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Poly[bis(μ_2-4-pyridinecarboxylato-κ^3N:O,O')cobalt(II)]: a triply interpenetrated structure with diamonoid topology

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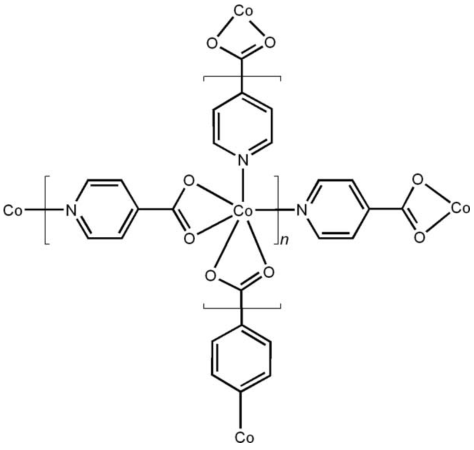
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.027; wR factor = 0.063; data-to-parameter ratio = 14.8.

The binary title complex, $[Co(C_6H_4NO_2)_2]_n$, is a three-dimensional coordination polymer that is triply interpenetrated with diamonoid topology. The asymmetric unit comprises half a Co atom, which lies on a twofold axis, and a 4-pyridinecarboxylate anion, in a general position. The Co atom is in a distorted *cis*-N_2O_4 octahedral geometry defined by two chelating carboxylate groups and two pyridyl N atoms.

Related literature

For related literature, see: Evans *et al.* (1999); Lu (2003); MacGillivray *et al.* (1998); Tong, Chen & Batten (2003); Tong, Li *et al.* (2003); Wang *et al.* (2003); Wei *et al.* (2004).



Experimental

Crystal data

$[Co(C_6H_4NO_2)_2]$
M_r = 303.13
Tetragonal, $P4_32_12$
a = 11.6304 (7) Å
c = 8.7665 (10) Å
V = 1185.81 (17) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.46 mm^{-1}
T = 293 (2) K
0.21 × 0.15 × 0.07 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
T_{min} = 0.749, T_{max} = 0.905
4769 measured reflections
1288 independent reflections
1219 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.063
S = 1.11
1288 reflections
87 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}
Absolute structure: (Flack, 1983)
Flack parameter: −0.03 (2)

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; 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: *SHELXTL* (Bruker, 1998).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2191).

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supplementary materials

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Poly[bis(μ_2-4-pyridinecarboxylato-κ^3N:*O*,*O*')cobalt(II)]: a triply interpenetrated structure with diamonoid topology

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Comment

Pyridinecarboxylates and their derivatives are good bridging ligands in the construction of 2- and 3-D functional metal-organic frameworks (Evans *et al.*, 1999; Lu, 2003; Tong, Chen & Batten, 2003; Tong, Li *et al.*, 2003; Wang *et al.*, 2003). The title complex, (I), was obtained unexpectedly in an attempt to prepare a bimetallic coordination network (see Experimental) with 4-pyridinecarboxylate (4-pya).

The structure of (I) is a three-dimensional coordination network. The Co(II) atom, which is located on a 2-fold axis (Fig. 1), is coordinated by four O atoms derived from two chelating carboxylate ligands and two pyridine-N atoms that define a distorted octahedral geometry within a *cis*-N_2O_4 donor set. The major distortion from the ideal octahedral geometry is caused by the acute chelate angle of 60.43 (7)° for O1—Co—O2.

The Co—N bond length [2.0723 (16) Å] is slightly shorter than those of 2.133 (3) Å, found in [Co(4-pya)$_2$]·0.5EtOH (Wei *et al.*, 2004), and 2.166 (4) Å, found in [Co(4,4-bipyridine)(4-pya)(H_2O)]NO_3.4,4'-bipyridine·1.5H_2O (MacGillivray *et al.*, 1998). By contrast, the Co—O bond distances of 2.1104 (16) and 2.2279 (16) Å are longer than those of 2.082 (4)–2.098 (4) Å formed by the 4-pya ligands in poly[tetrakis(μ_3-4-pya)dicobalt(II)] (Wei *et al.*, 2004).

In the crystal structure, the polymeric chains are triply interpenetrated with a diamonoid topology (Fig. 2). This resembles the situation in [Zn(4-pya)$_2$]$_n$ (Evans *et al.*, 1999) but, the structures are not isomorphous.

Experimental

To a ethanol-water solution (2:1 v:v, 10 ml) of Co(NO_3)$_2$·6H_2O (0.146 g, 0.5 mmol) and Gd(NO_3)$_3$·6H_2O (0.226 g, 0.5 mmol), a solution of 4-pyridinecarboxylic acid (0.123 g, 1.0 mmol) in EtOH (5 ml) was added slowly with stirring over 30 min at 333 K. This solution was transferred into a sealed 23-ml Teflon-lined stainless container and heated to 160 °C for 3 days. After slow cooling to room temperature over 8 h, red crystals of (I) separated from the solution (yield 75%).

Refinement

All the H atoms were included in the riding-model approximation, with C–H = 0.93 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$.

Figures

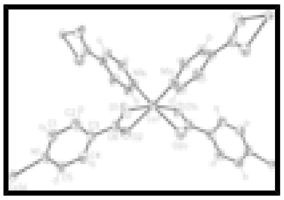

Fig. 1. Molecular structure of (I) extended to show the octahedral coordination geometry for the Co atom and the atom-labeling scheme. Displacement ellipsoids are shown at the 50% probability level. [Symmetry codes: (*a*) *x* − 1/2, −*y* + 1/2, −*z* − 3/4; (*b*) −*y* + 1/2, *x* − 1/2, *z* + 3/4; (*c*) *y*, *x*, −*z*; (*d*) *y* + 1/2, −*x* + 1/2, *z* − 3/4.]

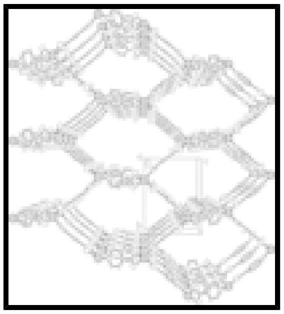

Fig. 2. Plot of a single diamonoid network in (I) viewed along the *a* axis.

Poly[bis(μ_2-4-pyridinecarboxylato-κ^3*N*:*O*,*O*')cobalt(II)]

Crystal data

$[Co(C_6H_4NO_2)_2]$

$M_r = 303.13$

Tetragonal, $P4_32_12$

Hall symbol: P 4nw 2abw

$a = 11.6304\ (7)$ Å

$b = 11.6304\ (7)$ Å

$c = 8.7665\ (10)$ Å

$\alpha = 90°$

$\beta = 90°$

$\gamma = 90°$

$V = 1185.81\ (17)$ Å^3

$Z = 4$

$F_{000} = 612$

$D_x = 1.698$ Mg m^{-3}

Mo *K*α radiation
λ = 0.71073 Å

Cell parameters from 1288 reflections

θ = 2.5–27.5°

$\mu = 1.46$ mm^{-1}

$T = 293\ (2)$ K

Block, red

0.21 × 0.15 × 0.07 mm

Data collection

Bruker SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293(2)$ K

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 2002)

$T_{min} = 0.749$, $T_{max} = 0.905$

4769 measured reflections

1288 independent reflections

1219 reflections with $I > 2\sigma(I)$

$R_{int} = 0.027$

$\theta_{max} = 27.5°$

$\theta_{min} = 2.5°$

$h = -10\rightarrow14$

$k = -14\rightarrow14$

$l = -11\rightarrow4$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.027$	$w = 1/[\sigma^2(F_o^2) + (0.033P)^2 + 0.0513P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.063$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.11$	$\Delta\rho_{max} = 0.39$ e Å^{-3}
1288 reflections	$\Delta\rho_{min} = -0.24$ e Å^{-3}
87 parameters	Extinction correction: none
Primary atom site location: structure-invariant direct methods	Absolute structure: (Flack, 1983)
Secondary atom site location: difference Fourier map	Flack parameter: −0.03 (2)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
Co1	0.27729 (2)	0.27729 (2)	0.0000	0.02511 (13)
O1	0.39522 (15)	0.18731 (17)	−0.13866 (18)	0.0475 (5)
O2	0.37226 (15)	0.37088 (16)	−0.18249 (19)	0.0457 (4)
N1	0.64350 (14)	0.24467 (16)	−0.59662 (19)	0.0299 (4)
C1	0.5913 (2)	0.15229 (19)	−0.5376 (2)	0.0369 (5)
H1	0.6066	0.0806	−0.5799	0.044*
C2	0.5157 (2)	0.1592 (2)	−0.4165 (3)	0.0370 (5)
H2	0.4812	0.0932	−0.3779	0.044*
C3	0.49211 (18)	0.2652 (2)	−0.3537 (2)	0.0315 (5)
C4	0.5420 (2)	0.36043 (19)	−0.4179 (3)	0.0354 (5)
H4	0.5257	0.4334	−0.3802	0.042*
C5	0.61669 (19)	0.34707 (18)	−0.5389 (2)	0.0331 (5)
H5	0.6497	0.4123	−0.5819	0.040*
C6	0.41504 (18)	0.2756 (2)	−0.2161 (2)	0.0352 (5)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.02932 (16)	0.02932 (16)	0.01668 (18)	−0.00108 (16)	0.00053 (11)	−0.00053 (11)
O1	0.0495 (10)	0.0624 (12)	0.0305 (8)	0.0157 (9)	0.0138 (8)	0.0114 (9)
O2	0.0435 (11)	0.0472 (11)	0.0464 (9)	−0.0054 (7)	0.0189 (8)	−0.0158 (9)
N1	0.0315 (9)	0.0357 (10)	0.0225 (8)	−0.0011 (7)	0.0037 (7)	0.0011 (7)
C1	0.0467 (14)	0.0288 (12)	0.0352 (12)	0.0008 (10)	0.0074 (11)	−0.0039 (10)
C2	0.0431 (13)	0.0349 (13)	0.0330 (11)	−0.0033 (11)	0.0104 (11)	0.0013 (10)
C3	0.0298 (11)	0.0408 (13)	0.0238 (9)	0.0012 (10)	0.0026 (9)	0.0011 (10)
C4	0.0412 (13)	0.0354 (13)	0.0294 (11)	0.0055 (10)	0.0035 (10)	−0.0063 (10)
C5	0.0414 (13)	0.0292 (11)	0.0288 (11)	−0.0013 (9)	0.0057 (9)	0.0034 (9)
C6	0.0291 (11)	0.0529 (14)	0.0235 (10)	−0.0028 (11)	0.0005 (8)	−0.0043 (11)

Geometric parameters (Å, °)

Co1—N1^{i}	2.0723 (16)	N1—Co1^{iv}	2.0723 (16)
Co1—N1^{ii}	2.0723 (16)	C1—C2	1.381 (3)
Co1—O1^{iii}	2.1104 (16)	C1—H1	0.9300
Co1—O1	2.1104 (16)	C2—C3	1.377 (3)
Co1—O2^{iii}	2.2279 (16)	C2—H2	0.9300
Co1—O2	2.2279 (16)	C3—C4	1.372 (3)
O1—C6	1.253 (3)	C3—C6	1.508 (3)
O2—C6	1.250 (3)	C4—C5	1.379 (3)
N1—C5	1.331 (3)	C4—H4	0.9300
N1—C1	1.338 (3)	C5—H5	0.9300
N1^{i}—Co1—N1^{ii}	103.65 (10)	C1—N1—Co1^{iv}	119.51 (15)
N1^{i}—Co1—O1^{iii}	94.67 (7)	N1—C1—C2	122.6 (2)
N1^{ii}—Co1—O1^{iii}	93.05 (7)	N1—C1—H1	118.7
N1^{i}—Co1—O1	93.05 (7)	C2—C1—H1	118.7
N1^{ii}—Co1—O1	94.67 (7)	C3—C2—C1	119.1 (2)
O1^{iii}—Co1—O1	167.50 (11)	C3—C2—H2	120.5
N1^{i}—Co1—O2^{iii}	153.36 (7)	C1—C2—H2	120.5
N1^{ii}—Co1—O2^{iii}	88.08 (6)	C4—C3—C2	118.33 (19)
O1^{iii}—Co1—O2^{iii}	60.43 (7)	C4—C3—C6	121.0 (2)
O1—Co1—O2^{iii}	109.99 (7)	C2—C3—C6	120.7 (2)
N1^{i}—Co1—O2	88.08 (6)	C3—C4—C5	119.4 (2)
N1^{ii}—Co1—O2	153.36 (7)	C3—C4—H4	120.3
O1^{iii}—Co1—O2	109.99 (7)	C5—C4—H4	120.3
O1—Co1—O2	60.43 (7)	N1—C5—C4	122.7 (2)
O2^{iii}—Co1—O2	91.79 (8)	N1—C5—H5	118.6
C6—O1—Co1	91.44 (14)	C4—C5—H5	118.6
C6—O2—Co1	86.20 (13)	O2—C6—O1	121.71 (19)
C5—N1—C1	117.73 (18)	O2—C6—C3	119.8 (2)

C5—N1—Co1^{iv}	122.20 (14)	O1—C6—C3	118.5 (2)

Symmetry codes: (i) $x-1/2, -y+1/2, -z-3/4$; (ii) $-y+1/2, x-1/2, z+3/4$; (iii) $y, x, -z$; (iv) $y+1/2, -x+1/2, z-3/4$.

Fig. 1

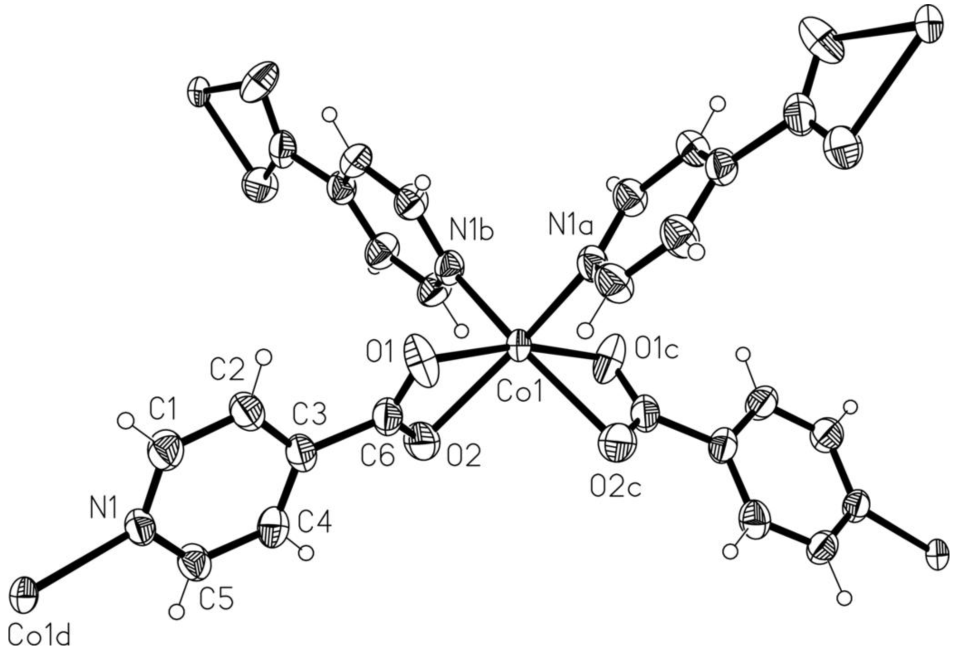

Fig. 2