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Key indicators

Single-crystal X-ray study

T = 173 K

Mean $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$

R factor = 0.065

wR factor = 0.188

Data-to-parameter ratio = 13.5

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.**catena-Poly[[[bis(μ -4-cyanobenzoato- $\kappa^2\text{O}:\text{O}$)-bis[(4-cyanobenzoato- $\kappa^2\text{O},\text{O}'$)]cobalt(II)]-di- μ -4,4'-bipyridine- $\kappa^4\text{N}:\text{N}'$]] dihydrate dimethylformamide tetrasolvate]**

The crystal structure of the title compound, $\{[\text{Co}_2(\text{C}_8\text{H}_4\text{NO}_2)_4(\text{C}_{10}\text{H}_8\text{N}_2)_2] \cdot 2\text{H}_2\text{O} \cdot 4\text{C}_3\text{H}_7\text{NO}\}_n$, features a centrosymmetric eight-membered $-\text{Co}-\text{O}-\text{C}-\text{O}-\text{Co}-\text{O}-\text{C}-\text{O}-$ ring that arises from the bridging of two Co atoms by two cyanobenzoate units across a center of symmetry. Each Co atom is also chelated by a cyanobenzoate unit and the two remaining coordination sites, *trans* to each other in the distorted octahedron, are occupied by the N atoms of the heterocycle, resulting in a polymeric ribbon structure. The water and dimethylformamide molecules occupy the space between the chains.

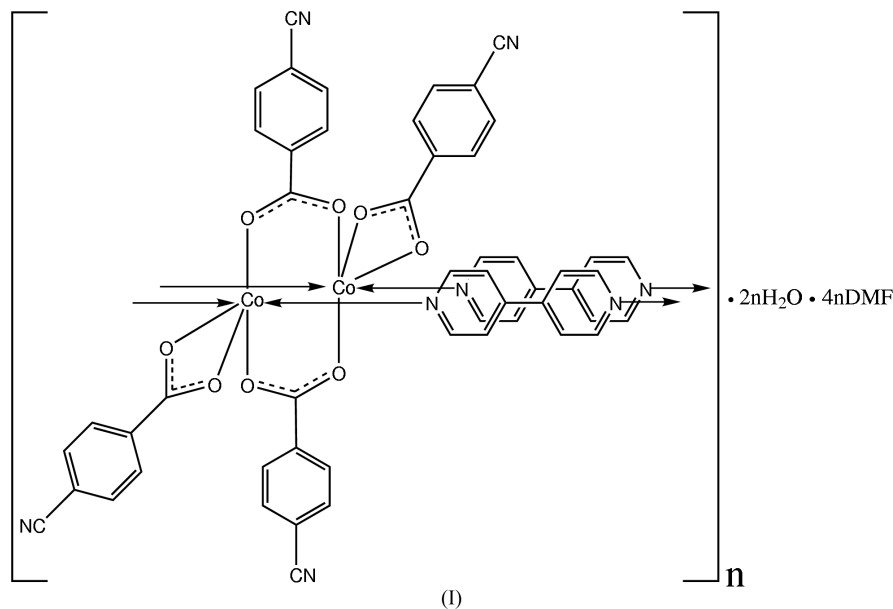
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Comment

In the crystal structure of the cobalt(II) derivative of 4-cyanobenzoic acid, the anionic units bridge adjacent metal atoms, giving rise to a layer motif. As the metal atom is coordinated by two water molecules, hydrogen-bonding interactions are present that further consolidate a tightly held layer motif (He *et al.*, 2004).



The introduction of 4,4'-bipyridine modifies the layer structure to one in which the amine ligand now serves as a bridging entity, but the resulting compound, *viz.* $[\text{Co}(\text{C}_8\text{H}_4\text{NO}_2)_2(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_2]$, (II), retains its two water molecules in the coordination sphere (He *et al.*, 2003).

A modification of the synthesis of (II), with dimethylformamide/water as solvent in place of methanol, has yielded a compound without water in the cobalt coordination sphere,

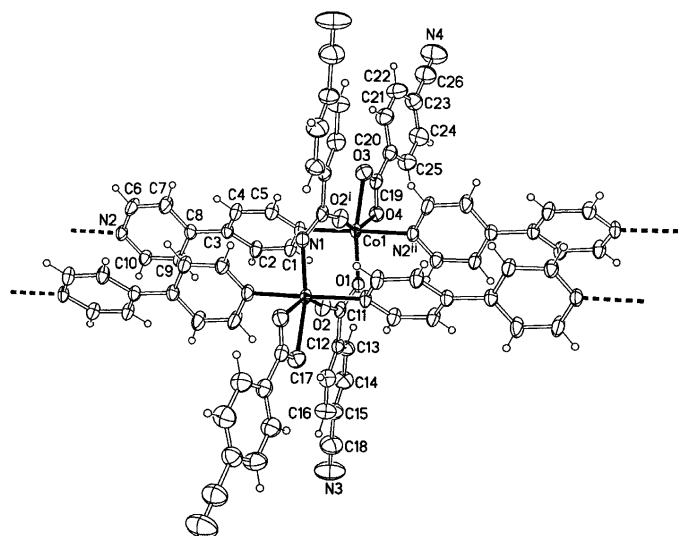


Figure 1
View of (I) showing 50% probability displacement ellipsoids and the H atoms as spheres of arbitrary radius. The water and dimethylformamide molecules are not shown. [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $x, 1 + y, z$.]

namely *catena*-poly[[[bis(μ -4-cyanobenzoato)bis[(4-cyanobenzoato)cobalt(II)]]-di- μ -4,4'-bipyridine] dihydrate dimethylformamide tetrasolvate], (I) (Fig. 1).

In (I), one anion bonds to two Co atoms to form, when inversion symmetry is taken into account, a centrosymmetric eight-membered $-\text{Co}-\text{O}-\text{C}-\text{O}-\text{Co}-\text{O}-\text{C}-\text{O}-$ ring. Each Co atom is also chelated by a 4-cyanobenzoate anion, resulting in a very acute $\text{O}3-\text{Co}1-\text{O}4$ bond angle (Table 1). The four O atoms surrounding the Co atom approximate to a square plane and the axial coordination sites of the octahedron are occupied by the N atoms of the *N*-heterocycle, thus forming a polymeric ribbon propagating along [010]. The two pyridyl rings of the heterocycle are twisted with respect to each other by $23.3(3)^\circ$.

The solvent (water and dimethylformamide) molecules occupy the space between the chains and may be disordered. There are probable $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds involving the water molecule (Table 2).

Experimental

Cobalt(II) acetate tetrahydrate (0.125 g, 0.5 mmol), 4-cyanobenzoic acid (0.159 g, 1.0 mmol) and 4,4'-bipyridine (0.078 g, 0.5 mmol) were dissolved in an *N,N*-dimethylformamide (20 ml), methanol (20 ml) and water (10 ml) mixture. Red block-shaped crystals of (I) separated from the solution after two weeks.

Crystal data

$[\text{Co}_2(\text{C}_8\text{H}_4\text{NO}_2)_4(\text{C}_{10}\text{H}_8\text{N}_2)_2] \cdot 2\text{H}_2\text{O} \cdot 4\text{C}_3\text{H}_7\text{NO}$	$D_x = 1.378 \text{ Mg m}^{-3}$
$M_r = 1343.14$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 29299 reflections
$a = 17.6227(9) \text{ \AA}$	$\theta = 1.2-27.5^\circ$
$b = 11.3661(5) \text{ \AA}$	$\mu = 0.59 \text{ mm}^{-1}$
$c = 17.1939(7) \text{ \AA}$	$T = 173(2) \text{ K}$
$\beta = 110.011(2)^\circ$	Block, red
$V = 3236.0(3) \text{ \AA}^3$	$0.30 \times 0.18 \times 0.09 \text{ mm}$
$Z = 2$	

Data collection

Rigaku R-Axis RAPID diffractometer	5653 independent reflections
ω scans	4559 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$R_{\text{int}} = 0.050$
$T_{\text{min}} = 0.641, T_{\text{max}} = 0.949$	$\theta_{\text{max}} = 25.0^\circ$
23077 measured reflections	$h = -20 \rightarrow 20$
	$k = -13 \rightarrow 11$
	$l = -20 \rightarrow 20$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0939P)^2 + 6.7732P]$
$R[F^2 > 2\sigma(F^2)] = 0.065$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.188$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.11$	$\Delta\rho_{\text{max}} = 1.06 \text{ e \AA}^{-3}$
5653 reflections	$\Delta\rho_{\text{min}} = -0.60 \text{ e \AA}^{-3}$
419 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

Co1—O1	2.046 (3)	Co1—O4	2.211 (3)
Co1—O2 ⁱ	2.025 (3)	Co1—N1	2.127 (3)
Co1—O3	2.181 (3)	Co1—N2 ⁱⁱ	2.135 (3)
O1—Co1—O2 ⁱ	119.1 (1)	O2 ⁱ —Co1—N2 ⁱⁱ	87.5 (1)
O1—Co1—O3	150.2 (1)	O3—Co1—O4	60.0 (1)
O1—Co1—O4	90.2 (1)	O3—Co1—N1	92.2 (1)
O1—Co1—N1	88.5 (1)	O3—Co1—N2 ⁱⁱ	89.0 (1)
O1—Co1—N2 ⁱⁱ	90.5 (1)	O4—Co1—N1	92.0 (1)
O2 ⁱ —Co1—O3	90.7 (1)	O4—Co1—N2 ⁱⁱ	88.7 (1)
O2 ⁱ —Co1—O4	150.5 (1)	N1—Co1—N2 ⁱⁱ	178.7 (1)
O2 ⁱ —Co1—N1	92.3 (1)		

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $x, 1 + y, z$.

Table 2

Hydrogen-bonding geometry ($\text{\AA}, ^\circ$).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O}1\text{w}-\text{H}1\text{w}1\cdots\text{O}3$	0.88	2.29	3.14 (2)	165
$\text{O}1\text{w}-\text{H}1\text{w}2\cdots\text{O}5$	0.89	2.15	3.02 (2)	165

The methyl H atoms were allowed to rotate to fit the electron density [$\text{C}-\text{H} = 0.98 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$]. The other carbon-bound H atoms were positioned geometrically and refined as riding [aromatic $\text{C}-\text{H} = 0.95 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$]. The H atoms of the water molecule were placed at chemically reasonable positions on the basis of possible hydrogen-bonding interactions with O atoms, but their positions were not refined. The structure apparently has some disorder in the two dimethylformamide molecules, but attempts at refinement using split-site models did not lead to a meaningful outcome. Similarly, the refinement of the water molecule as two half-occupancy water molecules was not undertaken. The largest peak in the final difference Fourier map is about 1 \AA from atoms O5 and N5.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSK, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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