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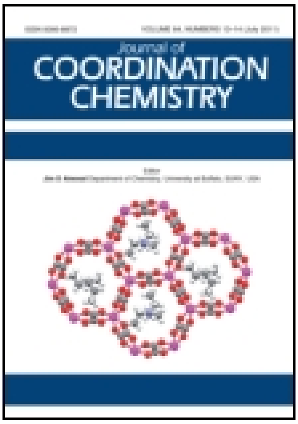

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Syntheses, crystal structures, and electrochemical properties of two cobalt complexes constructed with benzene tricarboxylates and 2,5-bipyridyl-1,3,4-oxadiazole

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Syntheses, crystal structures, and electrochemical properties of two cobalt complexes constructed with benzene tricarboxylates and 2,5-bipyridyl-1,3,4-oxadiazole

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Two new cobalt complexes based on benzene tricarboxylates 1,2,4-H_3BTC (1,2,4-H_3BTC = 1,2,4-benzenetricarboxylate) or 1,3,5-H_3BTC (1,3,5-H_3BTC = 1,3,5-benzenetricarboxylate), and the bent dipyridyl ligand 2,5-bis(3-pyridyl)-1,3,4-oxadiazole (3-bpo) or its 4-pyridyl *N*-donor analog (4-bpo), formulated as $[Co(1,3,5\text{-}BTC)(4\text{-}bpo)(H_2O)_3]_2[Co(H_2O)_6] \cdot 10H_2O$ (**1**) and $[Co_3(1,2,4\text{-}BTC)_2(3\text{-}bpo)_2(H_2O)_{12}]$ (**2**), have been hydrothermally synthesized and characterized by elemental analyses, IR spectroscopy, TG analyses, and single-crystal X-ray diffraction. Structure analysis reveals that **1** is a 3-D porous supramolecular network based on the 1-D polymer chain $[Co(1,3,5\text{-}BTC)(4\text{-}bpo)(H_2O)_3]_{2n}^{2n-}$, in which discrete $[Co(H_2O)_6]^{2+}$ units and lattice water molecules are dispersed. In **2**, bridging 3-bpo and 1,2,4-BTC connect cobaltions to form a trinuclear cobalt unit. Adjacent trinuclear cobalt units are further linked by π–π stacking interactions and hydrogen-bonding interactions to form a 3-D supramolecular framework. Electrochemical properties of cobalt(II) compounds bulk-modified carbon paste electrodes (**1**-CPE and **2**-CPE) have been studied.

Keywords: Cobalt compounds; Hydrothermal syntheses; Crystal structures; Electrochemical properties

1. Introduction

Rational syntheses of supramolecular coordination compounds are of great importance for developing new crystalline materials due to their promising applications in host–guest chemistry, catalysis, luminescence, and magnetism [1–4]. Judicious selection of ligands is a key factor because structural changes of organic building blocks such as length, flexibility, and symmetry can dramatically change structural motifs of these compounds. Aromatic polycarboxylates, such as 1,4-benzenedicarboxylate (1,4-H_2BDC), 1,3,5-benzenetricarboxylate (1,3,5-H_3BTC) and 1,2,4,5-benzenetetracarboxylate (1,2,4,5-H_4btec), have been popular choices of bridging ligands, not only as hydrogen-bond acceptors but also as hydrogen-bond donors for constructing high-dimensional supramolecular coordination compounds [5–8]. A series of coordination compounds with diverse topologies and interesting properties have been prepared based on these aromatic polycarboxylates [9–13].

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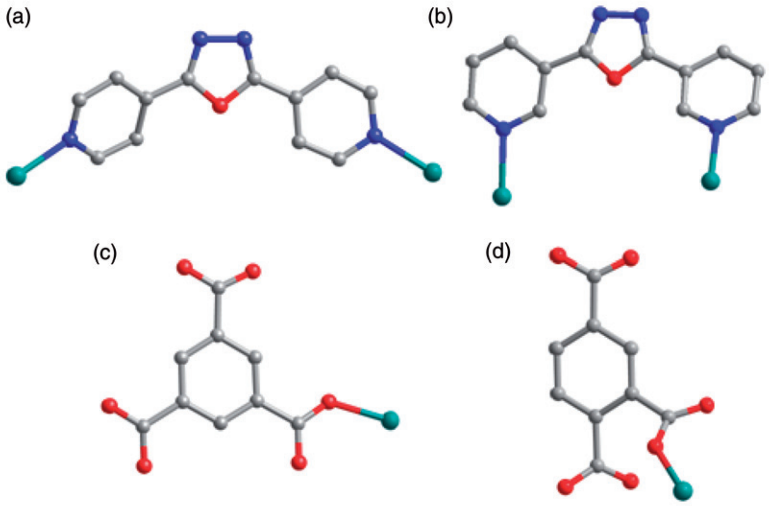

Scheme 1. Coordination modes of: (a) 4-bpo, (b) 3-bpo, (c) 1,3,5-BTC, and (d) 1,2,4-BTC in **1** and **2**.

Bent dipyridyl ligands, 2,5-bis(3-pyridyl)-1,3,4-oxadiazole (3-bpo) and 2,5-bis(4-pyridyl)-1,3,4-oxadiazole (4-bpo), can adopt different conformations according to the geometric requirements of different metals to construct polymers/supramolecules [14–17]. Coordination systems with both 3-bpo/4-bpo and aromatic polycarboxylates are quite rare [11, 18–21]. We prepared a 3-D cobalt complex based on 3-bpo and 1,3,5-H_3BTC, in which 3-bpo shows three different coordination modes [11]. As an extension of our previous work, we have focused on assembly of benzene tricarboxylates with metal cobalt *via* hydrothermal synthetic methods in various auxiliary ligands. In this article, 3-bpo and 4-bpo, as auxiliary ligands (scheme 1), possess relatively flexible conformation because of their ability to freely rotate, and the 1,3,4-oxadiazole groups may lead to the formation of hydrogen bonding interactions. We obtained two new cobalt coordination compounds with 3-bpo/4-bpo and benzene tricarboxylates (1,2,4-H_3BTC = 1,2,4-benzenetricarboxylate or 1,3,5-H_3BTC) as ligands: $[Co(1,3,5\text{-}BTC)(4\text{-}bpo)(H_2O)_3]_2[Co(H_2O)_6]\cdot 10H_2O$ (**1**) and $[Co_3(1,2,4\text{-}BTC)_2(3\text{-}bpo)_2(H_2O)_{12}]$ (**2**). Electrochemical behaviors for bulk-modified carbon paste electrodes (CPEs) of the two complexes have been examined.

2. Experimental

2.1. *Materials and methods*

All reagents were commercially available and used as received. 4-bpo and 3-bpo were synthesized by the literature method [22]. FT-IR spectra (KBr pellets) were taken on a Magna FT-IR 560 Spectrometer and elemental analyses (C, H, and N) were carried out on a Perkin-Elmer 240 C elemental analyzer. TG analyses were carried out with a Pyris Diamond TG-DTA instrument. Electrochemical experiments were carried out using a CHI 440 Electrochemical Quartz Crystal Microbalance. A conventional three-electrode cell was used at room temperature. The bulk-modified CPEs (**1**-CPE and **2**-CPE) were used as working electrodes. An SCE and a platinum wire were used as reference and auxiliary electrodes, respectively.

2.2. *Syntheses*

2.2.1. Synthesis of $[Co(1,3,5\text{-}BTC)(4\text{-}bpo)(H_2O)_3]_2[Co(H_2O)_6]\cdot 10H_2O$ (1). A mixture of $CoCl_2\cdot 2H_2O$ (0.047 g, 0.2 mmol), 1,3,5-H_3BTC (0.025 g, 0.12 mmol), 4-bpo (0.045 g, 0.2 mmol), H_2O (12 mL), and NaOH (0.017 g, 0.43 mmol) was stirred for 30 min in air, then transferred and sealed in a 25 mL Teflon reactor, which was heated at 120°C for 4 days leading to orange block crystals of **1**, washed by water, ethanol and dried in air. Yield: ~21% (based on Co). Anal. Calcd for $C_{42}H_{66}N_8O_{36}Co_3$ (%): C, 35.10; H, 4.63; N, 7.80. Found (%): C, 35.19; H, 4.55; N, 7.86. IR (KBr, cm^{-1}): 3398 s, 3218 m, 2357 m, 2323 m, 1616 s, 1552 s, 1490w, 1427 s, 1344 s, 1274w, 1177 m, 1094 m, 1059w, 1011 m, 838 m, 768 s, 715 s, 672 m, 539w, 505w.

2.2.2. Synthesis of $[Co_3(1,2,4\text{-}BTC)_2(3\text{-}bpo)_2(H_2O)_{12}]$ (2). Compound **2** was prepared by hydrothermal reaction of $CoCl_2\cdot 2H_2O$ (0.047 g, 0.2 mmol), 1,2,4-H_3BTC (0.025 g, 0.12 mmol), 3-bpo (0.023 g, 0.1 mmol), H_2O (12 mL), and NaOH (0.019 g, 0.47 mmol). The mixture was stirred for 30 min in air, then transferred and sealed in a 25 mL Teflon reactor, which was heated at 120°C for 4 days leading to formation of pink block crystals of **2** (~29% yield based on Co). Anal. Calcd for $C_{42}H_{46}N_8O_{26}Co_3$ (%): C, 40.14; H, 3.69; N, 8.92. Found (%): C, 40.22; H, 3.52; N, 8.82. IR (KBr, cm^{-1}): 3405 s, 3086w, 2364 m, 2335 m, 1705 s, 1614 s, 1537 s, 1482 m, 1434 s, 1357 s, 1246 s, 1170 m, 1103 m, 1052w, 1011w, 845w, 747 m, 705 s, 670 s, 518 m.

2.3. *Preparation of bulk-modified CPEs*

The title compounds bulk-modified CPEs were fabricated as follows: 0.5 g graphite powder and 0.031 g **1** (or **2**) were mixed and ground together by agate mortar and pestle for 20 min; to this mixture 0.18 mL paraffin oil was added and stirred with a glass rod; then the homogenized mixture was used to pack 3 mm inner diameter glass tubes. The electrical contact was established with a copper stick, and the CPEs were wiped with weighing paper. The same procedure was used for preparing bare CPE without cobalt compound.

2.4. *X-ray crystallographic study*

Crystallographic data for **1** and **2** were collected at 293(2) K on a Bruker Smart 1000 CCD diffractometer with Mo-Kα ($\lambda = 0.71073$ Å) by ω scan mode. The structures were solved by direct methods using SHELXS of the SHELXTL package and refined by full-matrix least-squares with SHELXL [23, 24]. Metals were located from the *E*-maps, and all non-hydrogen atoms were refined anisotropically. Hydrogens of the ligand were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. A summary of crystal data and structure refinement for the two cobalt

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

Formula	$C_{42}H_{66}Co_3N_8O_{36}$	$C_{42}H_{46}Co_3N_8O_{26}$
Formula weight	1435.82	1255.66
Crystal system	Monoclinic	Triclinic
Space group	$P21/c$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	6.8766(4)	6.8679(5)
b	20.0531(12)	10.3470(8)
c	20.8273(12)	17.3560(13)
α	90	90.3500(10)
β	95.478(1)	95.3340(10)
γ	90	102.6250(10)
Volume (Å^3), Z	2858.9(3), 2	1197.88(16), 1
Calculated density (g cm^{-3})	1.668	1.741
Absorption coefficient (mm^{-1})	0.971	1.131
$F(000)$	1486	643
θ_{max} (°)	24.99	25.00
R_{int}	0.0513	0.014
R_1^a $[I > 2\sigma(I)]$	0.0392	0.0302
wR_2^b (all data)	0.1038	0.0815
Good-of-fit on F^2	1.029	1.034
$\Delta\rho_{max}$ (e Å^{-3})	0.39	0.38
$\Delta\rho_{min}$ (e Å^{-3})	−0.53	−0.35

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

compounds are provided in table 1. Selected bond lengths and angles are listed in tables S1 and S2. Hydrogen-bonding geometries are summarized in tables S3 and S4. IR spectra of **1** and **2** are shown in figures S3 and S4.

3. Results and discussion

3.1. *Synthesis*

Many factors affect crystallization and structural construction of the products in the hydrothermal process, such as initial reactants, reactant ratio, and pH. We obtained $[Co_3(1,3,5\text{-BTC})_2(3\text{-bpo})_3(H_2O)_2] \cdot 5.25H_2O$, which presents the first example of a 3-D coordination polymer constructed from 3-bpo simultaneously showing three different coordination modes [11]. In order to investigate the effect of different reaction conditions on the hydrothermal system, we chose different auxiliary ligands, adjusting the reactant ratio and systematic pH. Under similar condition to that of reference 11, we expected that using 4-bpo in place of 3-bpo would lead to the similar complex as reference 11; however, we failed to isolate the expected single crystal. Only when the reactant ratio (Co: 1,3,5-BTC:4-bpo) was adjusted to 2 : 1.2 : 2 (in reference 11 the ratio of Co: 1,3,5-BTC:3-bpo is 2 : 1.2 : 1), we obtained **1**, whose structure is different from that of $[Co_3(1,3,5\text{-BTC})_2(3\text{-bpo})_3(H_2O)_2] \cdot 5.25H_2O$. To further investigate the structural diversity tuned by different bridging ligands, we extended our studies from 1,3,5-H_3BTC to 1,2,4-H_3BTC. Changing from 1,3,5-H_3BTC to 1,2,4-H_3BTC and adjusting the pH and temperature, **2** was obtained, which may be because the synthesis of the compound is affected not only by the stoichiometries of the reactants but also by the pH of the reaction media, and types of co-ligands in the reaction medium [25, 26].

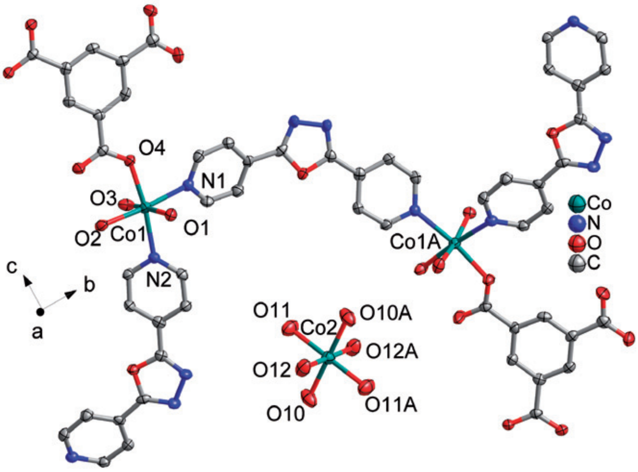

Figure 1. ORTEP showing the coordination environment for Co^{II} in **1** (at 30% probability level).

3.2. *Structure descriptions*

Aromatic tricarboxylates construct coordination polymers with metals by adopting various coordination modes [7, 27], due to complete or partial deprotonation of their carboxyl groups. In this article, both 1,3,5-H_3BTC and 1,2,4-H_3BTC adopted monodentate coordination (only one carboxyl of the tricarboxylates coordinated to Co^{II}) in **1** and **2** (scheme 1c and d); 4-bpo or 3-bpo only adopted one bridging coordination mode (scheme 1a and b).

3.2.1. [Co(1,3,5-BTC)(4-bpo)(H_2O)$_3$]$_2$[Co(H_2O)$_6$] • 10H_2O (1). Compound **1** is a 3-D supramolecular network constructed from 1-D $[Co(1,3,5\text{-}BTC)(4\text{-}bpo)(H_2O)_3]_{2n}^{2n-}$ and mononuclear cobalt building units $[Co(H_2O)_6]^{2+}$. As shown in figure 1, the fundamental building unit of the crystal structure for **1** is composed of two kinds of crystallographical independent Co^{II} ions [Co(1) and Co(2)]. Both Co^{II} ions have distorted octahedral geometry. Co(1) ion is coordinated by three oxygen atoms from three coordinated water molecules (Co–O distances of 2.109(2)–2.139(2) Å), one oxygen atom of carboxylate of 1,3,5-BTC ligand [Co(1)–O(4), 2.107(2) Å], and two nitrogen atoms of pyridyl groups from two 4-bpo ligands (2.154(2) [Co(1)–N(1)] and 2.162(2) Å [Co(1)–N(2)]). Co(2) is $[Co(H_2O)_6]^{2+}$, coordinated by six oxygen atoms [O(10), O(11), O(12), O(10 A), O(11 A), O(12 A)] of water with distances of 2.044(2)–2.092(2) Å.

Asymmetric tricarboxylates have been used to bind metal centers in different coordination modes to construct metal–organic frameworks with intriguing topologies. For example, $[Co_3(nbtb)_2(bpe)_3(H_2O)_2]_2 \cdot H_2O$ (nbtb = 5-nitro-1,2,3-benzenetricarboxylic acid, bpe = 1,2-bi(4-pyridyl)ethene) exhibits a 3-D (4,5)-connected motif containing $(4^2 \cdot 6^7 \cdot 8)(4^2 \cdot 6^7 \cdot 8)(6^4 \cdot 8^2)(4^2 \cdot 6^4)$ topology [7]. In the 3-D metal–organic framework of $[Co_3(1,3,5\text{-}BTC)_2(3\text{-}bpo)_3(H_2O)_2] \cdot 5.25H_2O$, all of the carboxylates of 1,3,5-BTC ligand coordinate to Co^{II} with chelating-bidentate-monodentate coordination [11]. In this article 1,3,5-BTC is monodentate for **1** (scheme 1c) with only one carboxyl coordinated with Co^{II}. Adjacent Co(1) ions are linked by bridging bidentate 4-bpo (scheme 1a) to form a 1-D wave polymer chain, as shown in figure 2. The π–π

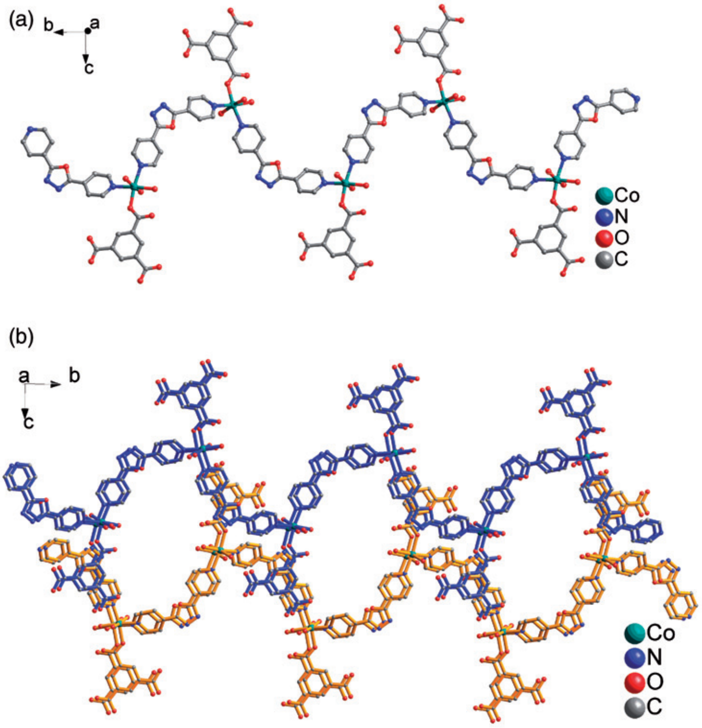

Figure 2. (a) 1-D polymeric chain of **1** along the *b*-axis; (b) 3-D supramolecular framework with channels constructed from 1-D chains by π–π stacking interactions (all hydrogen atoms, $[Co(H_2O)_6]^{2+}$ and lattice water molecules are omitted for clarity).

stacking interaction between aromatic rings of 1,3,5-BTC ligands and the 1,3,4-oxadiazole rings of 4-bpo ligands with centroid-to-centroid distance *ca* 3.63 Å (the dihedral angle of 0.20°) links adjacent polymer chains to construct a 3-D supramolecular framework with elliptical channels (*ca* 22.13 × 12.89 Å) (figure 2b and figure S1). The $[Co(H_2O)_6]^{2+}$ and lattice water molecules are encapsulated in channels of the 3-D supramolecular framework (figure 3). Stability of the 3-D framework is strengthened by hydrogen-bonding interactions between the carboxylate oxygen atoms and oxygen atoms of coordinated water [O1–H1B $\cdots$ O9 (x, $1/2 - y$, $-1/2 + z$) = 1.93 Å, O1 $\cdots$ O9 = 2.772(3) Å; O1–H1C $\cdots$ O6 ($1 - x$, $1 - y$, $1 - z$) = 1.85 Å, O1$\cdots$O6 = 2.699(3) Å, O2–H2B $\cdots$ O8 (x, $1/2 - y$, $-1/2 + z$) = 1.90 Å, O2$\cdots$O8 = 2.730(3) Å; O3–H3C $\cdots$ O8 ($-1 + x$, $1/2 - y$, $-1/2 + z$) = 1.90 Å, O3$\cdots$O8 = 2.975(4) Å].

3.2.2. $[Co_3(1,2,4\text{-}BTC)_2(3\text{-}bpo)_2(H_2O)_{12}]$ (2). Compound **2** is a 3-D supramolecular network based on trinuclear cobalt units composed of bridging 3-bpo and 1,2,4-BTC. The coordination environment of Co^{II} is shown in figure 4. In the trinuclear cobalt unit, there are two crystallographical independent Co^{II} ions [Co(1) and Co(2)]. Co(1) is coordinated by one nitrogen atom from a 3-bpo with Co(1)–N(1) distance of 2.1401(19) Å, one oxygen atom of carboxylate of 1,2,4-BTC (the distance: Co(1)–O(1), 2.0523(15) Å), and four oxygen atoms from four coordinated water molecules

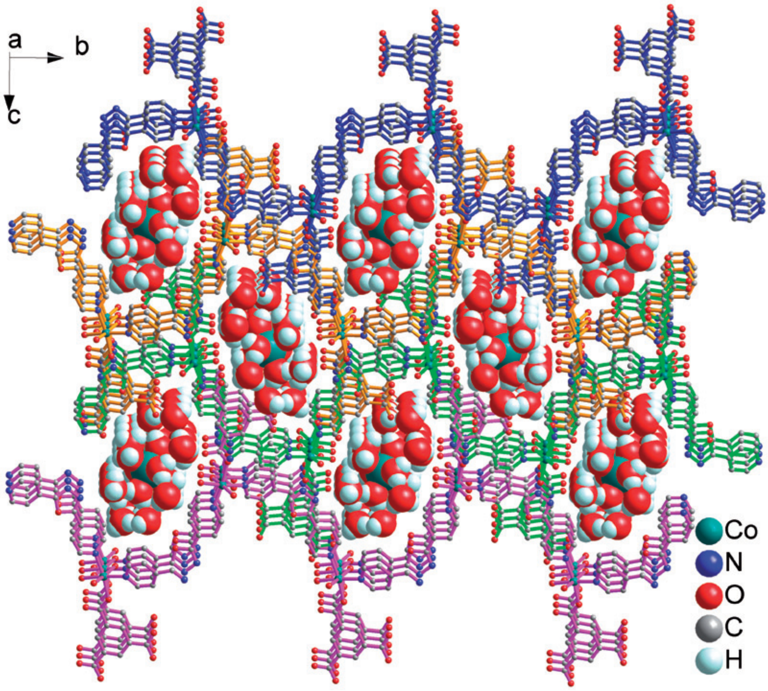

Figure 3. The 3-D packing structure of **1** containing lattice water and $[Co(H_2O)_6]^{2+}$ (part of the hydrogen atoms are omitted for clarity).

with Co(1)–O distances of 2.045(2)–2.090(2) Å, showing a six-coordinate environment.

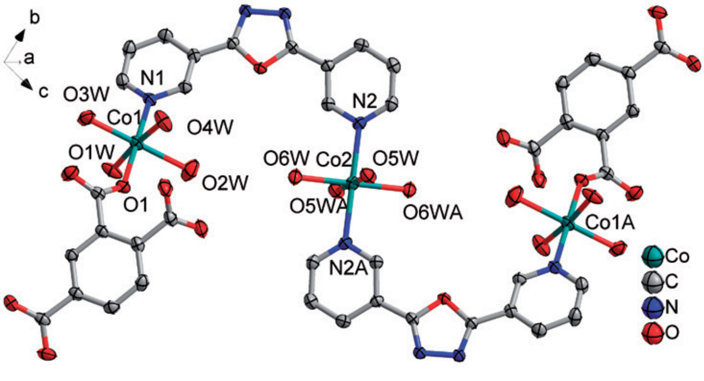

Figure 4. ORTEP showing the coordination environment for Co^{II} in **2** (at 30% probability level).

Only one carboxylate of 1,2,4-BTC displays monodentate coordination (scheme 1 d), similar to 1,3,5-BTC in **1**. Co(2) is six-coordinate from four oxygen atoms [O(5 W), O(5WA), O(6 W), O(6WA)] of four coordinated water molecules (2.0801(19)–2.1066(18) Å and O–Co(2)–O angle 180.0°), two nitrogen atoms from pyridyl groups of two bridging 3-bpo with Co–N distance of 2.1782(18) Å [Co(2)–N(2), Co(2)–N(2 A)]

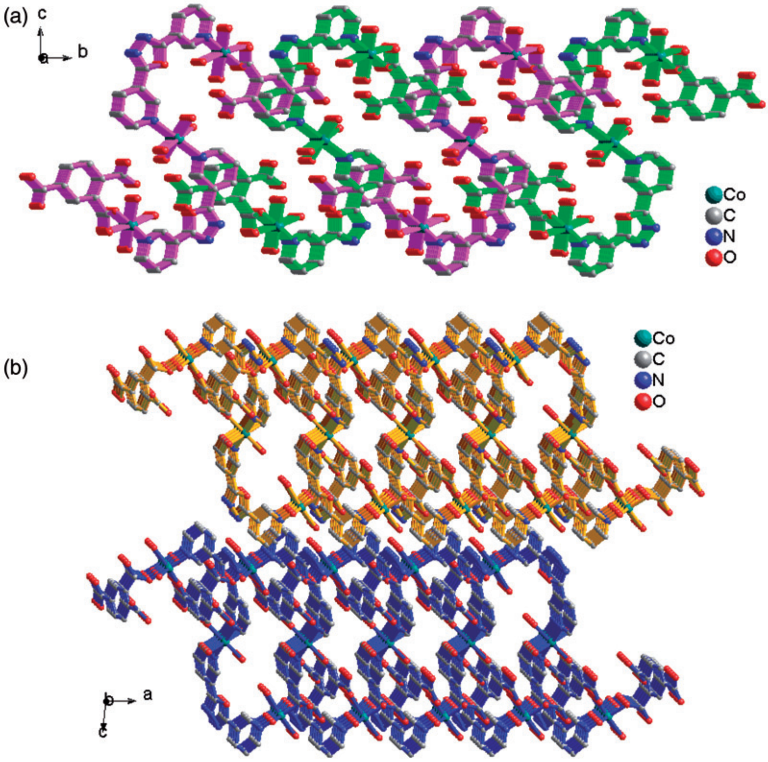

Figure 5. (a) 2-D supramolecular layer of **2** along the *b*-axis by π–π stacking interactions (all hydrogen atoms and lattice water molecules are omitted for clarity); (b) 3-D supramolecular network of **2** (all hydrogen atoms are omitted for clarity).

and N–Co(2)–N angle 180.0°. The five-membered unit O(5 W)–O(6 W)–Co(2)–O(5WA)–O(6WA) is planar.

The 2-D layer structure of **2** is formed by π–π stacking interactions between aromatic rings of 1,2,4-BTC ligands and 1,3,4-oxadiazole of 3-bpo ligands with centroid-to-centroid distance *ca* 3.51 Å (dihedral angle of 4.11°) among adjacent trinuclear cobalt units, as shown in figure 5(a). The 2-D layers are extended to a 3-D supramolecular network by π–π stacking interactions among pyridyl rings of 3-bpo ligands (the distance between ring centroids is 3.59 Å and the dihedral angle is 0°), as shown in figure 5(b) (and figure S2). O–H $\cdots$ N hydrogen bonds between coordinated water and nitrogen from 1,3,4-oxadiazole of 3-bpo [O3W–H3WA $\cdots$ N3 $(1-x, -y, 1-z) = 2.02$ Å, O3W $\cdots$ N3 $= 2.914(3)$ Å; O1W–H1WB $\cdots$ N4 $(1+x, 1+y, z) = 2.02$ Å, O1W $\cdots$ N4 $= 2.798(3)$ Å], and O–H $\cdots$ O hydrogen bonds between lattice water and carboxylate oxygen atoms consolidate the 3-D supramolecular structure of **2** [O6W–H6WB $\cdots$ O5 $(-1+x, y, z) = 1.91$ Å, O6W $\cdots$ O5 $= 2.710(3)$ Å; O2W–H2WA $\cdots$ O3 $(-1+x, y, z) = 2.06$ Å, O2W $\cdots$ O3 $= 2.790(3)$ Å; O1W–H1WA $\cdots$ O2 $(-1+x, y, z) =$ 1.90 Å, O1W $\cdots$ O2 $= 2.678(3)$ Å; O6W–H6WA $\cdots$ O3 $(-1+x, y, z) = 1.99$ Å, O6W $\cdots$ O3 $= 2.763(3)$ Å; O5W–H5WA $\cdots$ O5 $(2-x, 1-y, -z) = 2.20$ Å, O6W $\cdots$ O3 $= 2.843(3)$ Å; O4W–H4WA $\cdots$ O6 $(-1+x, y, z) = 1.70$ Å, O4W $\cdots$ O6 $= 2.603(3)$ Å; O5W–H5WB $\cdots$ O4 $(1-x, -y, -z) = 1.76$ Å, O5W $\cdots$ O4 $= 2.641(3)$ Å].

3.3. *IR spectra*

The main features in IR spectra of **1** and **2** concern the tricarboxylates (1,3,5-BTC and 1,2,4-BTC) and 4-bpo (or 3-bpo) (figures S3 and S4). Very strong band at $1615\,\mathrm{cm}^{-1}$ can be attributed to the asymmetric stretching (ν_{as}) of the carboxyl groups, while the symmetrical stretch (ν_s) appears at 1344–$1490\,\mathrm{cm}^{-1}$. The skeletal vibrations of the aromatic rings are at 1400–$1600\,\mathrm{cm}^{-1}$. Bands at 1545, 1485, 1100, and $710\,\mathrm{cm}^{-1}$ may be attributed to the $\nu_{C\text{–}N}$ of the pyridyl ring or 1,3,4-oxadiazole group of bpo. The strong broad band at $3400\,\mathrm{cm}^{-1}$ is assigned to hydroxyl groups.

3.4. *Thermal gravimetric analysis*

TG curves of **1** and **2** are determined from 30°C to 600°C in air (Supplementary material). For **1**, the first weight loss beginning at 160°C is attributed to loss of lattice water (13.09%, calculated value of 12.54%). The second weight loss from 300°C to 550°C is loss of coordinated water, 1,3,5-BTC and 4-bpo. The TG curve of **2** reveals only one obvious weight loss, between 320°C and 400°C, which should be attributed to the decomposition of **2**. The observed weight loss 81.32% is in agreement with the calculated value 82.10%. The remaining weight (15.23% for **1**, 18.68% for **2**) corresponds to CoO (15.66% for **1**, 17.90% for **2**).

3.5. *Electrochemical behaviors of the 1-CPE and 2-CPE*

For cobalt compounds, the ability to undergo reversible one-electron redox processes makes them attractive in electrochemistry [28, 29]. Thus **1** and **2** bulk-modified CPEs (**1**-CPE, **2**-CPE) are used as working electrodes due to their insolubility in water. The electrochemical studies of modified CPEs are carried out in 1 M H_2SO_4 at $60\,\mathrm{mV\ s^{-1}}$. Cyclic voltammograms at a bare CPE and the modified CPEs are provided in Supplementary material. In the potential range 800 to −600 mV, there is no redox peak at the bare CPE. While at the modified CPEs, a reversible redox couple attributed to redox of Co(II)/Co(I) is observed [28, 30] with mean peak potentials $E_{1/2} = (E_{pa} + E_{pc})/2$ are + 125 mV ($60\,\mathrm{mVs^{-1}}$) for **1**-CPE and +155 mV for **2**-CPE. The electrochemical behaviors of **1**-CPE and **2**-CPE are similar to other cobalt complexes [28]. The slight difference of peak potential for **1**-CPE and **2**-CPE might be attributed to the different structures.

4. Conclusion

We have synthesized two new 3-D supramolecular compounds from benzene tricarboxylates and bent dipyridyl ligands, $[Co(1,3,5\text{-}BTC)(4\text{-}bpo)(H_2O)_3]_2[Co(H_2O)_6]\cdot 10H_2O$ (**1**) and $[Co_3(1,2,4\text{-}BTC)_2(3\text{-}bpo)_2(H_2O)_{12}]$ (**2**). The presence of the 1,3,4-oxadiazole from 4-bpo and 3-bpo and non-coordinated carboxyl groups of 1,3,5-BTC or 1,2,4-BTC ligands provide hydrogen-bonding interactions. Compounds **1** and **2** were employed to fabricate bulk-modified CPEs due to their insolubility.

Preliminary results of **1**-CPE and **2**-CPE display that the cobalt compounds may be potential candidates for electrochemical materials.

Supplementary material

CCDC 724741 for **1** and 822998 for **2** contain the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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