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Synthesis, Crystal Structure, and Electrochemical Property of the Complex [Co(tfbdc)(DMF)$_2$(H$_2$O)$_2$] (tfbdc = Tetrafluoroterephthalate; DMF = *N,N*-Dimethylformamide)

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One complex [Co(tfbdc)(DMF)$_2$(H$_2$O)$_2$] (tfbdc = tetrafluoroterephthalate) was synthesized by the reaction of tetrafluoroterephthalatic acid with cobalt(II) nitrate hexahydrate in mixture solvent. This complex was characterized by elemental analysis, infrared (IR) spectra, cyclic voltammetry, and x-ray single-crystal structure analysis. This complex crystallizes in the monoclinic system with space group P2(1)/n. The Co(II) ion has a distorted octahedral geometry coordinated by two O atoms from two tetrafluoroterephthalate (tfbdc), two O atoms from two water molecules, and two O atoms from two *N,N*-dimethyl formamide molecules. Each tfbdc ligand bridges two Co(II) ions in end-to-end fashion, forming a straight chain. These chains are connected by hydrogen bonds, forming a two-dimensional supramolecular network structure.

Keywords cobalt(II), coordination polymer, crystal structure, electrochemical property, tetrafluoroterephthalatic acid

INTRODUCTION

Synthesis and structural characterization of framework materials involving metal dicarboxylate functions have attracted considerable attention these days owing to their ability to form structurally diverse assemblies with interesting network topologies and material properties that make them very useful candidates for applications relating to sorption, storage, host–guest, catalytic, magnetic, and optical materials.[1–10] Compared to malonic, succinic, glutaric, and adipic acids, which have flexible –CH$_2$– spacer functions of varying lengths, benzenedicarboxylic acids have a rigid aromatic unit as the spacer, which can make them a very special system that can have interesting electronic and magnetic interactions between the metal ions in the network through possible conjugative interaction.[11,12] In spite of the rich coordination chemistry exhibited by 1,4-benzenedicarboxylatic acid, 1,3-benzenedicarboxylatic acid, 1,3,5- benzenetricarboxylatic acid, Br-benzenedicarboxylatic acid, 1,3-tetrafluoroterephthalatic acid, and 1,2,4,5-benzenetetracarboxylic acid,[13–24] studies on tetrafluoroterephthalatic acid (H$_2$tfbdc) are less reported.[25–30] With the aim of understanding the coordination chemistry of H$_2$tfbdc, we recently began to study the assembly reactions of H$_2$tfbdc with metal ions via general solution synthetic methods.[31] Considering the abundant physical and chemical property of cobalt carboxylate complexes,[32] such as magnetic and catalytic properties, we focused our work on the Co(II) and H$_2$tfbdc system. In this work, we report synthesis, structural, spectral, and electrochemical features of one-dimensional zigzag-type coordination polymers [Co(tfbdc)(DMF)$_2$(H$_2$O)$_2$], obtained from the assembly reaction of the Co(II) ion and H$_2$tfbdc in a mixture solvent of dimethylformamide (DMF) and anhydrous ethanol.

EXPERIMENTAL

Material

Tetrafluoroterephthalatic acid (H$_2$tfbdc), cobalt(II) nitrate hexahydrate, *N,N*-dimethyl formamide (DMF), and anhydrous ethanol were of reagent grade without further purification before use.

Physical Measurements

Elemental analysis (C, H, N) was performed on a Perkin-Elmer 2400 Series II element analyzer. Fourier-transform infrared (FTIR) spectra were recorded on a Nicolet 460 spectrophotometer in the form of KBr pellets.

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TABLE 1

Crystal structure parameters of the title complex

Formula	$C_{14}H_{18}F_4CoN_2O_6$	Calculated Density (g cm^{-3})	1.688
Formula weight	477.23	Mu(Mo K_α) (mm^{-1})	0.999
Color	Purple	Limiting indices	h: –6,6; k: –13,13; l: –22,22
Crystal system	Monoclinic	F(000)	486
Space group	P2(1)/n	Crystal size (mm)	0.30 × 0.23 × 0.19
Scan type	ψ-ω	θ range for data collection (°)	2.31 to 27.60
a, nm	0.53295(14)	A total reflections collected	7918
b, nm	1.0246(3)	Independent reflections	2157 (Rint = 0.0252)
c, nm	1.7239(5)	Observed reflections	2010
β (°)	94.207(3)	μ(Mo Kα) (mm^{-1})	0.071073
V (nm^3)	0.9388(4)	Goodness-of-fit on F^2	1.005
Z	2	R_1, wR_2[I>2σ(I)]	0.0316, 0.0996
Temperature (K)	296(2)	R_1, wR_2(all data)	0.0334, 0.1014

TABLE 2

Selected bond lengths (nm)[a] and bond angles (°) of the complex

Co1–O4	0.21017 (14)	Co1–O4A	0.21017(14)
Co1–O1	0.21034 (12)	Co1–O1A	0.21034 (12)
Co1–O3	0.21259 (14)	Co1–O3A	0.21259 (14)
O4–Co1–O4A	180.0	O4–Co1–O1	88.18 (5)
O4A–Co1–O1	91.82 (5)	O4–Co1–O1A	91.82 (5)
O4A–Co1–O1A	88.18 (5)	O1A–Co1–O1	180.000 (1)
O4–Co1–O3A	90.10 (6)	O4A–Co1–O3A	89.90 (6)
O3A–Co1–O1	93.96 (6)	O1A–Co1–O3A	86.04 (6)
O4–Co1–O3	89.90 (6)	O4A–Co1–O3	90.10 (6)
O1–Co1–O3	86.04 (6)	O1A–Co1–O3	93.96 (6)
O3A–Co1–O3	180.0		

[a] Symmetry code: A, –x, –y + 2, –z + 1.

Electrochemical measurements were performed using a Shanghai Company 440A electrochemical analyzer, with a three-electrode system consisting of a Pt-piece working electrode, a Pt-wire counterelectrode, and a saturated calomel electrode (SCE) reference electrode. All measurements were carried out at room temperature with a sweep rate of 100 mV s^{-1} under N_2, in degassed solvents, using 0.1 *M* NaC1 aqueous solution as a supporting electrolyte. The complex concentrations were 5.0 × 10^{-4} *M* in aqueous solutions. The half-wave potentials $E_{1/2}$ were obtained from (E_{pa} + E_{pc})/2.

Synthesis of [Co(tfbdc)(DMF)$_2$(H$_2$O)$_2$]

A 5-ml anhydrous ethanol solution of Co(NO$_3$)$_2$·6H$_2$O (0.0239 g, 0.082 mmol) was slowly added to a 3-ml *N,N*-dimethylformamide solution that contained H$_2$tfbdc (0.0195 g, 0.082 mmol) to afford a purple solution. Upon slow evaporation of the solvent at room temperature for 3 weeks, purple block crystals were obtained. Anal.: Calc. for $C_{14}H_{18}F_4CoN_2O_6$ (477.23): C, 35.23; H, 3.77; N, 5.87%. Found: C, 35.25; H, 3.72; N, 5.83%. IR data (cm^{-1}, KBr pellet): 3511(s), 2989(s), 1658(vs), 1620(vs), 1496 (s), 1468 (s), 1438(vs), 1418(s),

TABLE 3

Hydrogen bond distances and angles in the complex

D-H–A[a]	D-H (nm)	H–A (nm)	D–A (nm)	D-H–A (°)
O4—H4A–O1^C	0.0820	0.2580	0.32181(19)	136.00
O4—H4A–O3^C	0.0820	0.2320	0.3040(2)	147.00
O4—H4B–O2^A	0.0820	0.1850	0.2650(2)	165.00

[a] Symmetry code: A, –x, –y + 2, –z + 1; C, –x + 1, –y + 1, –z + 1.

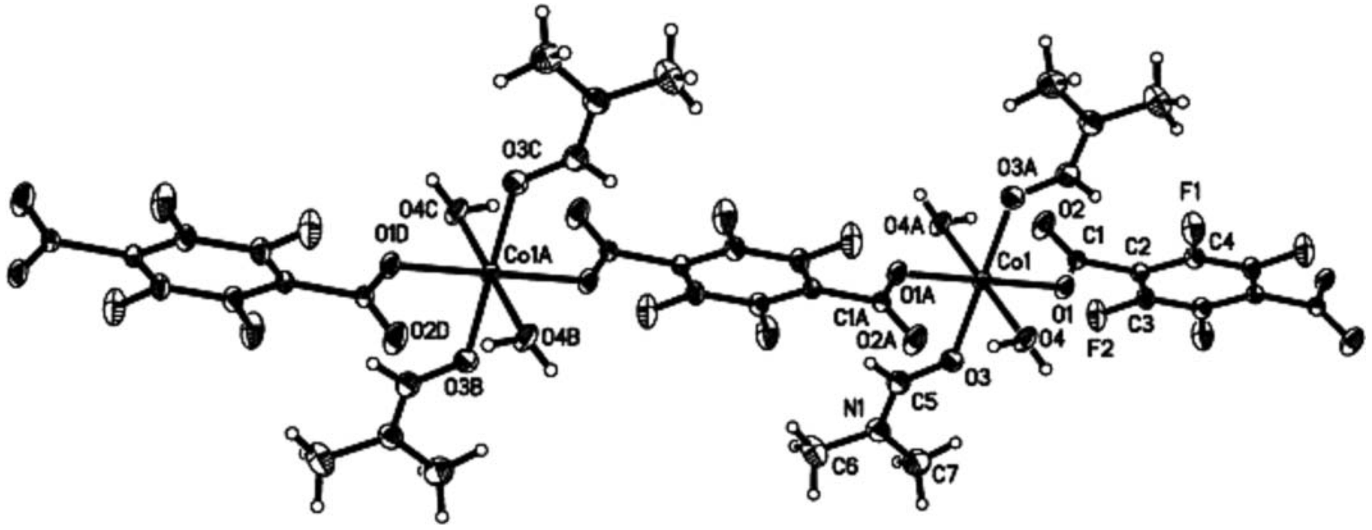

FIG. 1. The molecular structure of the title complex; atoms are shown as 30% thermal ellipsoids.

1387(vs), 1370(vs), 1247(s), 1115(s), 1066(m), 984(s), 911 (m), 850(m), 771(m), 731(vs), 681(s), 650(m), 489(s), 418(m).

X-Ray Crystallography

Single-crystal x-ray diffraction measurement of the title complex was carried out with a Bruker Smart Apex CCD diffractometer at 296(2) K. Intensities of reflections were measured using graphite-monochromatized Mo Kα radiation ($\lambda = 0.071073$ nm) with the ψ-ω scans mode in the range of $2.31 < \theta < 27.60^\circ$. The structures were solved by direct methods using SHELXS-97[33] computer program and refined by full-matrix least-squares methods on F^2 with the SHELXS-97 program package. Anisotropic thermal factors were assigned to all the non-hydrogen atoms. Hydrogen atoms were included in calculated position and refined with isotropic thermal parameters riding on the parent atoms. Crystallographic data and experimental details for structural analyses are summarized in Table 1, the selected bond lengths (nm) and bond angles (°) are given in Table 2, and the hydrogen bonds parameters are presented in Table 3, respectively.

RESULTS AND DISCUSSION

Crystal Structure Description of [Co(tfbdc)(DMF)$_2$(H$_2$O)$_2$]

Figure 1 represents the molecular structure coordination with atom numbering scheme. As shown in Figure 1, tetrafluoroterephthalate (tfbdc) ligands attached to the Co(II) atom adopt a monodentate coordination mode, which is involved in end-to-end bridging with the metal center. The other two oxygen atoms from two water molecules and two oxygen atoms from two *N,N*-dimethyl formamide (DMF) molecules are also coordinated to the metal center. The coordination environment of each cobalt(II) center can be described as a distorted octahedral geometry. The equatorial position is governed by four oxygen atoms, two from tfbdc ligands [Co1–O1 = 0.21034(12) nm and Co1–O1A = 0.21034(12) nm], the other two from two water molecules [Co1–O4 = 0.21017(14), Co1–O4A = 0.21017(14) nm]. The apical position is occupied by O3, O3A, from oxygen atoms of *N,N*-dimethyl formamide [Co1–O3 = 0.21259(14) and Co1–O3A = 0.21259(14) nm]. The bond distance of Co–O from the tfbdc ligand is shorter than that from the DMF molecule, indicating that the strength of the Co(II) ion chelated with tfbdc is stronger than that of the DMF molecule. Moreover, the bond

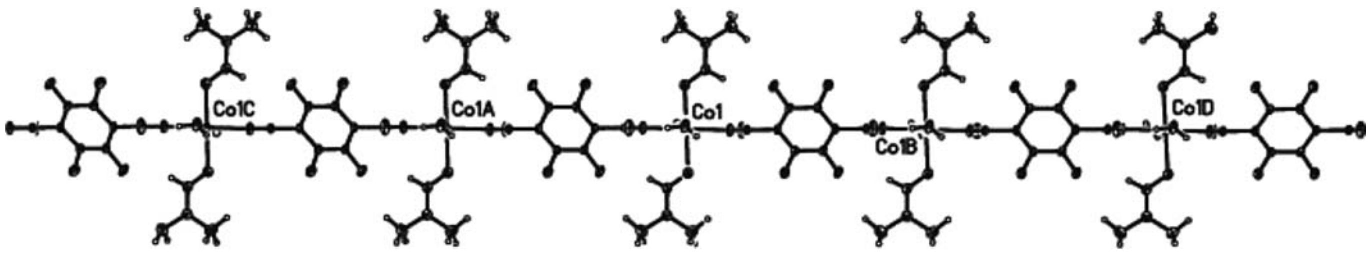

FIG. 2. One-dimensional straight chain of the title compound.

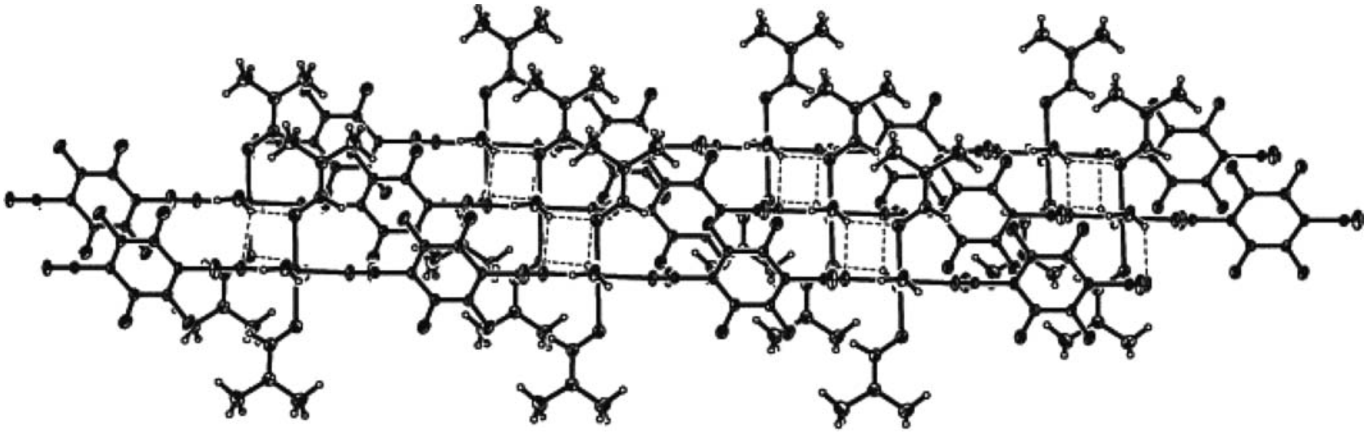

FIG. 3. The packing of the title compound; dashed lines indicate there are hydrogen bonds between the chains.

angle of O3–Co1–O3A lying in the axial position is 180.0°, which indicates that the three atoms are in the same line, and bond angles of O4–Co1–O4, O1A–Co1–O1 are also 180.0 and 180.0(1)°, respectively, which indicate O1, O1A, O4, and O4 atoms are on the same plane, but bond distances of Co1–O4, Co1–O1, Co1–O3 are different, leading to the conclusion that the Co(II) ion has a distorted octahedral geometry. The distance between Co1–Co1A is 1.1549 nm. Each tfbdc ligand in equatorial plane bridges two Co(II) ions in end-to-end fashion, forming a straight chain, as shown in Figure 2. This one-dimensional chain is quite similar to that of $\{[Co(4,\ 4'\text{-bipy})(H_2O)_4]\cdot(\alpha\text{-furacrylic acid})_2\cdot(H_2O)\}_n$ reported by Yang et al.[34] The formation of hydrogen bonds between chains [O4–H4A- - -O1* = 0.32181(19) and 0.3040(2) nm], and O3–H3A- - -O2^A = 0.2650(2) nm], as shown in Figure 3, leads to the production of a two-dimensional network. The shortest Co(II)- - -Co(II) distance between the closest neighbors in the same layer via hydrogen bonds is 0.5329 nm.

Infrared Spectrum

The IR spectrum of the title complex reflects the binding patterns of water, *N,N*-dimethyl formamide, and tetrafluoroterephthalate moieties. The strong absorption band in the 3600–3000 cm^{-1} regions corresponds to ν(OH) of the coordination water molecules in the complex. All carboxylic groups of the organic ligand in the compound are deprotonated, in agreement with the IR spectral results, where no absorption peak around 1730 cm^{-1} for a protonated carboxylic group is observed. The strong peaks at 1658 cm^{-1} and at 1468 cm^{-1}, 1438 cm^{-1} are the ν_{as}(OCO) and ν_s(OCO) stretching mode of the coordinated tetrafluoroterephthalate, while strong absorption at ~731 cm^{-1} is the δ (OCO) bent vibration of tetrafluoroterephthalate. The different values of 220 cm^{-1} and 190 cm^{-1} between ν_{as}(OCO) and ν_s(OCO) indicate that the tetrafluoroterephthalate ligands adopt both monodentate coordination and bridging mode,[35,36] as proved by the x-ray crystal structure analysis of $[Co(tfbdc)(DMF)_2(H_2O)_2]$.

Thermogravimetric Analysis

The thermogravimetric (TG) measurement of the title complex was determined in the range of 20–800°C in N_2. The weight loss of 28.17% occurs at a temperature range of about 110 to 240°C, which is attributed to the volatilization of two DMF molecules (calcd. 30.59%). The weight loss of 53.38% from 240 to 750°C corresponds to the elimination of two coordinated H_2O molecules and the pyrolysis of tfbdc ligands. The remaining weight of 16.03% at 750°C corresponds to the percentage (15.70%) of final product CoO. Because hydrogen bond action exists between hydrogen atoms of the coordinated water molecules and the oxygen atoms of the tfbdc ligands, losing the coordinated water molecules is harder than for DMF molecules under the compound heated.

Electrochemical Property

The redox behavior of the $[Co(tfbdc)(DMF)_2(H_2O)_2]$ complex was studied by cyclic voltammetry (CV) in aqueous solution. As shown in Figure 4, during scanning from –1.1 to 1.1 V, the CV diagram of the complex in aqueous solution displays one pair of anodic and cathodic peaks with peak potentials of

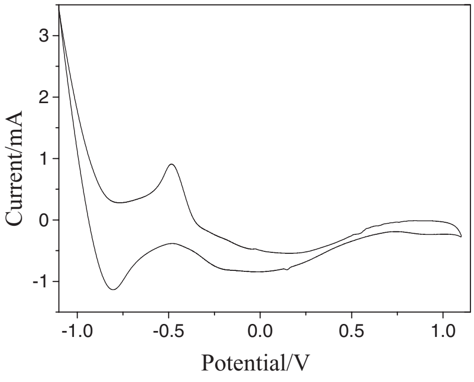

FIG. 4. Cyclic voltammogram of $[Co(tfbdc)(DMF)_2(H_2O)_2]$ in aqueous solution, concentration 0.5 m*M* (scan rate 100 mV s^{-1}).

E_{pa} = –0.476 V and E_{pc} = –0.796 V (vs. SCE) respectively, which corresponds to a Co^{III}/Co^{II} redox process.[37] The value of the half-wave potential, $E_{1/2}$, was calculated to be –0.636 V. The ratio of i_{pa} and i_{pc} is 0.82. The peak separation between the anodic and cathodic peaks at a scan rate 100 mV s^{-1} is 320 mV. These features are indicative of a quasi-reversible Co^{III}/Co^{II} redox process.

CONCLUSION

In conclusion, a one-dimensional straight-chain coordination polymer [Co(tfbdc) $(DMF)_2(H_2O)_2$] was readily prepared via reaction of $Co(NO_3)_2{\cdot}6H_2O$ with ligand of H_2tfbdc in the mixture solvent of DMF and anhydrous ethanol. The electrochemical behavior of the title complex is a quasi-reversible Co^{III}/Co^{II} redox process.

SUPPLEMENTARY MATERIAL

CCDC 705175 for [Co(tfbdc)$(DMF)_2(H_2O)_2$] contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.hmtl [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB21EZ, UK; fax (Internet) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

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