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Poly[[diaquacobalt(II)]-di-μ-4-cyano-benzoato-κ^4O:O']

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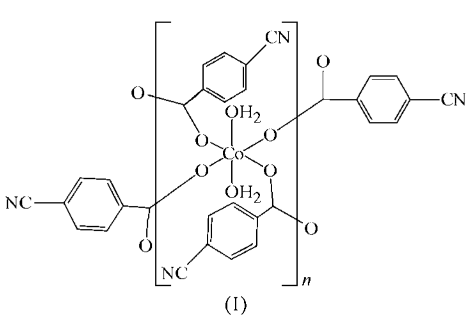
The title compound, $[Co(C_8H_4NO_2)_2(H_2O)_2]_n$, which was obtained by the reaction of $CoCl_2\cdot6H_2O$ with 4-cyanobenzoic acid, is the first two-dimensional 4-cyanobenzoate cobalt(II) polymer. The Co atom lies on a centre of symmetry and its coordination polyhedron is a slightly distorted octahedron, defined by two water and four carboxylate O atoms. The 4-cyanobenzoate (cba) anion is bridging in a *syn*-skew coordination mode, which ensures a two-dimensional architecture with the building block $Co_4(cba)_4$.

Comment

The design and construction of frameworks in the field of coordination polymers have been extensively studied due to their potential applications as functional materials (Alam, 2003; Liddle & Clegg, 2002; Seo *et al.*, 2000). Recently, complexes with 4-cyanobenzoic acid (Hcba) have received considerable attention due to their potential application as strongly fluorescent materials (Yuan *et al.*, 2001) and their structural interest (Wang *et al.*, 2003). However, all examples of 4-cyanobenzoate–metal complexes reported to date are monomers [with Co^{II} (Xie *et al.*, 2004; He & Zhu, 2003*a*) or Cu^{II} (Zhou *et al.*, 2003; Wang *et al.*, 2003)], dimers [with Rh^{II} (Schiavo *et al.*, 2003)] or one-dimensional polymers [with Ca^{II} (Yuan *et al.*, 2001), Cu^{II} (He & Zhu, 2003*b*) or Co^{II} (He *et al.*, 2003)]. In this paper, we report the title compound, (I), which is the first two-dimensional compound constructed with the cba ligand.



(I)

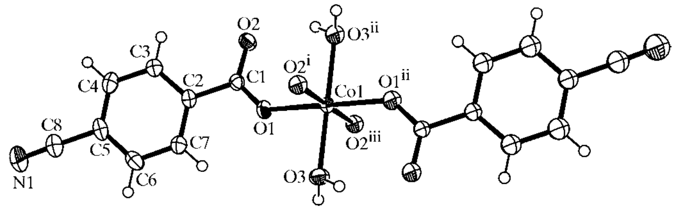


Figure 1
A view of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $1 - x, -y, 1 - z$; (iii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$.]

The Co atom in (I) lies on a centre of symmetry and the structure is two-dimensional, with the Co atom in a slightly distorted octahedral geometry defined by two O-atom donors from two water molecules and four O atoms from four cba ligands (Fig. 1 and Table 1). Atoms O1, $O1^{ii}$, O3 and $O3^{ii}$ occupy the basal plane, while atoms $O2^{iii}$ and $O2^{i}$ occupy the apical positions [symmetry codes: (i) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $1 - x, -y, 1 - z$; (iii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$]. The Co—O*W* bond distances [2.0913 (15) Å] in (I) are shorter than those in the analogous compounds $[Co(cba)_2(phen)(H_2O)_2]$, (II) [2.114 (2) and 2.156 (2) Å; Xie *et al.*, 2004], $[Co(cba)_2(4,4'\text{-bipy})(H_2O)_2]_n$, (III) [2.155 (2) Å; He *et al.*, 2003] and $[Co(cba)_2(3\text{-}NH_2\text{-py})_2(H_2O)_2]\cdot2H_2O$, (IV) [2.120 (2) Å; He & Zhu, 2003*a*]. In compounds (II)–(IV), the carboxylate groups are all in a *syn*-monodentate coordination mode and the Co—O(COO^-) bond distances [2.071 (2)–2.110 (2) Å] are shorter than the Co—O*W* distances [2.114 (2)–2.156 (2) Å]. In (I), the carboxylate group has a bridging mode and two kinds of Co—O(COO^-) bond distances are observed, namely the Co1—O1 distance of 2.0527 (14) Å in the *syn*-coordination mode, which is shorter than the Co—O*W* distance, and the Co1—$O2^{i}$ distance of 2.1437 (14) Å in the skew-coordination mode.

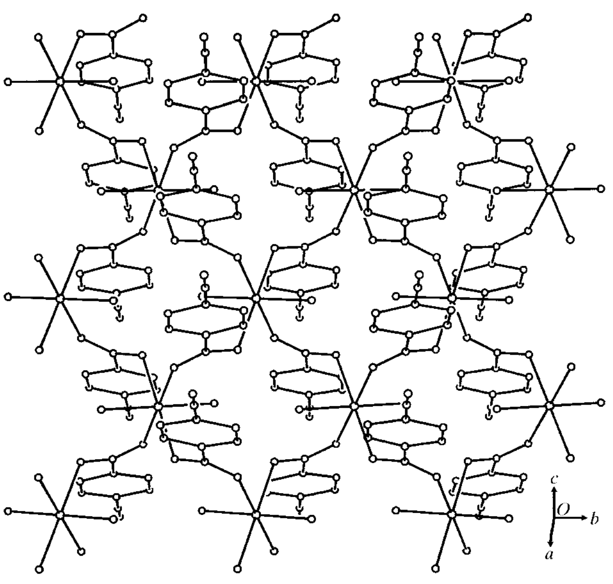


Figure 2
A view of the two-dimensional framework of (I), projected along $(10\bar{1})$. H atoms have been omitted for clarity.

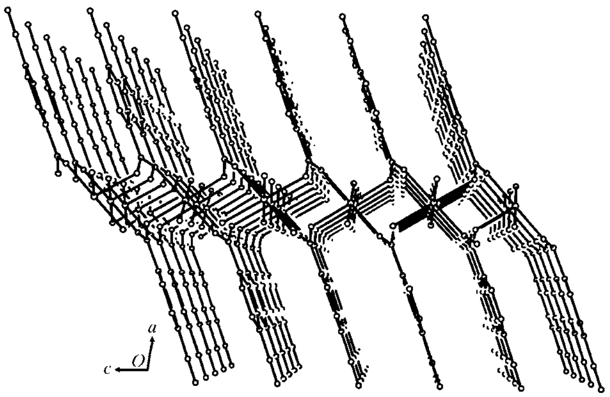


Figure 3
A view of the π–π interactions in (I).

In (I), the carboxylate group is not coplanar with the attached benzene ring, the dihedral angle between the planes being 15.2 (2)°. Moreover, the bridging mode of the 4-cyanobenzoate ligand is *syn*-skew and the Co···Co separation bridged by the cba ligand is 4.9471 (4) Å. The bridging skew coordination of the cba ligand leads to a building unit of $Co_4(cba)_4$, which is the basic unit in the two-dimensional framework (Fig. 2).

In most of the previously reported 4-cyanobenzoate complexes, there is an $[M(cba)_2(H_2O)_2]$ motif. The two water molecules can be arranged in a *cis* or *trans* pattern. In (II), the two water molecules are arranged *cis*, while in (III) and (IV) the two water molecules are in *trans* positions. Although *cis*- or *trans*-(O*W*, O*W*) types could be found in (II)–(IV), the $[Co(cba)_2(H_2O)_2]$ structures in these three compounds are monomeric, with the cba ligands in a *syn*-monodentate mode. In the one-dimensional structure of $[Ca(cba)_2(H_2O)_2]$ (Yuan *et al.*, 2001), the cba ligand is in a *syn*-skew bridging mode and the two water molecules are *cis*. In contrast, the aqua ligands in (I) are *trans*. Therefore, the combination of the bridging coordination mode and the *trans* arrangement of the aqua ligands leads to the two-dimensional architecture observed in (I).

In the crystal structure of (I), π–π interactions between cba ligands are observed (Fig. 3). The shifts of atoms C2–C7 at (x, y, z) from the plane defined by atoms C2–C7 at $(x, \frac{1}{2} - y, \frac{1}{2} + z)$ are in the range 3.305 (4)–3.586 (3) Å. In the two-dimensional framework, these π–π interactions of the cyanophenyl groups are extended into one-dimensional stacking columns along the *c* axis. Moreover, hydrogen bonds (Table 2) are observed in the two-dimensional framework. The coordinated water molecule forms hydrogen bonds with neighbouring carboxylate groups. Therefore, π–π and hydrogen-bonding interactions enhance the stability of the crystal structure.

Experimental

A solution of $CoCl_2\cdot 6H_2O$ (0.0717 g, 0.3 mmol) in water (10 ml) was mixed with a previously prepared solution of 4-cyanobenzoic acid (0.0833 g, 0.57 mmol) and 4-aminopyridine (0.0536 g, 0.57 mmol) in dimethylformamide (10 ml). The resulting solution was set aside and allowed to evaporate slowly. After three months, dark-red crystals of (I) had formed and these were collected for X-ray analysis.

Crystal data

$[Co(C_8H_4NO_2)_2(H_2O)_2]$
$M_r = 387.21$
Monoclinic, $P2_1/c$
$a = 15.5951 (18)$ Å
$b = 6.6087 (7)$ Å
$c = 7.3635 (8)$ Å
$\beta = 96.979 (2)°$
$V = 753.28 (14)$ Å^3
$Z = 2$
$D_x = 1.707$ Mg m^{-3}

Mo *K*α radiation
Cell parameters from 2419 reflections
$\theta = 5.3–56.4°$
$\mu = 1.18$ mm^{-1}
$T = 293 (2)$ K
Block, dark red
0.48 × 0.32 × 0.18 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.639$, $T_{\max} = 0.809$
4306 measured reflections
1656 independent reflections

1473 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.077$
$\theta_{\max} = 27.1°$
$h = -19 \rightarrow 19$
$k = -8 \rightarrow 7$
$l = -7 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.097$
$S = 1.10$
1656 reflections
121 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0445P)^2 + 0.1431P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.49$ e Å^{-3}
$\Delta\rho_{\min} = -0.38$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—O1	2.0527 (14)	O1—C1	1.247 (2)
Co1—O3	2.0913 (15)	O2—C1	1.270 (2)
Co1—O2^{i}	2.1437 (14)		
O1—Co1—O3	87.70 (6)	O3—Co1—O2^{i}	89.13 (6)
O1—Co1—O2^{i}	95.49 (6)	O1—Co1—O2^{iii}	84.51 (6)
Co1—O1—C1—O2	19.6 (3)	Co1^{iv}—O2—C1—O1	100.8 (2)

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*A*···O2^{i}	0.88 (2)	2.01 (2)	2.881 (2)	170 (3)
O3—H3*B*···O2^{ii}	0.88 (2)	2.14 (2)	2.867 (2)	140 (2)
O3—H3*B*···O1^{iii}	0.88 (2)	2.35 (2)	3.087 (2)	142 (2)

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

H atoms bonded to C atoms were located geometrically and treated as riding, with C—H distances of 0.93 Å and with $U_{\rm iso}(H) = 1.2U_{\rm eq}(C)$. The water H atoms were located from difference Fourier maps and refined, with restraints on the O—H distances [0.88 (1) Å] and with $U_{\rm iso}(H) = 0.05$ Å^2.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1199). Services for accessing these data are described at the back of the journal.

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