metal-organic compounds

Polymeric dihydroxydiphthalato-tricobalt(II)

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In the crystal structure of dihydroxydiphthalatotricobalt(II), $[Co_3(C_8H_4O_4)_2(OH)_2]_n$, two of the four independent Co atoms lie at special positions of site symmetry 2. The hydroxy groups link three Co atoms to form a pyramidal Co_3O unit, and adjacent Co_3O units are linked through the Co base atoms into a honeycomb layer motif. Each of the phthalate dianions uses the O atoms of one carboxyl group to bind to three Co atoms, the bonding mode giving rise to six-coordinate Co atoms.

Comment

Hydrothermally synthesized cobalt(II) derivatives of benzene polycarboxylic acids exist as hydroxides. The tetracarboxylate compound adopts a framework architecture that constitutes roughly only half the volume of the unit cell (Gutschke *et al.*, 2001*a*). Cobalt hydroxide benzene-1,4-dicarboxylate, on the other hand, packs in such a manner that the π systems of adjacent carboxylate anions interact magnetically (Huang *et al.*, 2000). Other than a tricarboxylate derivative (Gutschke *et al.*, 2001*b*), there are no further reports to date of such cobalt hydroxide derivatives of benzene polycarboxylic acids.

Unlike the reaction of cobalt(II) carbonate with phthalic acid in water, which affords hexaaquacobalt hydrogen phthalate (Kariuki & Jones, 1993), the reaction of cobalt(II) nitrate and potassium hydrogen phthalate under hydrothermal conditions yielded the title cobalt(II) hydroxide derivative, (I), and its structure is presented here.

The crystal structure of (I) is built up of a layer motif consisting of corner-sharing pyramidal Co_3O units. These units are linked through the Co corners to form a hexagonal unit, which also shares its Co corners, giving rise to a honeycomb motif (Fig. 1). The layers that make up the structure feature a Co_3O core, and the aromatic groups protrude from the top and bottom of each layer. Where the layers come together,

aromatic–aromatic edge–face interactions exist. The Co_3O unit is also documented in the other compounds mentioned above. For example, in the terephthalate derivative $[Co_2(C_8H_4O_4)(OH)_2]$, the Co_3O units form layer structures by edge- and corner-sharing (Huang *et al.*, 2000). This layer motif is not adopted by the tri- and tetracarboxylates.

(I)
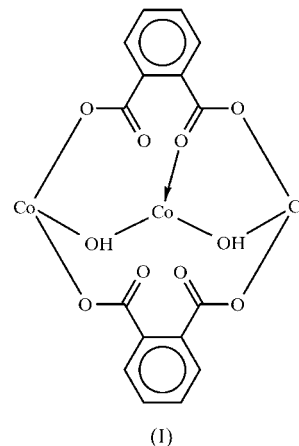
The four independent Co atoms in (I) exist in an octahedral environment (Fig. 2), and each is coordinated by four O atoms from carboxyl groups and two O atoms from hydroxyl groups.
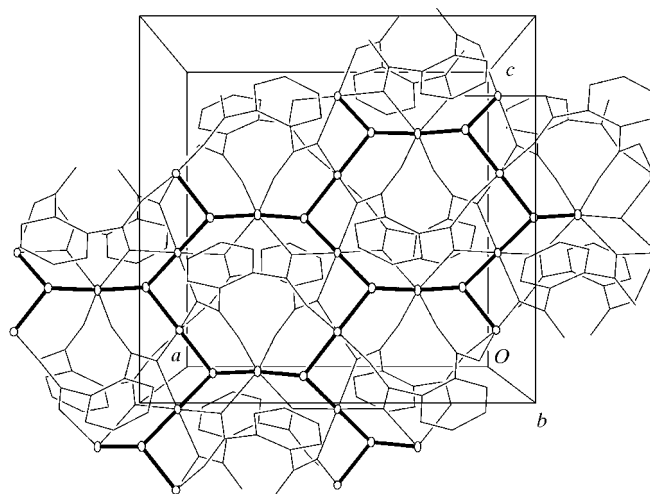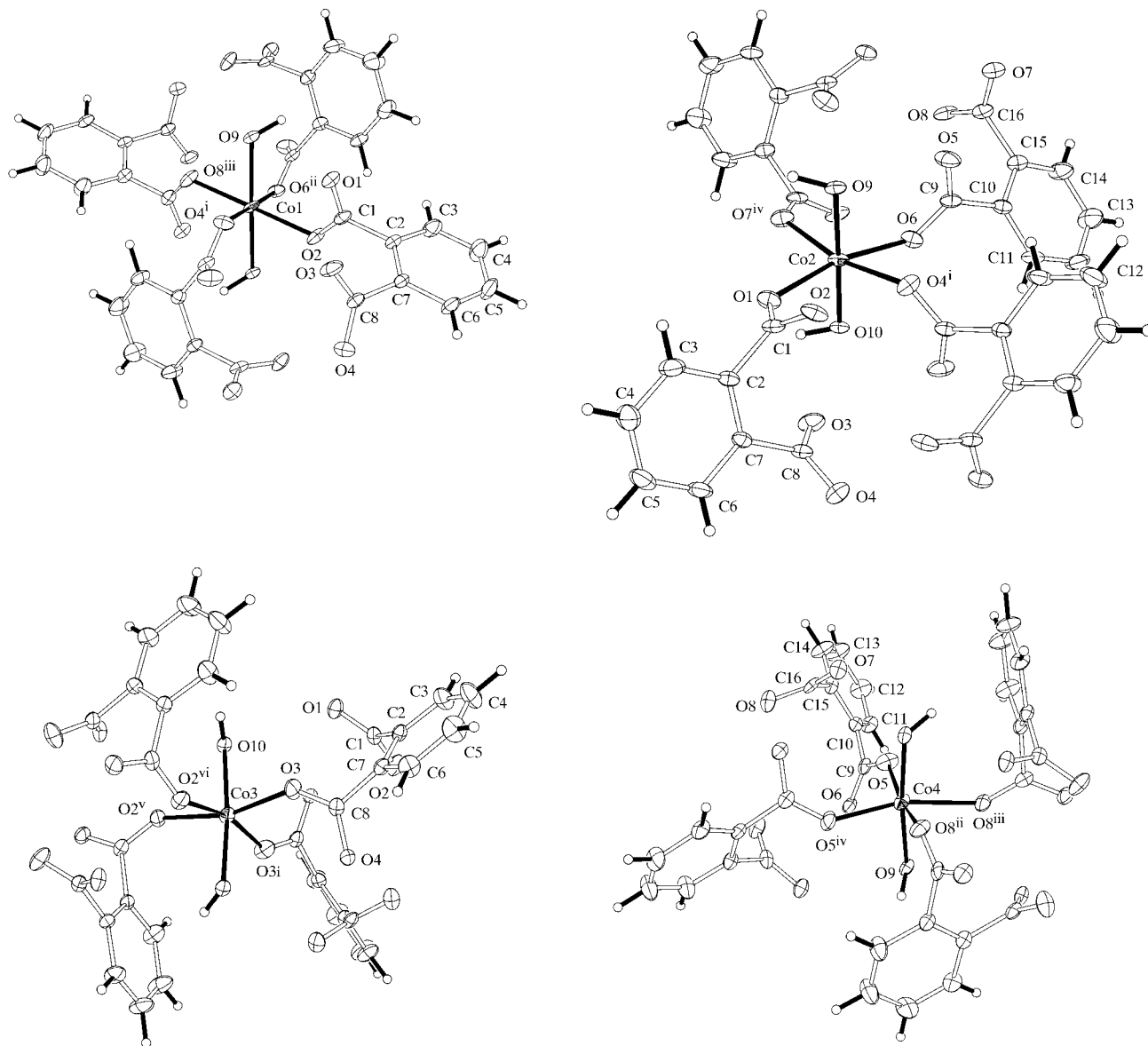

Figure 1
A view of the layer structure of (I), illustrating the honeycomb motif built from Co_3O pyramids.

Each hydroxyl group bridges three Co atoms. For both independent phthalate dianions, each carboxyl $-CO_2$ group is linked to three Co atoms.

Experimental

Cobalt(II) nitrate hexahydrate (0.17 g, 0.6 mmol) and potassium hydrogen phthalate (0.37 g, 1.8 mmol) were dissolved in water (15 ml). The solution was placed in a Teflon-lined stainless-steel vessel, which was then heated to 473 K for 60 h. The vessel was then allowed to cool to room temperature and needle-shaped crystals of

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Figure 2
Views of the coordination environments of the four independent Co atoms in (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} - y, z$; (ii) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (iii) $\frac{3}{2} - x, y, z - \frac{1}{2}$; (iv) $\frac{3}{2} - x, \frac{1}{2} - y, z$; (v) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (vi) $\frac{1}{2} - x, y, \frac{1}{2} + z$.]

(I) deposited from the solution in about 10% yield. Analysis calculated for $C_{16}H_{10}Co_3O_{10}$: C 35.65, H 1.87%; found: C 35.51, H 1.86%. FT–IR (KBr, v, cm^{-1}): 3596 (s), 3422 (br), 3070 (w), 2930 (w), 1625 (s), 1599 (vs), 1581 (s), 1568 (s), 1494, 1448, 1425, 1389 (s), 1280 (w), 1156, 1093, 1040, 947 (w), 868, 842, 806, 788, 767, 738, 699, 658, 588 (w), 469, 452.

Crystal data

$[Co_3(C_8H_4O_4)_2(OH)_2]$
$M_r = 539.03$
Orthorhombic, $Pccn$
$a = 12.1121\,(5)$ Å
$b = 22.6847\,(9)$ Å
$c = 11.8730\,(5)$ Å
$V = 3262.2\,(2)$ Å^3
$Z = 8$
$D_x = 2.195$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 8115 reflections
$\theta = 1.8–28.3°$
$\mu = 3.08$ mm^{-1}
$T = 298\,(2)$ K
Needle, pink
$0.45 \times 0.13 \times 0.03$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.692$, $T_{max} = 0.912$
26 490 measured reflections

3904 independent reflections
2518 reflections with $I > 2\sigma(I)$
$R_{int} = 0.057$
$\theta_{max} = 28.3°$
$h = -16 \rightarrow 15$
$k = -30 \rightarrow 30$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.104$
$S = 0.89$
3904 reflections
263 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0664P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.71$ e Å^{-3}
$\Delta\rho_{min} = -0.82$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—O2	2.119 (2)	Co2—O7[iv]	2.115 (2)
Co1—O4[i]	2.105 (2)	Co2—O9	2.087 (2)
Co1—O6[ii]	2.097 (2)	Co2—O10	2.086 (2)
Co1—O8[iii]	2.115 (2)	Co3—O2[v]	2.340 (2)
Co1—O9	2.094 (2)	Co3—O3	2.063 (2)
Co1—O10[ii]	2.089 (2)	Co3—O10	2.018 (2)
Co2—O1	2.108 (2)	Co4—O5	2.056 (2)
Co2—O4[i]	2.116 (2)	Co4—O8[ii]	2.379 (2)
Co2—O6	2.110 (2)	Co4—O9	2.010 (2)
O2—Co1—O4[i]	81.7 (1)	O6—Co2—O7[iv]	93.4 (1)
O2—Co1—O6[ii]	98.5 (1)	O6—Co2—O9	102.0 (1)
O2—Co1—O8[iii]	179.4 (1)	O6—Co2—O10	79.2 (1)
O2—Co1—O9	100.6 (1)	O7[iv]—Co2—O9	93.0 (1)
O2—Co1—O10[ii]	78.5 (1)	O7[iv]—Co2—O10	86.6 (1)
O4[i]—Co1—O6[ii]	178.8 (1)	O9—Co2—O10	178.8 (1)
O4[i]—Co1—O8[iii]	97.8 (1)	O2[v]—Co3—O2[vi]	99.4 (1)
O4[i]—Co1—O9	78.8 (1)	O2[v]—Co3—O3	162.9 (1)
O4[i]—Co1—O10[ii]	101.8 (1)	O2[v]—Co3—O3[i]	83.3 (1)
O6[ii]—Co1—O8[iii]	82.0 (1)	O2[v]—Co3—O10	74.9 (1)
O6[ii]—Co1—O9	100.0 (1)	O2[v]—Co3—O10[i]	101.5 (1)
O6[ii]—Co1—O10[ii]	79.4 (1)	O3—Co3—O3[i]	99.1 (1)
O8[iii]—Co1—O9	79.5 (1)	O3—Co3—O10	88.0 (1)
O8[iii]—Co1—O10[ii]	101.4 (1)	O3—Co3—O10[i]	95.5 (1)
O9—Co1—O10[ii]	178.8 (1)	O10—Co3—O10[i]	174.6 (1)
O1—Co2—O4[i]	93.7 (1)	O5—Co4—O5[iv]	99.4 (1)
O1—Co2—O6	167.7 (1)	O5—Co4—O8[ii]	163.7 (1)
O1—Co2—O7[iv]	95.2 (1)	O5—Co4—O8[iii]	82.1 (1)
O1—Co2—O9	86.3 (1)	O5—Co4—O9	96.0 (1)
O1—Co2—O10	92.6 (1)	O5—Co4—O9[iv]	88.5 (1)
O4[i]—Co2—O6	79.3 (1)	O8[ii]—Co4—O8[iii]	101.0 (1)
O4[i]—Co2—O7[iv]	167.5 (1)	O8[ii]—Co4—O9[iv]	75.1 (1)
O4[i]—Co2—O9	78.7 (1)	O8[ii]—Co4—O9	100.3 (1)
O4[i]—Co2—O10	101.9 (1)	O9—Co4—O9[iv]	173.0 (1)

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} - y, z$; (ii) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (iii) $\frac{3}{2} - x, y, z - \frac{1}{2}$; (iv) $\frac{3}{2} - x, \frac{1}{2} - y, z$; (v) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (vi) $\frac{1}{2} - x, y, \frac{1}{2} + z$.

The aromatic and hydroxyl H atoms were generated geometrically (C—H = 0.93 Å and O—H = 0.98 Å) and were allowed to ride on their parent atoms in riding-model approximations, with U_{iso}(H) values set at $1.2U_{eq}$(parent). The final difference map had peaks of more than 1 e Å^{-3} near the four Co atoms.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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