THE SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF A TWO-DIMENSIONAL COORDINATION POLYMER $[Co(H_2O)(phen)(\mu_4\text{-bta})_{1/2}]_n$ (H_4bta = BENZENETETRACARBOXYLIC ACID)

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Complex $[Co(H_2O)(phen)(\mu_4\text{-bta})_{1/2}]_n$ was hydrothermally synthesized from sodium benzene-1,2,4,5-tetracarboxylate, 1,10-phenanthroline and $CoCl_2 \cdot 6H_2O$, and structurally characterized by single-crystal X-ray crystallography, showing that it possesses a novel two-dimensional polymeric structure.

Keywords: Crystal structure; Benzene-1,2,4,5-tetracarboxylate; 1,10-Phenanthroline; Cobalt complexes; Coordination polymers; Hydrothermal synthesis; X-ray diffraction.

The design of multi-dimensional coordination polymers has recently attracted considerable attention not only because of their novel structures and geometry, but also for their interesting properties such as optical and magnetic functions, as well as catalytic properties[1,2]. A valuable conceptual approach to building and describing extended framework is based on the idea of a network. Multiconnecting ligands which provide two or more didentate metal-binding sites, can be building blocks for coordination polymers because they promise robust networks with good electronic communication between metal centers[3,4]. They also offer new network architectures, many of which do not exist in natural solids. “Clay mimics” or “zeolite mimics” have gross analogues but are based upon very different chemical components and, most importantly, they are inherently modular and therefore fine-tunable[5]. At present, there has been much effort devoted to the research area of designing polycarboxylate-metal assemblies[6–11]. A particular case is the construction of metal and tma^{3-} (benzene-1,3,5-tricarboxylate) assemblies. By using tma^{3-} as a bridging ligand, a lot of supramolecular isomers have been prepared, such as multi-dimensional

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structures of coordination polymers $[Cu_3(tma)_2(H_2O)]_n$ (ref.[6]), $[M_3(tma)_2\cdot 12H_2O]$ (M = Co, Ni, Zn)[7]. Also other organic ligands for cooperative binding to metal centers have been described, such as in the two-dimensional structure of $[Ni(C_{12}H_3ON_6O_2)_3(tma)_2]\cdot 18H_2O$ (ref.[10]). As a multiconnecting ligand, benzene-1,2,4,5-tetracarboxylate anion (bta^{4-}) is also an excellent candidate for the design of coordination polymers, but few examples of its use in crystal engineering of coordination polymers have been described. We have therefore conducted an investigation of a system $CoCl_2$–Na_4bta–phen–H_2O by hydrothermal method. The compound obtained, $[Co(H_2O)(phen)(\mu_4\text{-bta})]_n$ (**1**), is unprecedented, exhibiting two-dimensional polymeric structure by linking metal ions with bta bridging units. We report here the synthesis and structure characterization of such a novel compound.

EXPERIMENTAl

Synthesis of Compound **1**

A mixture of $CoCl_2\cdot 6H_2O$ (2.0 g), Na_4bta (1.8 g), phen (0.70 g), H_2O (18 ml) (molar ratio 1 : 2 : 0.7 : 1 300) was fully stirred at room temperature for 30 min, and was sealed in a Teflon-lined stainless steel reactor and heated at 160 °C for three days. After the reaction system slowly cooled to room temperature, brown crystals were collected and washed with distilled water. The yield is *ca* 15% (based on Co). IR (KBr, cm^{-1}): 3 445.80 vs, 2 358.83 m, 1 622.50 w, 1 557.87 s, 1 515.81 s, 1 488.65 s, 1 427.38 s, 1 378.41 vs, 1 322.49 m, 1 140.03 m, 922.04 m, 853.75 s, 814.07 m, 726.99 s, 678.53 m, 532.11 m, 458.29 m. For $C_{17}H_{11}CoN_2O_5$ (382.2) calculated: 54.42% C, 2.90% H, 7.33% N, 15.42% Co; found: 55.50% C, 2.85% H, 7.40% N, 15.4% Co.

X-Ray Structure Determination

Crystals of compound **1** was studied on a Siemens P4 four-circle diffractometer using graphite-monochromatized MoKα radiation (λ = 0.71073 Å) and ω–2θ scans. The structure was solved using SHELXTL program, and refined by full-matrix least-square techniques. Crystal data: T = 293(2) K; crystal size 0.48 × 0.36 × 0.32 mm; empirical formula $C_{17}H_{11}CoN_2O_5$, M_w = 382.21; monoclinic, space group $P2_1/n$; a = 10.129(2) Å, b = 9.206(2) Å, c = 15.765(3) Å, β = 92.34(3)°, V = 1478.0(5) Å^3; Z = 4, μ(MoKα) = 1.195 mm^{-1}, D_{calc} = 1.718 g cm^{-3}, $F(000)$ = 776; θ range for data collection is from 2.34 to 25.01°; 3 582 reflections were measured, of which 2 592 reflections are unique [R_{int} = 0.1065], and used in all calculations; final R indices, R_1 = 0.0301, wR_2 = 0.0621. Crystallographic data for the structure **1** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-147728. Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk.

RESULTS AND DISCUSSION

Selected bond lengths and angles are listed in Table I. Figure 1 shows that the asymmetric unit of compound consists of half a bta^{4-} anion, one H_2O and one molecule of phenanthroline and one Co(II) ion, the Co(II) ion is six-coordinated by two bta^{4-}, one phen and one H_2O. The four carboxylate groups of each (μ_4-bta) unit are alternately used as mono- and didentate ligands to bind to Co(II) ions. Six oxygen atoms from one (μ_4-bta) unit are used to link four [Co(H_2O)(phen)] moieties. Two phenanthroline rings in the opposite two [Co(H_2O)(phen)] moieties are parallel, but the other two in the neighboring two [Co(H_2O)(phen)] moieties exhibit a dihedral angle of 83.9°. Around a (μ_4-bta) unit, the four phenanthroline rings in the four moieties are alternately located above and below the unit. A two-dimensional network layer of compound **1** is thus constructed as showed in Fig. 2. The phenanthroline rings in this network layer are divided into two parallel groups. Large thirty-membered-ring holes exist in the structure. Around each hole, there are four (μ_4-bta) units and four cobalt atoms which form a square metal-ion grid in the layer with dimension of 9.36(8) × 5.45(2) Å. The local geometry around each Co(II) center can be described as a slightly distorted octahedron. The Co(II) ion coordinates to three carboxylate oxygen atoms O3A, O1 and O2, two phenanthroline nitrogen

TABLE I
Selected bond lengths (in Å) and angles (in °) for compound **1**

Atoms	Bond lengths, angles	Atoms	Bond lengths, angles
Co–O3A	2.055(2)	Co–N2	2.130(2)
Co–OW	2.057(2)	Co–O1	2.168(2)
Co–N1	2.102(2)	Co–O2	2.175(2)
O3A–Co–OW	89.35(8)	O3A–Co–O2	158.35(7)
O3A–Co–N2	86.76(8)	N2–Co–O2	114.49(8)
O3A–Co–O1	8.49(8)	OW–Co–N1	171.75(9)
N2–Co–O1	172.40(8)	N1–Co–N2	78.43(9)
N1–Co–O2	94.41(8)	N1–Co–O1	95.64(9)
O3A–Co–N1	93.98(8)	OW–Co–O2	85.11(8)
OW–Co–N2	94.25(9)	O1–Co–O2	60.82(7)
OW–Co–O1	91.32(9)		

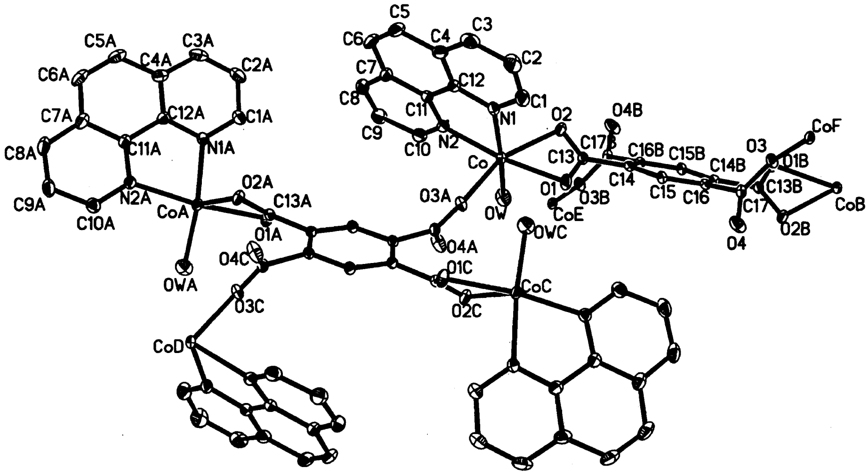

FIG. 1
A view of the molecular structure of [Co(H_2O)(phen)(μ_4-bta)$_{1/2}$]$_n$

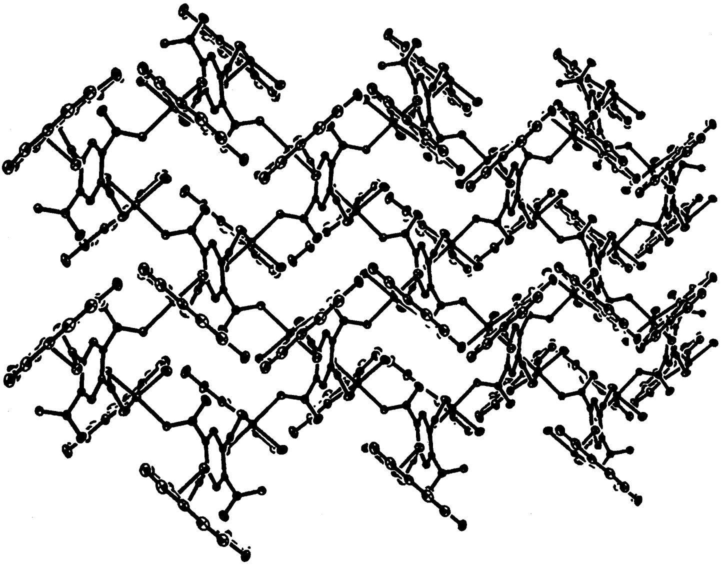

FIG. 2
A view of the polymeric layer of [Co(H_2O)(phen)(μ_4-bta)$_{1/2}$]$_n$

atoms N1 and N2, and one water molecule. The angles between two neighboring bonds around a Co(II) ion range from 78.43(9) to 98.49(8)° (see Table I).

In Fig. 3, the two-dimensional layers are packed along crystallographic axis *b*. The interlayer distance is 8.71(6) Å. Between two neighboring layers, the phenanthroline rings on different layers interdigitate.

Figure 4 reveals that the phenanthroline rings identified between two neighboring layers are parallel (the phenanthroline plane CP, CQ; CF, CH and CC, CB are parallel groups). The average distance of the two adjacent parallel phenanthroline planes is close (3.44(9) Å), indicating weak π–π interactions between the adjacent parallel phenanthroline rings. This type of π–π packing may be of high interest in the designing of advanced materials.

In synthesis of multidimensional solids consisting of carboxylate ligands and metal ions, a major challenge may come from the control of dimensionality. There are at least following four problems. First, since water molecules are excellent ligands for hard Co(II) metal ions, ancillary ligation of metal ions by water may result in low dimensionality such as in discrete $[Co(H_2O)_6(H_2bta)]$ (ref.[12]). Second, with Co(II) and two kinds of organic ligands, low dimensionality may come from the competition between the two

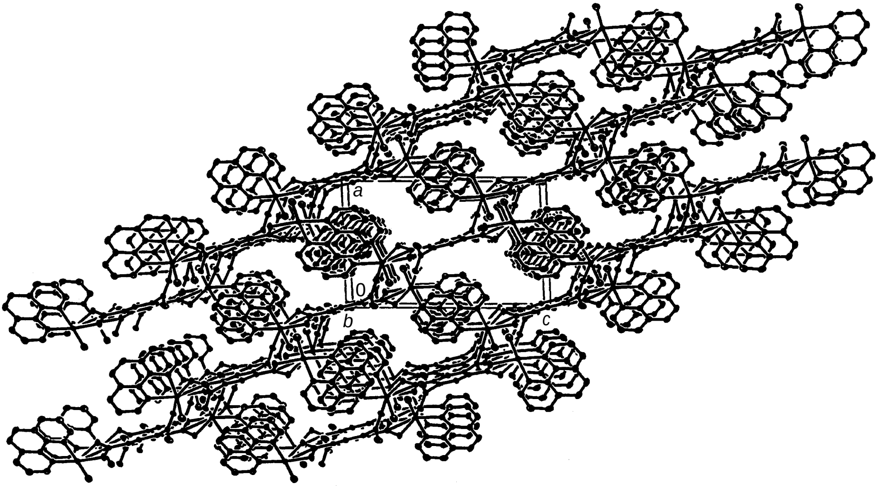

FIG. 3
Packing of $[Co(H_2O)(phen)(\mu_4\text{-}bta)_{1/2}]_n$ along the crystallographic axis *b*

kinds of coordinating organic ligands, *e.g.* full occupation of six sites per Co(II) ion with three phenanthroline ligands, and forming discrete complex cations $[Co(phen)_3]^{2+}$. Third, the low dimensionality may be caused by competition of polycarboxylate itself, because of its easy formation of hydrogen-bonded dimers or polymers[13]. Last, in alkaline and even neutral aqueous solutions, the construction of low-molecular-weight complexes from organic ligands and Co(II) ions will compete with the process of forming hydroxo- and oxo-bridging metal networks[14].

During our exploration of the above mentioned system, we found that maintaining the mole ratio of Co(II) : phen lower then unity favors the formation of compound **1**. As the ratio grew, the $[Co(phen)_3]^{2+}$ cations formed easily and resulted in the products of low dimensionality. pH of the reaction system is also an important factor. It must be controlled over pH 9.5 to obtain the target complex.

The herein determination of structure of compound **1** may help in better understanding of function of polycarboxylate ligands as building blocks in the engineering of new supramolecular architectures.

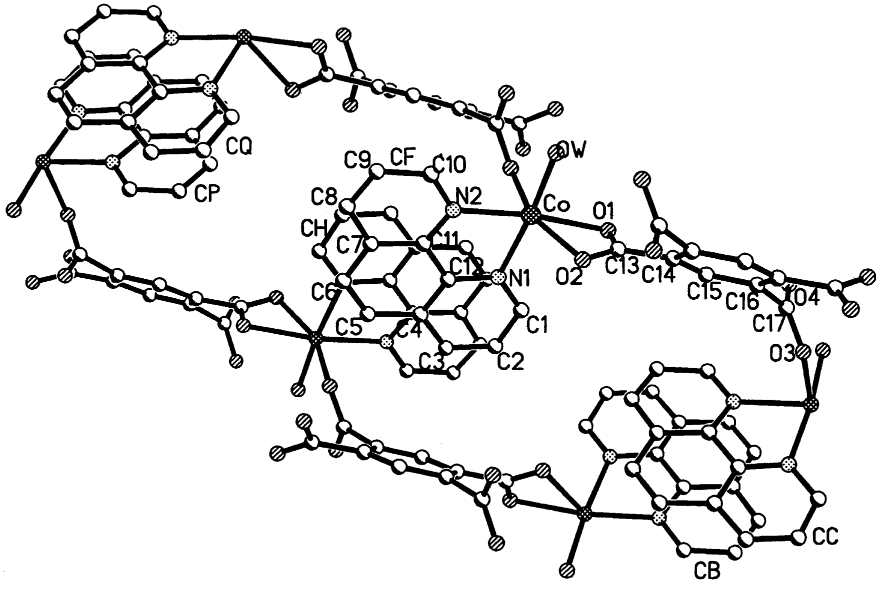

FIG. 4
The parallel π–π packing of the phenanthroline plane between two polymeric layers in the crystal. The planes CP, CQ; CF, CH and CC, CB are parallel groups

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