Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

OPEN ACCESS

ISSN 2056-9890

Crystal structure of *catena*-poly[bis(formato-κO)bis[μ_2-1,1′-(1,4-phenylene)bis(1*H*-imidazole)-$\kappa^2N^3:N^{3'}$]cobalt(II)]

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Received 18 July 2015; accepted 28 July 2015

Edited by K. Fejfarova, Institute of Macromolecular Chemistry, AS CR, v.v.i, Czech Republic

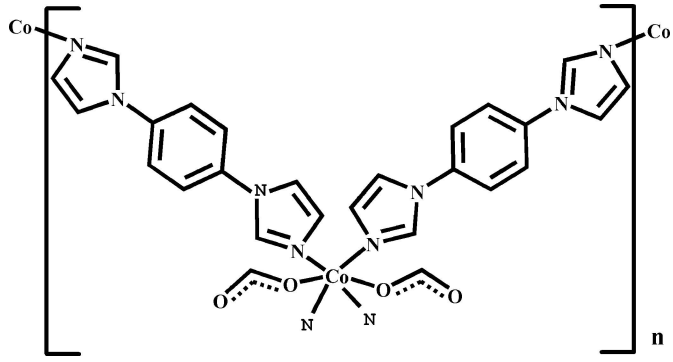
A red block-shaped crystal of the title compound, $[Co(HCOO)_2(C_{12}H_{10}N_4)_2]_n$, was obtained by the reaction of cobalt(II) nitrate hexahydrate, formic acid and 1,1′-(1,4-phenylene)bis(1*H*-imidazole) (bib) molecules. The asymmetric unit consists of one Co^{II} cation, one formate ligand and two halves of a bib ligand. The central Co^{II} cation, located on an inversion centre, is coordinated by two carboxylate O atoms and four N atoms from bib ligands, completing an octahedral coordination geometry. The Co^{II} centres are bridged by bib ligands, giving a two-dimensional net. Topologically, taking the Co^{II} atoms as nodes and the bib ligands as linkers, the two-dimensional structure can be simplified as a typical **sql**/Shubnikov tetragonal plane network. The structure features C—H···O hydrogen-bonding interactions between formate and bib ligands, resulting in a three-dimensional supramolecular network.

Keywords: crystal structure; Co complex; 1,4-bis(1-imidazolyl)benzene; hydrogen bonding.

CCDC reference: 1415558

1. Related literature

For metal–organic framework structures, see: Yang *et al.* (2011, 2012); Guo & Sun (2012).



2. Experimental

2.1. Crystal data

$[Co(CHO_2)_2(C_{12}H_{10}N_4)_2]$
M_r = 569.44
Monoclinic, $P2_1/c$
a = 7.601 (6) Å
b = 11.715 (9) Å
c = 13.791 (10) Å
β = 99.017 (9)°
V = 1212.8 (16) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.76 mm^{-1}
T = 293 K
0.20 × 0.18 × 0.17 mm

2.2. Data collection

Bruker SMART 1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
T_{min} = 0.732, T_{max} = 1
12595 measured reflections
2773 independent reflections
2059 reflections with $I > 2\sigma(I)$
R_{int} = 0.092

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.121
S = 1.07
2773 reflections
178 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···O2^{i}	0.93	2.40	3.330 (5)	173
C6—H6···O1^{i}	0.93	2.49	3.383 (5)	161
C8—H8···O2^{ii}	0.93	2.13	3.038 (5)	164

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

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT-Plus* (Bruker, 2007); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL*; software used to prepare material for publication: *publCIF* (Westrip, 2010).

Acknowledgements

This work was supported financially by the Graduate Student Research Innovation Fund of CTGU (CX2014094) and the Training Excellent Masters Thesis Fund of CTGU (Nos. PY2015074 and PY2015030), China.

Supporting information for this paper is available from the IUCr electronic archives (Reference: FF2140).

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supporting information

Acta Cryst. (2015). E**71**, m156–m157 [https://doi.org/10.1107/S2056989015014255]

Crystal structure of *catena*-poly[bis(formato-κO)bis[μ_2-1,1′-(1,4-phenylene)bis-(1*H*-imidazole)-κ^2N^3:$N^{3'}$]cobalt(II)]

Guo-Wang Xu, Ye-Nan Wang, Hong-Xu Xia and Zhong-Long Wang

S1. Chemical context

Many fantastic structures of metal-organic frameworks have been reported based on 1,4-bis(1-imidazolyl)benzene. A lot of the them were constructed by mixed ligands including carboxylate ligand, other N-donor molecule and wolframic acid or molybdic acid, see: Guo *et al.* (2012), Yang *et al.* (2011), Yang *et al.* (2012), Compared with those compounds constructed by mixed organic ligands, coordination polymers established by a single ligand, especially N-donor molecules, are much more useful and easier for understanding the theory of formation of supramolecules. Accordingly, we selected 1,4-bis(1-imidazolyl) benzene and cobalt(II), which always shows one or two coordinated ligands, to construct a new supramolecule and study the structure of the title compound.

S2. Synthesis and crystallization

The title complex was synthesized by the reaction of 1,4-bis(1-imidazolyl)benzene (10.5 mg, 0.05 mmol) in 8 ml of deionized water with cobalt(II) nitrate hexahydrate (29.1 mg, 0.1 mmol) in 20ml of methanol and the mixture was refluxed for 1 hour. To the above mixture, 0.5 ml of formic acid was added and the result fluid was placed in a Teflon-lined, stainless-steel reactor. The reactor was heated to 413 K for 96 hours. It was then cooled to room temperature. Red block crystals were isolated in 69% yield (based on bib ligand).

S3. Refinement details

All the hydrogen atoms in the molecule were identified from the difference electron density map, further idealized and treated as riding with a distance d(C—H)=0.93Å In all cases Uiso(H)=-1.2Ueq.

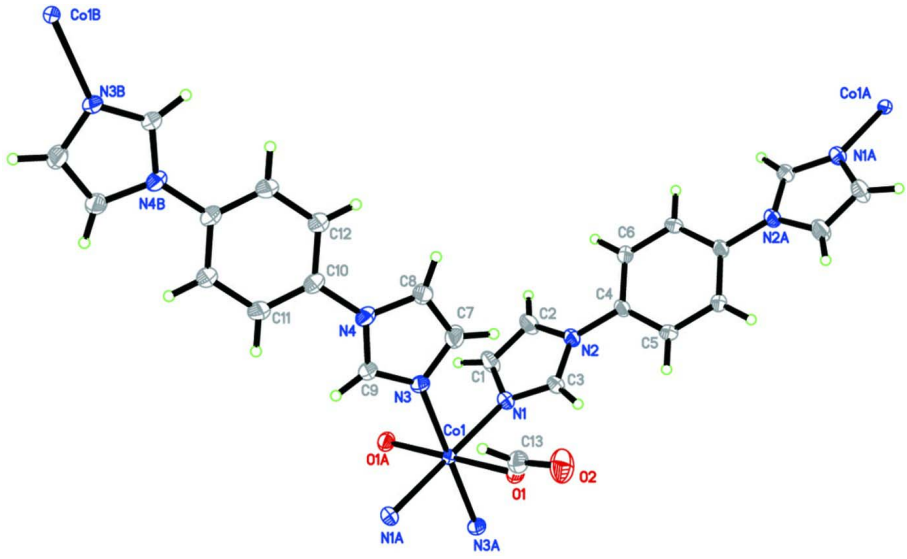

Figure 1

A part of the crystal structure of the title compound with labeling and displacement ellipsoids drawn at the 30% probability level, The H atoms have been removed for clarity. Symmetry codes: (A) -*x*, 2 - *y*, 1 - *z*; (B) 1 - *x*, 1 - *y*, -*z*.

***catena*-Poly[bis(formato-κO)bis[μ_2-1,1′-(1,4-phenylene)bis(1*H*-imidazole)-κ^2N^3:$N^{3'}$]cobalt(II)]**

Crystal data

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a = 7.601 (6) Å
b = 11.715 (9) Å
c = 13.791 (10) Å
β = 99.017 (9)°
V = 1212.8 (16) Å^3
Z = 2
$F(000)$ = 586
D_x = 1.559 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2599 reflections
θ = 2.3–27.5°
μ = 0.76 mm^{-1}
T = 293 K
Block, red
0.20 × 0.18 × 0.17 mm

Data collection

Bruker SMART 1000 CCD diffractometer
Detector resolution: 13.6612 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
T_{min} = 0.732, T_{max} = 1
12595 measured reflections
2773 independent reflections
2059 reflections with $I > 2\sigma(I)$
R_{int} = 0.092
θ_{max} = 27.5°, θ_{min} = 2.7°
h = −9→9
k = −15→15
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.121
S = 1.07
2773 reflections
178 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0395P)^2 + 0.7123P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.0000	1.0000	0.0000	0.02562 (17)
O1	0.1750 (3)	1.11742 (17)	0.07673 (16)	0.0356 (5)
N4	0.3551 (3)	0.7072 (2)	0.0552 (2)	0.0357 (6)
N2	−0.0995 (4)	0.9605 (2)	0.29716 (18)	0.0327 (6)
N3	0.1856 (4)	0.8626 (2)	0.04773 (19)	0.0340 (6)
C4	−0.0494 (4)	0.9811 (2)	0.4001 (2)	0.0294 (6)
N1	−0.1089 (4)	0.9758 (2)	0.13562 (18)	0.0340 (6)
C6	−0.0753 (4)	0.8960 (3)	0.4668 (2)	0.0330 (7)
H6	−0.1252	0.8265	0.4446	0.040*
C11	0.4328 (5)	0.5795 (3)	−0.0706 (3)	0.0452 (9)
H11	0.3879	0.6324	−0.1184	0.054*
C5	0.0263 (4)	1.0845 (3)	0.4333 (2)	0.0336 (7)
H5	0.0442	1.1410	0.3885	0.040*
C1	−0.2136 (5)	0.8854 (3)	0.1559 (2)	0.0454 (9)
H1	−0.2780	0.8386	0.1087	0.055*
C10	0.4314 (4)	0.6030 (3)	0.0271 (2)	0.0361 (7)
C2	−0.2098 (5)	0.8742 (3)	0.2544 (2)	0.0459 (9)
H2	−0.2689	0.8198	0.2864	0.055*
C9	0.2525 (4)	0.7840 (2)	−0.0035 (2)	0.0343 (7)
H9	0.2326	0.7808	−0.0717	0.041*
C3	−0.0435 (4)	1.0190 (3)	0.2222 (2)	0.0346 (7)
H3	0.0318	1.0820	0.2310	0.041*
C13	0.3415 (5)	1.1113 (3)	0.0969 (2)	0.0422 (8)
H13	0.3948	1.0518	0.0675	0.051*
O2	0.4414 (4)	1.1735 (3)	0.1501 (2)	0.0710 (9)
C12	0.4980 (5)	0.5242 (3)	0.0977 (3)	0.0448 (9)
H12	0.4969	0.5402	0.1636	0.054*
C7	0.2476 (5)	0.8367 (3)	0.1452 (3)	0.0527 (10)
H7	0.2220	0.8785	0.1986	0.063*
C8	0.3512 (5)	0.7414 (3)	0.1518 (3)	0.0494 (10)
H8	0.4076	0.7064	0.2088	0.059*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0335 (3)	0.0221 (3)	0.0210 (3)	0.0044 (2)	0.0034 (2)	−0.0006 (2)
O1	0.0393 (13)	0.0303 (11)	0.0360 (12)	0.0005 (10)	0.0022 (10)	−0.0054 (10)
N4	0.0356 (15)	0.0274 (13)	0.0432 (16)	0.0054 (11)	0.0030 (12)	−0.0014 (12)
N2	0.0405 (15)	0.0345 (13)	0.0238 (13)	−0.0026 (11)	0.0080 (11)	−0.0009 (11)

N3	0.0392 (15)	0.0287 (13)	0.0324 (14)	0.0093 (11)	0.0006 (11)	0.0020 (11)
C4	0.0326 (16)	0.0344 (16)	0.0215 (13)	0.0027 (13)	0.0057 (12)	−0.0011 (12)
N1	0.0426 (15)	0.0347 (14)	0.0254 (12)	0.0002 (11)	0.0082 (11)	−0.0004 (11)
C6	0.0431 (18)	0.0277 (15)	0.0283 (15)	−0.0018 (13)	0.0062 (14)	−0.0029 (13)
C11	0.054 (2)	0.0387 (18)	0.043 (2)	0.0143 (17)	0.0071 (17)	0.0073 (16)
C5	0.0444 (19)	0.0303 (16)	0.0268 (15)	−0.0013 (14)	0.0080 (14)	0.0061 (13)
C1	0.052 (2)	0.058 (2)	0.0268 (16)	−0.0157 (18)	0.0059 (15)	−0.0035 (16)
C10	0.0327 (17)	0.0296 (16)	0.0461 (19)	0.0053 (13)	0.0063 (14)	0.0000 (14)
C2	0.058 (2)	0.051 (2)	0.0287 (17)	−0.0178 (18)	0.0064 (16)	0.0003 (16)
C9	0.0393 (18)	0.0290 (15)	0.0343 (17)	0.0070 (14)	0.0046 (14)	0.0017 (13)
C3	0.0447 (19)	0.0346 (17)	0.0258 (15)	0.0006 (14)	0.0100 (13)	0.0012 (13)
C13	0.045 (2)	0.0397 (19)	0.0398 (19)	−0.0021 (16)	0.0017 (16)	−0.0043 (15)
O2	0.0624 (19)	0.078 (2)	0.0664 (19)	−0.0092 (16)	−0.0096 (15)	−0.0266 (17)
C12	0.057 (2)	0.0379 (18)	0.0400 (18)	0.0143 (16)	0.0079 (17)	0.0024 (15)
C7	0.064 (3)	0.047 (2)	0.043 (2)	0.0232 (19)	−0.0058 (18)	−0.0095 (17)
C8	0.063 (3)	0.043 (2)	0.0364 (19)	0.0180 (18)	−0.0110 (17)	−0.0037 (16)

Geometric parameters (Å, º)

Co1—O1^{i}	2.083 (2)	N3—C7	1.387 (4)
Co1—O1	2.083 (2)	C4—C5	1.387 (4)
Co1—N3^{i}	2.173 (3)	C4—C6	1.391 (4)
Co1—N3	2.173 (3)	N1—C3	1.320 (4)
Co1—N1	2.179 (3)	N1—C1	1.379 (4)
Co1—N1^{i}	2.179 (3)	C6—C5^{ii}	1.389 (4)
O1—C13	1.254 (4)	C11—C10	1.377 (5)
N4—C9	1.369 (4)	C11—C12^{iii}	1.397 (4)
N4—C8	1.396 (4)	C5—C6^{ii}	1.389 (4)
N4—C10	1.431 (4)	C1—C2	1.361 (5)
N2—C3	1.363 (4)	C10—C12	1.379 (4)
N2—C2	1.385 (4)	C13—O2	1.212 (4)
N2—C4	1.432 (4)	C12—C11^{iii}	1.397 (4)
N3—C9	1.311 (4)	C7—C8	1.360 (5)
O1^{i}—Co1—O1	180.0	C9—N3—Co1	130.2 (2)
O1^{i}—Co1—N3^{i}	90.15 (11)	C7—N3—Co1	124.2 (2)
O1—Co1—N3^{i}	89.84 (11)	C5—C4—C6	120.1 (3)
O1^{i}—Co1—N3	89.85 (11)	C5—C4—N2	120.4 (3)
O1—Co1—N3	90.16 (11)	C6—C4—N2	119.5 (3)
N3^{i}—Co1—N3	180.00 (13)	C3—N1—C1	105.0 (3)
O1^{i}—Co1—N1	92.97 (10)	C3—N1—Co1	125.9 (2)
O1—Co1—N1	87.03 (10)	C1—N1—Co1	125.6 (2)
N3^{i}—Co1—N1	92.33 (10)	C5^{ii}—C6—C4	119.6 (3)
N3—Co1—N1	87.67 (10)	C10—C11—C12^{iii}	119.7 (3)
O1^{i}—Co1—N1^{i}	87.04 (10)	C4—C5—C6^{ii}	120.2 (3)
O1—Co1—N1^{i}	92.96 (10)	C2—C1—N1	110.7 (3)
N3^{i}—Co1—N1^{i}	87.67 (10)	C11—C10—C12	119.9 (3)
N3—Co1—N1^{i}	92.33 (10)	C11—C10—N4	120.1 (3)

N1—Co1—N1^{i}	180.0	C12—C10—N4	119.9 (3)
C13—O1—Co1	128.1 (2)	C1—C2—N2	105.7 (3)
C9—N4—C8	106.2 (3)	N3—C9—N4	112.1 (3)
C9—N4—C10	128.2 (3)	N1—C3—N2	112.0 (3)
C8—N4—C10	125.0 (3)	O2—C13—O1	127.9 (4)
C3—N2—C2	106.5 (3)	C10—C12—C11^{iii}	120.3 (3)
C3—N2—C4	127.0 (3)	C8—C7—N3	110.4 (3)
C2—N2—C4	126.5 (3)	C7—C8—N4	105.8 (3)
C9—N3—C7	105.5 (3)		

Symmetry codes: (i) −*x*, −*y*+2, −*z*; (ii) −*x*, −*y*+2, −*z*+1; (iii) −*x*+1, −*y*+1, −*z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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C8—H8···O2^{v}	0.93	2.13	3.038 (5)	164

Symmetry codes: (iv) −*x*, *y*−1/2, −*z*+1/2; (v) −*x*+1, *y*−1/2, −*z*+1/2.