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A new supramolecular framework through hydrogen bonds in *catena*-poly[[[tetraaquacobalt(II)]-μ-4,4-bipyridine-$\kappa^2N:N'$] 2-carboxylatocinnamate dihydrate]

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Key indicators

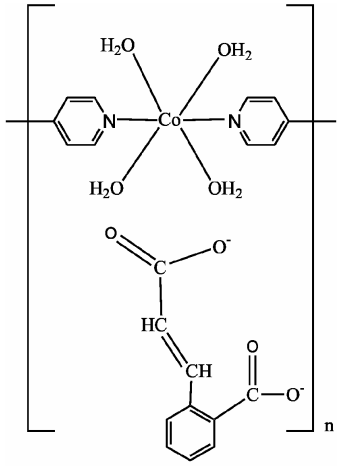
Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.003 Å
R factor = 0.022
wR factor = 0.045
Data-to-parameter ratio = 9.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title complex, $\{[Co(4,4'\text{-bipy})(H_2O)_4](CCA)\cdot 2H_2O\}_n$ (where bipy is bipyridine, $C_{10}H_8N_2$, and CCA^{2-} is 2-carboxylatocinnamate, $C_{10}H_6O_4$), is a linear polymer constructed from cobalt and 4,4′-bipy, and which contains uncoordinated CCA^{2-} counter-ions. There are two independent formula units in the asymmetric unit. O—H···O hydrogen bonds connect the structure into a three-dimensional network.

Comment

The utility of linear bifunctional ligands, such as 4,4′-bipyridine (4,4′-bipy), has been well explored in studies of the crystal engineering of coordination polymers (Briadha & Fujita, 2001). We are interested in the synthesis of novel compounds which contain not only 4,4′-bipy but also carboxylate groups in the crystal structure (Almeida Paz *et al.*, 2003). In this paper, we report the synthesis and crystal structure of the title compound, (I), of which the asymmetric unit is shown in Fig. 1.



(I)

The cation shows a slightly distorted octahedral coordination environment composed of a central Co atom with four water molecules (forming the equatorial plane) and two coordinated 4,4′-bipy N atoms at the axial positions (see Table 1 for selected geometric parameters). The 4,4′-bipy ligand bridges the Co atoms directly to form a one-dimensional chain. The 2-carboxylatocinnamate (CCA^{2-}) anion does not take part in coordination, but acts as a charge balance with two deprotonated carboxylate groups, and supplies hydrogen-bonding acceptor O atoms. O—H···O hydrogen bonds exist between carboxylate groups, uncoordinated water and coordinated water molecules (see Table 2 for hydrogen-

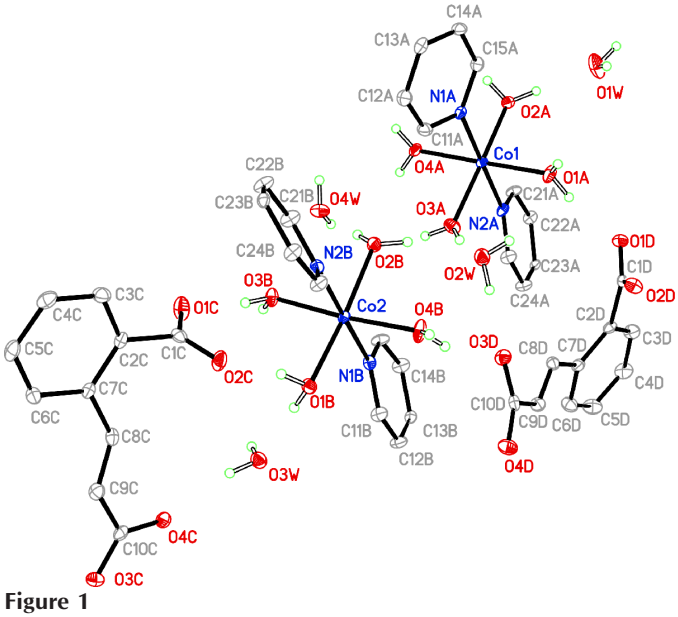


Figure 1
A view of the asymmetric unit of the title compound with displacement ellipsoids drawn at the 50% probability level. Carbon-bound H atoms have been omitted.

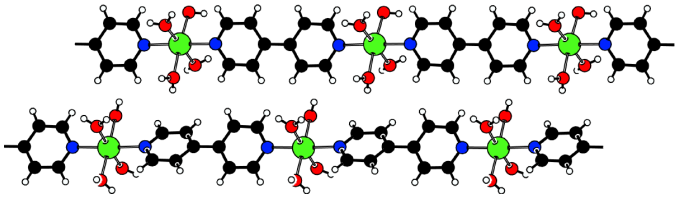


Figure 2
View (Spek, 2004) of two portions of the one-dimensional chain structure of the title compound. The deprotonated 2-carboxylatocinnamate counter-ions and the solvent water molecules are not shown. Colour code: green Co, red O, blue N and black C.

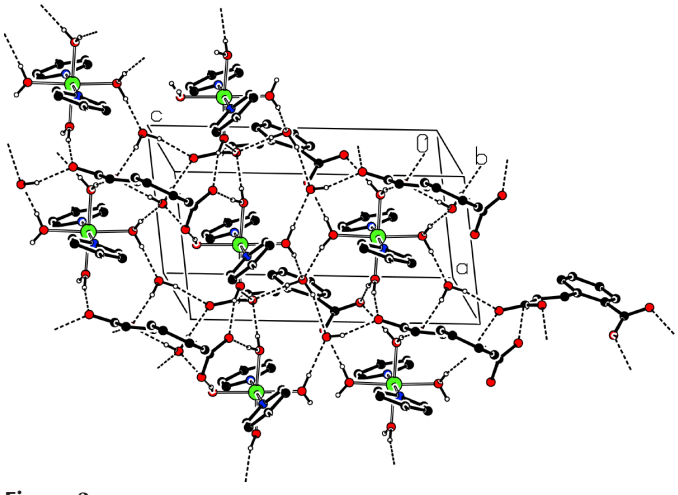


Figure 3
View (Spek, 2004) of the three-dimensional hydrogen-bonded network (shown as dashed lines) in the title compound.

bonding geometries), which connect the one-dimensional Co–bipy chain (Fig. 2) and the free CCA^{2-} ligands into a three-dimensional supramolecular network (Fig. 3).

Experimental

The title compound, (I), was obtained unexpectedly. 4,4′-Bipyridine (0.0156 g, 0.1 mmol), 2-carboxycinnamic acid (0.0192 g, 0.01 mmol), KOH (0.012 g, 0.02 mmol) and $Co(NO_3)_2$ (0.0183 g, 0.1 mmol) were dissolved in a mixture of water (8 ml) and ethanol (8 ml). After stirring for 2 h, a clear yellow solution was produced from which yellow prismatic crystals of the title compound were collected after evaporation of the solvent, in a yield of 35.6%.

Crystal data

$[Co(C_{10}H_8N_2)(H_2O)_4]$-$(C_{10}H_6O_4)\cdot 2H_2O$
M_r = 513.36
Triclinic, $P\overline{1}$
a = 7.3854 (15) Å
b = 11.432 (2) Å
c = 13.625 (3) Å
α = 92.88 (3)°
β = 98.04 (3)°
γ = 97.18 (3)°
V = 1127.4 (4) Å^3
Z = 2
D_x = 1.512 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3522 reflections
θ = 3.1–27.5°
μ = 0.82 mm^{-1}
T = 173 (2) K
Prism, yellow
0.60 × 0.35 × 0.20 mm

Data collection

Rigaku Mercury70 diffractometer
φ and ω scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2001)
T_{min} = 0.729, T_{max} = 0.850
8640 measured reflections
6621 independent reflections
6236 reflections with $I > 2\sigma(I)$
R_{int} = 0.015
θ_{max} = 27.5°
$h = -8 \rightarrow 9$
$k = -14 \rightarrow 13$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.022
$wR(F^2)$ = 0.046
S = 0.93
6621 reflections
667 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.006
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}
Absolute structure: Flack (1983), 1443 Friedel pairs
Flack parameter = 0.008 (6)

Table 1
Selected geometric parameters (Å, °).

Co1—O4*A*	2.0494 (18)	Co2—O2*B*	2.1530 (18)
Co1—O1*A*	2.0499 (18)	Co2—N2*B*	2.159 (2)
Co1—O2*A*	2.1073 (18)	Co2—N1*B*	2.169 (2)
Co1—O3*A*	2.1125 (18)	O3*C*—C10*C*	1.262 (3)
Co1—N2*A*	2.163 (2)	O4*C*—C10*C*	1.270 (3)
Co1—N1*A*	2.181 (2)	O3*D*—C10*D*	1.273 (3)
Co2—O4*B*	2.0435 (18)	O4*D*—C10*D*	1.255 (3)
Co2—O3*B*	2.0676 (18)	C8*C*—C9*C*	1.332 (3)
Co2—O1*B*	2.0764 (18)	C8*D*—C9*D*	1.329 (3)
N2*A*—Co1—N1*A*	178.05 (9)	N2*B*—Co2—N1*B*	178.90 (9)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1A—H1A1···O1D	0.834 (16)	1.924 (16)	2.750 (3)	170 (3)
O1A—H1A2···O3C^{i}	0.863 (16)	1.858 (16)	2.711 (3)	169 (3)
O2A—H2A2···O1W	0.840 (16)	1.825 (16)	2.663 (3)	175 (3)
O2A—H2A1···O3W^{ii}	0.835 (16)	1.955 (17)	2.782 (3)	171 (2)
O3A—H3A2···O2W	0.818 (16)	1.925 (16)	2.726 (3)	166 (3)
O3A—H3A1···O2D^{iii}	0.830 (16)	1.907 (16)	2.734 (3)	174 (3)
O4A—H4A2···O4C^{ii}	0.837 (16)	1.917 (16)	2.738 (3)	166 (2)
O4A—H4A1···O1D^{iii}	0.836 (16)	1.899 (16)	2.735 (3)	178 (2)
O1B—H1B1···O2C	0.844 (15)	1.747 (16)	2.582 (2)	170 (2)
O1B—H1B2···O3W	0.864 (16)	1.918 (17)	2.774 (3)	171 (2)
O2B—H2B2···O4W	0.820 (15)	2.005 (16)	2.825 (3)	179 (3)
O2B—H2B1···O2W	0.867 (15)	1.996 (16)	2.842 (3)	165 (3)
O3B—H3B2···O3D^{iii}	0.844 (16)	1.954 (17)	2.791 (3)	171 (2)
O3B—H3B1···O1C	0.843 (15)	1.834 (16)	2.673 (2)	173 (3)
O4B—H4B2···O3D	0.839 (16)	1.923 (16)	2.732 (2)	162 (3)
O4B—H4B1···O1C^{iv}	0.848 (16)	1.883 (18)	2.706 (3)	163 (2)
O1W—H1W1···O4C^{i}	0.838 (17)	1.928 (17)	2.754 (3)	169 (3)
O1W—H1W2···O4D^{ii}	0.851 (16)	1.987 (18)	2.825 (2)	167 (3)
O2W—H2W2···O4W^{iv}	0.835 (16)	2.19 (2)	2.968 (3)	156 (3)
O2W—H2W1···O3D	0.861 (16)	1.845 (17)	2.692 (2)	168 (3)
O3W—H3W2···O4D^{iii}	0.848 (16)	1.884 (16)	2.731 (2)	178 (3)
O3W—H3W1···O4C	0.830 (15)	2.002 (17)	2.813 (2)	165 (3)
O4W—H4W2···O2D^{iii}	0.850 (15)	1.951 (16)	2.775 (2)	163 (3)
O4W—H4W1···O3C^{ii}	0.813 (16)	1.945 (18)	2.730 (2)	162 (3)

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

H atoms bonded to C atoms were positioned geometrically, with a C—H distance of 0.95 Å. They were included in a riding-model approximation, with $U_{iso} = 1.2U_{eq}$(C). The positions of H atoms bonded to O atoms were allowed to refine with $U_{iso} = 1.5U_{eq}$(O), subject to the restraints O—H = 0.85 Å and H···H = 1.34 Å.

Data collection: *CrystalClear* (Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXTL* (Siemens, 1994); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL*.

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