New butane-1,2,3,4-tetracarboxylato bridged cobalt(II) complexes

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ABSTRACT

Four butane-1,2,3,4-tetracarboxylato bridged supramolecular complexes $[Co_2(H_2O)_5(BTC)]\cdot 2H_2O$ **1**, $[Co_2(H_2O)_5(BTC)]\cdot 2H_2O$ **2**, $[Co_2(H_2O)_6(bpy)_2(BTC)]\cdot 4H_2O$ **3** and $[Co_2(H_2O)_2(bpy)_2(BTC)]$ **4**, (H_4BTC = butane-1,2,3,4-tetracarboxylic acid, 2,2-bpy = 2,2-bipydine) are synthesized and characterized by single-crystal X-ray diffraction. IR spectroscopy, TG-DTA analyses, elemental analyses, powder X-ray diffraction and magnetic measurements for **3** and **4** are carried out. The dinuclear Co unit in **2** is bridged by BTC^{4-} anions into 2D layers, which are assembled *via* interlayer hydrogen bonds into a 3D $(4^4 \cdot 6^2)(4^5 \cdot 6^5)_2$-$(4^6 \cdot 6^8 \cdot 8)$ topological supramolecular architecture. In **3**, the $[Co_2(H_2O)_6(bpy)_2(BTC)]$ molecules are aggregated to 2D layers *via* π–π stacking interactions, the resulting layers are engaged in hydrogen bonding leading to a novel 3D supramolecular architecture with the schläfli symbol of $(10^2 \cdot 12)_2(4 \cdot 10^2)_2$-$(4^2 \cdot 10^2 \cdot 12^2)$. The Co atoms in **4** are linked by BTC^{4-} anions into a 1D chain, then the hydrogen bonding and π–π stacking interactions result in formation of a 3D novel $(4^3 \cdot 6^2 \cdot 8)_2(4^6 \cdot 6^6 \cdot 8^3)(6^3)_2$ topological networks. The variable temperature magnetic characterizations on **3** and **4** suggest weak antiferromagnetic or ferromagnetic coupling exchange *via* π···π stacking interactions (J = –0.03 cm^{-1} for **3**, J = 0.11 cm^{-1} for **4**).

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1. Introduction

The current interest in the crystal engineering of coordination polymer frameworks and supramolecular systems stem from not only their potential applications in host–guest chemistry, catalysis, separations, gas storage, optical properties and magnetic properties, but also their intriguing variety of architectures and topologies [1–5]. Net-topology represents an important and essential problem of the construction and analysis of coordination frameworks, which has also been the subject of several related studies, with fundamental contributions by Wells [6], Smith [7], and O'Keeffe et al. [8].

Nodes of 3-, 4-, and 6-connectivity are most common in the topological nets, and a variety of such uninodal net-topologies have been realized by 3D coordination frameworks, for instance, Srs, dia, cds, nbo, pcu, etc. [9–13]. Meanwhile, the binodal nets with relevant connectivity such as (3, 6), (4, 6), (4, 8) also be described in the literature [14–16]. However, the multi-nodal topology nets have rarely been reported so far, especially for construction *via* hydrogen bonds and aromatic π···π stacking interactions [17,18]. Thus, the construction of new or unusual multi- connectivity topologies is of great interest at a current stage.

For the construction of a specific supramolecular architecture with multi-nodal topological nets, design of the ligands and selec-

tion of metal ions are extremely crucial [19,20]. Polycarboxylate ligands have been extensively employed in the preparation of carboxylato bridged coordination polymers with high porosity and new topology [21–23]. In the family of the polycarboxylic acids, butane-1,2,3,4-tetracarboxylic acid (H_4BTC) is of special interest and has attracted much attention because its four carboxylate groups allows it to serve as either a multidentate ligand or bridging building block in supramolecular assemblies. Furthermore, ligand based on H_4BTC as building blocks for constructing coordination complexes have been less studied, and such ditopic ligand may become a type of building block to construct coordination polymers with novel topologies and properties [24,25]. In this paper, we report the synthesis, structural characterization and magentic properties of three cobalt complexes with butane-1,2,3,4-tetracarboxylic acid derived in the presence of 2,2-bipydine.

2. Experimental section

2.1. Materials

All chemicals of reagent grade were commercially available and used without further purification.

2.2. Physical methods

Powder X-ray diffraction measurements were carried out with a Bruker D8 Focus X-ray diffractometer to check the phase purity.

The C, H and N microanalyses were performed with a PE 2400II CHNO/S elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Shimadzu FTIR-8900 spectrometer. Thermogravimetric measurements were carried out from room temperature to 900 °C on preweighed samples using a Seiko Exstar 6000 TG/DTA 6300 apparatus with a heating rate of 10 °C/min. Single crystal X-ray diffraction data were collected by Rigaku Raxis-Rapid X-ray diffractometer. The temperature-dependent magnetic susceptibilities were determined with a Quantum Design SQUID magnetomer (Quantum Design Model MPMS-7) in the temperature range 2–300 K with an applied field of 5 KOe.

2.3. Synthesis of two polymorphs 1 and 2 of composition [Co$_2$(H$_2$O)$_5$(BTC)]·2H$_2$O

Addition of 1.0 mL (1.0 M) Na$_2$CO$_3$ to an aqueous solution of 0.2899 g (0.99 mmol) Co(NO$_3$)$_2$·6H$_2$O in 8.0 mL H$_2$O produced purple precipitate, which was separated by centrifugation, washed with distilled water for several times and then transferred into an aqueous solution of 0.1140 g (0.49 mmol) butane-1,2,3,4-tetracarboxylic acid (H$_4$BTC) in 20.0 ml water. The mixture was stirred for 30 min to give a clear solution (pH 4. 91). Slow evaporation for two weeks yielded a rose-colored crystalline mixture consisting of two polymorphs 1 and 2 of composition [Co$_2$(H$_2$O)$_5$(BTC)]·2H$_2$O. 1 and 2 crystallize in a orthorhombic space group F2dd and a monoclinic space group C2/c, respectively. The orthorhombic polymorph was very recently reported by Delgado et al. [24], and the monoclinic one is a new coordination polymer. Due to their extreme similarity in habitus and color, manual separation of the individuals from each other is impossible. Furthermore, all attempts to prepare compound 1 and 2 separately as a unique product have failed unfortunately so far.

2.4. [Co$_2$(H$_2$O)$_6$(bpy)$_2$(BTC)]·4H$_2$O (3)

Purple precipitate resulted from addition of 1.0 mL (1.0 M) Na$_2$CO$_3$ to an aqueous solution of 0.2940 g (1.01 mmol) Co(NO$_3$)$_2$·6H$_2$O in 8.0 mL H$_2$O was separated by centrifugation and washed with distilled water for several times, then transferred into a mixed solvent consisted of 10.0 ml methanol and 10.0 ml water. To the mixture, 0.1178 g (0.50 mmol) butane-1,2,3,4-tetracarboxylic acid was added and stirred for 10 min showing a clear solution, and subsequently 0.077 g (0.49 mmol) 2,2′-bipyridine was added. The resulting orange solution (pH 4.93) was further stirred for 10 min, and then allowed to stand at room temperature. Slow evaporation for two months afforded orange plate-like crystals of 3 (yield 51.5% based on the initial Co(NO$_3$)$_2$·6H$_2$O input). Anal. Calc. for C$_{14}$H$_{21}$CoN$_2$O$_9$: C, 40.01; H, 5.04; N, 6.67. Found: C, 40.34; H, 5.28; N, 6.46%. IR data (cm^{-1}, KBr): 3424w, 3079w, 2976w, 2953w, 1566vs, 1475w, 1447m, 1408vs, 1385m, 1317m, 1284m, 1252m, 1184m, 1063w, 1023m, 992w, 885w, 775s, 738m, 653w, 594w, 555w.

2.5. Co$_2$(H$_2$O)$_2$(bpy)$_2$(BTC) (4)

Na$_2$CO$_3$ (0.5 mL, 1.0 M) was added to an aqueous solution of 0.1467 g (0.50 mmol) Co(NO$_3$)$_2$·6H$_2$O in 8.0 mL H$_2$O to yield purple precipitate, which was separated by centrifugation and washed with distilled water for several times. The gathered precipitate was then transferred into a 23 ml Teflon-lined stainless-steel autoclave charged with a mixture of 0.058 g (0.25 mmol) butane-1,2,3,4-tetracarboxylic acid, 0.039 g (0.25 mmol) 2,2′-bipyridine (bpy) and 10 mL water. The reactor was heated to 140 °C and kept at this temperature for 4 days under autogenous pressure, then spontaneously cooled to room temperature. Pink block crystals of

4 were collected from the reaction vessel and air-dried (yield 45.3% based on the initial Co(NO$_3$)$_2$·6H$_2$O input). Anal. Calc. for C$_{28}$H$_{26}$Co$_2$N$_4$O$_{10}$: C, 48.29; H, 3.76; N, 8.05. Found: C, 48.18; H, 3.93; N, 8.17%. IR data (cm^{-1}, KBr): 3239w, 3075w, 2976w, 2914w, 1604s, 1566vs, 1484m, 1449m, 1405vs, 1316m, 1282m, 1198w, 1168w, 1059w, 1022m, 885m, 814w, 775s, 737s, 672m, 535m.

2.6. X-ray crystallography

Suitable single crystals were selected under a polarizing microscope and fixed with epoxy cement on respective fine glass fibers which were then mounted on a Rigaku R-Axis Rapid IP X-ray diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) for cell determination and subsequent data collection. The reflection intensities in suitable θ ranges were collected at 293 K using the ω scan technique. The employed single crystals exhibit no detectable decay during the data collection. The data were corrected for Lp and empirical absorption effects. The SHELXS-97 and SHELXL-97 programs [26,27] were used for structure solution and refinement. The structure were solved by using direct methods. Subsequent difference Fourier syntheses enabled all non-hydrogen atoms to be located. After several cycles of refinement, all hydrogen atoms associated with carbon atoms were geometrically generated, and the rest hydrogen atoms were located from the successive difference Fourier syntheses. Finally, all non-hydrogen atoms were refined with anisotropic displacement parameters by the full-matrix least-squares technique and hydrogen atoms with isotropic displacement parameters set to 1.2 times of the values for the associated heavier atoms. Detailed information about the crystal data and structure determination is summarized in Table 1. Selected interatomic distances and bond angles are tabulated in Tables 2–4.

Table 1
Summary of crystal data, data collection, structure solution and refinement details for 2–4 (T = 293(2)).

Compounds	2	3	4
Empirical formula	C$_8$H$_{22}$Co$_2$O$_{16}$	C$_{28}$H$_{42}$Co$_2$N$_4$O$_{18}$	C$_{28}$H$_{26}$Co$_2$N$_4$O$_{10}$
Formula weight	490.10	840.562	696.38
Description	pink block	orange block	pink block
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	C2/c	P$\bar{1}$	P$\bar{1}$
a (Å)	28.060(6)	8.923(2)	7.638(2)
b (Å)	8.138(2)	9.176(2)	9.596(2)
c (Å)	16.229(3)	11.770(2)	10.284(2)
α (°)		97.13(3)	79.24(3)
β (°)	119.90(3)	91.98(3)	71.78(3)
γ (°)		107.85(3)	68.96(3)
Volume (Å^3)	3212.9(1)	907.6(3)	665.9(2)
Z	8	1	1
D_{calc} (g cm^{-3})	2.026	1.538	1.737
F(0 0 0)	2000	436	356
Absorption coefficient	2.152	0.995	1.316
θ Range (°)	3.15–27.44	3.08–27.46	3.11–27.45
Total number of data collected	3649	4109	3006
Number of observed data (I ⩾ 2σ(I))	3323	3613	2346
Number of variables	235	235	199
Goodness-of-fit on F^2	1.085	1.080	1.269
R$_1$, wR$_2$ [I ⩾ 2σ(I)]^a	0.0379, 0.1040	0.0284, 0.0737	0.0348, 0.0682
R$_1$, wR$_2$ (all data)^a	0.0423, 0.1109	0.0382, 0.0813	0.0594, 0.1088
δρ$_{max}$, δρ$_{min}$ (e Å^{-3})	1.172, −0.875	0.432, −0.471	0.729, −0.741

^{a} R$_1$ = $\sum(|F_o|-|F_c|)/\sum F_o$, wR$_2$ = $[\sum w(F_o^2 - F_c^2)^2/w(F_o^2)^2]^{1/2}$, and w = $[\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$ where P = $(F_o^2 + 2 F_c^2)/3$. For **2**, a = 0.0514 and b = 14.3779. For **3**, a = 0.0391 and b = 0.2355. For **4**, a = 0.0000 and b = 1.4758.