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The first pillared three-dimensional structure constructed by carboxylate ligands bridging heterometallic trilayers

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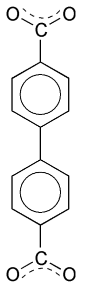
Reaction of an aqueous solution of Na_2bpdc (H_2bpdc = biphenyldicarboxylic acid) with an organic solution of $Co(NO_3)_2$ *via* a diffusion route leads to a pillared three-dimensional structure in which the heterometallic sodium(I)–cobalt(II) trilayers are connected by carboxylate groups of the pillared ligand bpdc^{2-}.

One of the challenges in crystal engineering is to predict the crystal packing from molecular structures. A reasonable approach to build three-dimensional structures based on layered structural motifs is to control the packing of layers by organic pillars of changeable length and/or type. This approach has been demonstrated to be effective towards assembly of both non-covalent and covalent pillared networks.[1] Pillared structures are potentially important for applications in absorption, separation and catalysis.[2] A variety of pillar-layered structures including positively and negatively charged or neutral layers have been synthesized.[3] Organically templated molybdenum oxides MOXI-1, -8, -24, -37 and indium phosphate (InPO) involve nitrogen donor pillars that connect to oxide layers.[4] Metal phosphonates of the type $M^{z+}_{4/z}(O_3P–R–PO_3)$ use phosphonate pillars $O_3P–R–PO_3$ where R is an alkyl or aryl group.[5] However, only a few pillared structures are built upon ligands containing carboxylate groups. Limited examples include exo-bicarboxylate in bilayer[6] and isonicotinate (with a carboxylate group and a pyridine nitrogen) in three-dimensional pillared structures.[7] In this contribution, we report a three-dimensional structure consisting of sodium(I)–cobalt(II) heterometallic trilayers and biphenylenecarboxylate pillars, **1**. It is interesting to note that this structure represents the first example of carboxylate pillared structures containing heterometallic layers.



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The title compound was synthesized by mixing organic and aqueous solutions *via* slow diffusion techniques. A DMF solution of $Co(NO_3)_2$ (0.1 M, 1 mL) was carefully layered on an aqueous solution of Na_2bpdc (0.1 M, 1 mL), through a 2 mL mixed (buffer) solution of EtOH–water (2:3). Pink block crystals of $Na_2Co(bpdc)_2(H_2O)$ **2**, suitable for X-ray diffraction analysis,† appeared after several days. Single crystal X-ray analysis revealed that each sodium ion has a distorted triangular bipyramidal (tbp) coordination. The apical positions of the tbp are occupied by two carboxylate oxygen atoms (O1, O2) from two bpdc^{2-}, while the equatorial positions are occupied by a η^2-oxygen atom (O5) of a water molecule and two carboxylate oxygen atoms (O3, O4) from another two bpdc^{2-}. Each sodium metal is connected with four adjacent sodium atoms located in the same plane through four carboxylate groups *via anti–anti* mode, leading to a two-dimensional grid-like metal network with Na···Na distances of 6.083 Å (along the *b*-axis) and 6.809 Å (along the *c*-axis). Two of these topologically identical Na planes are interconnected by Co. The octahedrally coordinated cobalt ion is located at the inversion center as a node, connected to four adjacent sodium ions through four O atoms at equatorial positions, two of which are *trans* η^2-oxygen atoms (O5, O5^i) of water molecules, and the other two, *trans* carboxylate η^2-oxygen (O1, O1^i). The remaining two (axial) positions around Co(II) are occupied by terminal water molecules (O6, O6^i). This arrangement results in a heterometallic metal slab consisting of a Na(I)–Co(II)–Na(I) trilayer running parallel to the *bc* plane, with the edge-shared sodium(I) and cobalt(II) separated by 3.397(2) Å. A view of the metal slab is illustrated in Fig. 1. This metal trilayer is quite different from that of a pillared zinc biphenylylenebis(phosphonate) $Zn_2(O_3PC_{12}H_8PO_3)\cdot 2H_2O$,[8] in which not only the metal atoms are connected to five neighboring metals by four PO_3 groups, but also they form a monometallic single layer.

The unique heterometallic trilayers in **2** are cross-linked by bpdc^{2-} ligands to form a pillared three-dimensional structure (Fig. 2). Two CO_2^- groups of each bicarboxylate attach the adjacent metal layers as a stud. Each group adopts a different coordination mode. One binds a metal layer through its two oxygen atoms to two sodium ions in a bidentate *anti–anti* mode. The other, at the opposite end of the bpdc^{2-}, forms tridentate bonds with the neighboring layer through its two oxygen atoms, coordinating to two sodium ions (in an *anti–anti* mode) and to one cobalt ion (with the η^2-oxygen). The twisting of the bpdc^{2-} ligand is a result of orientation adjustment to achieve a stable coordination geometry for both carboxylate and the metal ions from the layers above and below the pillar, and the *skew–skew* mode of the CO_2^- groups. The width of the heterometallic

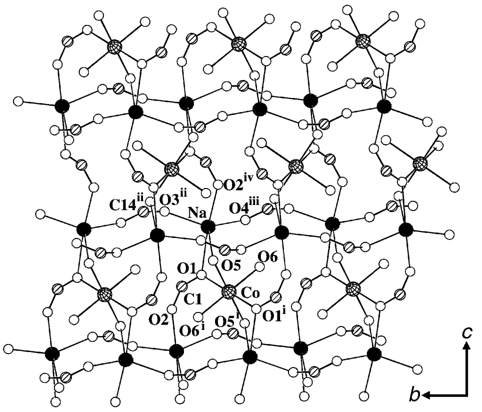

Fig. 1 View of **2** along the crystallographic *a*-axis. Solid and cross-shaded circles are Na and Co, and open and shaded circles are O and C atoms, respectively. Selected bond lengths (Å) and angles (°): Na–Co 3.397(2), Co–O(1) 2.042(3), Co–O(6) 2.044(3), Co–O5 2.210(3), Na–O(1) 2.530(4), Na–O(5) 2.509(3), Na–O(2)^{iv} 2.487(4), Na–O(4)^{iii} 2.271(4), Na–O(3)^{ii} 2.238(5); Na–Co–Na^i 180, Na–O(5)–Co 91.88(11), Na–O(1)–Co 95.36(14). Symmetry codes: i $-x + 1/2, -y + 1/2, -z-1$; ii $-x, y, -z + 1/2$; iii: $-x, y + 1, -z + 1/2$; iv: $x, -y, z - 1/2$.

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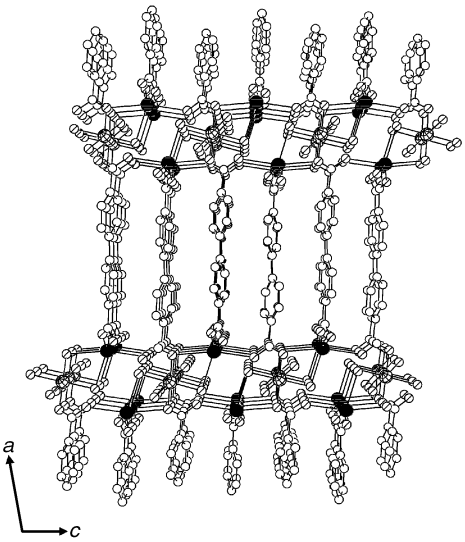

Fig. 2 Perspective view of **2** down the *b*-axis, The same labeling scheme as in Fig. 1 is used. The width of heterometallic trilayer is 3.75 Å and the interlayer distance is 11.5 Å.

trilayer is 3.75 Å. The distance between the two neighboring trilayers is 11.5 Å. The shortest average distance between neighboring benzene rings is 3.75 Å, falling in the range of π–π interactions. This non-covalent interaction may stabilize the pillared structure. However, the closely packed biphenylene groups in the title compound are too close to accommodate guest solvent molecules. The connectivity of bpdc^{2-} (μ_5) in this heterometallic structure cannot be obtained by mixing different ratios of aqueous solutions of Na_2bpdc (0.1 M) and $Co(NO_3)$ (0.1 M), ($V_{Na_2bpdc}/V_{Co(NO_3)_2}$ = 1:1, 1:5, 1:10, 10:1, 5:1; V = volume). The product from these reactions is a one-dimensional structure with a single Co ion center, $^{1}_{\infty}[Co(bpdc)(H_2O)_2]$,[9] which was confirmed by powder XRD. The one-dimensional chain in this structure was formed by connecting six-coordinated Co ions through the four μ-H_2O, and two *trans* μ-bpdc.

The present work has shown that heterometallic pillared structures can be effectively synthesized using a bicarboxylate as a pillar molecule. Furthermore, it is likely that other transition metal elements with similar coordination habits and pillars of different length may replace Na/Co and bpdc^{2-}, respectively, to form other related pillared structures. Suitable choices of ligands may also lead to porous, 3D pillared networks.

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Notes and references

† *Crystal data* for **2**: $Na_2CoC_{28}H_{24}O_{12}$, M = 657.38, monoclinic, space group $C2/c$ (no.15), a = 3.746(6), b = 6.083(1), c = 13.363(3) Å, Z = 4, V = 2500.0(8) Å^3, D_c = 1.747 g cm^{-3}, crystal size 0.10 × 0.06 × 0.04 mm, μ(Mo-Kα) = 0.795 mm^{-1}. The intensity data were collected with an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). 196 unique reflections of which 1097 were measured; $R_1[I > 2\sigma(I)]$ = 0.063, wR_2 (all data) = 0.0668, GOF = 0.951. The structure were solved by direct methods (SHELXS-86) and refined by full-matrix least-squared methods (SHELXL-97). All non-hydrogen atoms were refined anisotropically.

CCDC 182/1862. See http://www.rsc.org/suppdata/cc/b0/b007344j/ for crystallographic files in .cif format.

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