

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