

catena-Poly[[bis(nitrato- κ^2 O,O')-cobalt(II)]- μ -4,4'-bis(pyrazol-1-yl-methyl)biphenyl- κ^2 N 2 :N 2 ']

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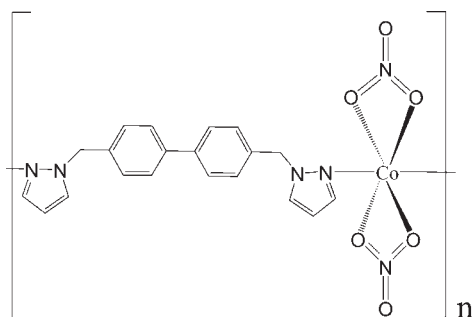
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Key indicators: single-crystal X-ray study; $T = 291$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.036; wR factor = 0.091; data-to-parameter ratio = 15.6.

In the title compound, $[\text{Co}(\text{NO}_3)_2(\text{C}_{20}\text{H}_{18}\text{N}_4)]_n$, the Co^{II} atom lies on a crystallographic twofold axis and the coordination geometry can be considered as a slightly distorted tetrahedron defined by two O atoms from two nitrate groups and two N atoms from two ligand molecules. A distorted octahedron may be assumed when two of the symmetry-related nitrate O atoms with $\text{Co}-\text{O}$ distances of 2.3449 (19) Å are added to the coordination environment. Another twofold axis, passing through the middle of the biphenyl bonds, is observed in the crystal structure. A chain is built up by the ligands linking the Co^{II} ions along [101].

Related literature

For a related polymeric bis(pyrazole) dinitratocobalt(II) structure, see: Chen *et al.* (1997). For the isotopic Zn structure, see: Wang *et al.* (2010). For the synthesis and structure of a three-dimensional polymeric Zn(II) network compound, see: Zhu *et al.* (2002).



Experimental

Crystal data

$[\text{Co}(\text{NO}_3)_2(\text{C}_{20}\text{H}_{18}\text{N}_4)]$
 $M_r = 497.33$

Monoclinic, $C2/c$

$a = 14.133$ (6) Å

$b = 13.631$ (8) Å

$c = 10.806$ (5) Å

$\beta = 96.211$ (18)°

$V = 2069.5$ (18) Å³

$Z = 4$

Mo $K\alpha$ radiation

$\mu = 0.88$ mm⁻¹

$T = 291$ K

$0.24 \times 0.23 \times 0.21$ mm

Data collection

Rigaku R-Axis RAPID
 diffractometer

Absorption correction: multi-scan
 (ABSCOR; Higashi, 1995)

$T_{\text{min}} = 0.814$, $T_{\text{max}} = 0.834$

9940 measured reflections

2346 independent reflections

1931 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.043$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.091$

$S = 1.07$

2346 reflections

150 parameters

H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.39$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.31$ e Å⁻³

Table 1

Selected bond lengths (Å).

Co1—O1	2.0395 (18)	Co1—O2	2.3444 (19)
Co1—N1	2.0463 (18)		

Data collection: *RAPID-AUTO* (Rigaku 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2260).

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supplementary materials

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***catena*-Poly[[bis(nitrato- κ^2O,O')cobalt(II)]- μ -4,4'-bis(pyrazol-1-ylmethyl)biphenyl- $\kappa^2N^2:N^2'$]**

J.-S. Gao, X. Wang, Z.-Y. Ding and G.-F. Hou

Comment

The structures of the metal derivative 1,4-bis(pyrazole) benzene are known for zinc and cobalt (Chen *et al.*, 1997). In order to enrich the research of this kinds of ligand, a new ligand 4,4'-bis(pyrazole) biphenyl with longer spacer was synthesized. In here, we report the structure of the title compound, which is a isomorphous compound of our previous report (Wang *et al.*, 2010).

The central Co atom lies on a crystallographic twofold axis and the coordination geometry can be considered as a slightly distorted tetrahedron defined by two O atoms from two nitrate groups and two N atoms from two ligand molecules. A distorted octahedron may be assumed when two of the C₂ related nitrate oxygen atoms with Co—O distances of 2.345 (2) Å are added to the coordination environment. Another twofold axis, passing through the middle of the biphenyl bonds, is observed in the crystal structure (Figure 1, Table 1).

A one dimensional chain is built up by the ligands linking the Co^{II} ions along the [1 0 1] direction (Figure 2).

Experimental

The 4,4'-bis(pyrazole-1-ylmethyl) biphenyl was synthesized by the reaction of pyrazole and 4,4'-bis(chloro) bibenzene under alkaline condition (Zhu *et al.*, 2002). Cobalt(II) dinitrate hexahydrate (0.582 g, 2 mmol) and 4,4'-bis(pyrazole-1-ylmethyl) biphenyl (0.628 g, 2 mmol) were dissolved in ethanol (20 ml), purple block-shaped crystals separated from the filtered solution after several days.

Refinement

H atoms bound to C atoms were placed in calculated positions and treated as riding on their parent atoms, with C—H = 0.93 Å (aromatic), C—H = 0.97 Å (methylene), and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures

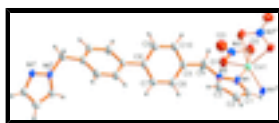


Fig. 1. The molecular structure of title compound, showing the atom-labeling scheme and displacement ellipsoids drawn at the 50% probability level. Symmetry codes: i = $-x + 1, y, -z - 1/2$; ii = $-x + 2, y, -z + 1/2$.



Fig. 2. A section of the chain structure of the title compound extending along the [1 0 1] direction.

supplementary materials

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Crystal data

$[\text{Co}(\text{NO}_3)_2(\text{C}_{20}\text{H}_{18}\text{N}_4)]$	$F(000) = 1020$
$M_r = 497.33$	$D_x = 1.596 \text{ Mg m}^{-3}$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: $-C 2yc$	Cell parameters from 7566 reflections
$a = 14.133 (6) \text{ \AA}$	$\theta = 3.0\text{--}27.5^\circ$
$b = 13.631 (8) \text{ \AA}$	$\mu = 0.88 \text{ mm}^{-1}$
$c = 10.806 (5) \text{ \AA}$	$T = 291 \text{ K}$
$\beta = 96.211 (18)^\circ$	Block, brown
$V = 2069.5 (18) \text{ \AA}^3$	$0.24 \times 0.23 \times 0.21 \text{ mm}$
$Z = 4$	

Data collection

Rigaku R-Axis RAPID diffractometer	2346 independent reflections
Radiation source: fine-focus sealed tube graphite	1931 reflections with $I > 2\sigma(I)$
ω scan	$R_{\text{int}} = 0.043$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 3.0^\circ$
$T_{\text{min}} = 0.814$, $T_{\text{max}} = 0.834$	$h = -18 \rightarrow 18$
9940 measured reflections	$k = -17 \rightarrow 17$
	$l = -14 \rightarrow 12$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.036$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.091$	H-atom parameters constrained
$S = 1.07$	$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.959P]$
2346 reflections	where $P = (F_o^2 + 2F_c^2)/3$
150 parameters	$(\Delta/\sigma)_{\text{max}} < 0.001$
0 restraints	$\Delta\rho_{\text{max}} = 0.39 \text{ e \AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$

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.

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.88489 (15)	-0.14358 (16)	0.29942 (19)	0.0386 (5)
H1	0.9333	-0.1663	0.3575	0.046*
C2	0.79651 (15)	-0.18759 (17)	0.2749 (2)	0.0420 (5)
H2	0.7746	-0.2436	0.3119	0.050*
C3	0.74852 (14)	-0.13104 (15)	0.1848 (2)	0.0367 (5)
H3	0.6867	-0.1416	0.1484	0.044*
C4	0.78951 (16)	0.02164 (16)	0.0679 (2)	0.0449 (6)
H4A	0.8434	0.0250	0.0195	0.054*
H4B	0.7869	0.0830	0.1128	0.054*
C5	0.69915 (14)	0.01146 (16)	-0.02073 (19)	0.0350 (5)
C6	0.68227 (14)	-0.06955 (16)	-0.0965 (2)	0.0385 (5)
H6	0.7242	-0.1223	-0.0887	0.046*
C7	0.60311 (14)	-0.07260 (16)	-0.18418 (19)	0.0364 (5)
H7	0.5914	-0.1284	-0.2330	0.044*
C8	0.54120 (13)	0.00614 (15)	-0.20021 (17)	0.0301 (4)
C9	0.55799 (14)	0.08674 (16)	-0.1228 (2)	0.0391 (5)
H9	0.5169	0.1402	-0.1312	0.047*
C10	0.63546 (14)	0.08820 (16)	-0.0331 (2)	0.0402 (5)
H10	0.6447	0.1419	0.0199	0.048*
Co1	1.0000	0.03534 (3)	0.2500	0.03214 (14)
N1	0.89123 (11)	-0.06439 (12)	0.22882 (15)	0.0327 (4)
N2	0.80555 (11)	-0.05793 (12)	0.15780 (15)	0.0304 (4)
N3	1.06867 (12)	0.16070 (13)	0.10362 (17)	0.0382 (4)
O1	1.00539 (10)	0.09498 (12)	0.07781 (14)	0.0456 (4)
O2	1.10495 (11)	0.16308 (13)	0.21497 (15)	0.0497 (4)
O3	1.09153 (13)	0.21630 (14)	0.02403 (17)	0.0627 (5)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0360 (11)	0.0383 (12)	0.0379 (11)	-0.0004 (9)	-0.0118 (9)	0.0046 (9)
C2	0.0409 (12)	0.0387 (12)	0.0445 (12)	-0.0066 (9)	-0.0036 (10)	0.0068 (9)
C3	0.0260 (9)	0.0406 (12)	0.0412 (11)	-0.0070 (8)	-0.0065 (8)	-0.0005 (9)
C4	0.0351 (11)	0.0422 (13)	0.0508 (13)	-0.0093 (9)	-0.0255 (10)	0.0112 (10)
C5	0.0261 (10)	0.0404 (12)	0.0349 (11)	-0.0042 (8)	-0.0127 (8)	0.0051 (9)
C6	0.0305 (10)	0.0395 (11)	0.0420 (12)	0.0085 (9)	-0.0115 (9)	0.0005 (9)
C7	0.0328 (10)	0.0365 (11)	0.0366 (11)	0.0047 (8)	-0.0120 (9)	-0.0068 (9)

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C8	0.0213 (9)	0.0374 (11)	0.0292 (10)	-0.0002 (7)	-0.0088 (8)	0.0017 (8)
C9	0.0315 (10)	0.0393 (12)	0.0431 (12)	0.0081 (9)	-0.0116 (9)	-0.0053 (9)
C10	0.0372 (11)	0.0381 (12)	0.0412 (12)	0.0003 (9)	-0.0145 (9)	-0.0090 (9)
Co1	0.0226 (2)	0.0312 (2)	0.0390 (2)	0.000	-0.01331 (15)	0.000
N1	0.0240 (8)	0.0335 (9)	0.0366 (9)	-0.0004 (6)	-0.0146 (7)	0.0010 (7)
N2	0.0225 (7)	0.0329 (9)	0.0327 (8)	-0.0018 (6)	-0.0111 (6)	0.0002 (7)
N3	0.0337 (9)	0.0333 (9)	0.0462 (10)	-0.0007 (7)	-0.0020 (8)	-0.0011 (8)
O1	0.0419 (8)	0.0440 (9)	0.0471 (9)	-0.0118 (7)	-0.0125 (7)	0.0013 (7)
O2	0.0416 (8)	0.0530 (10)	0.0504 (9)	-0.0103 (7)	-0.0142 (7)	-0.0041 (8)
O3	0.0737 (12)	0.0549 (12)	0.0594 (11)	-0.0208 (9)	0.0064 (9)	0.0111 (9)

Geometric parameters (Å, °)

C1—N1	1.330 (3)	C7—H7	0.9300
C1—C2	1.385 (3)	C8—C9	1.386 (3)
C1—H1	0.9300	C8—C8 ⁱ	1.498 (3)
C2—C3	1.364 (3)	C9—C10	1.382 (3)
C2—H2	0.9300	C9—H9	0.9300
C3—N2	1.334 (3)	C10—H10	0.9300
C3—H3	0.9300	Co1—O1	2.0395 (18)
C4—N2	1.457 (3)	Co1—O1 ⁱⁱ	2.0395 (18)
C4—C5	1.517 (3)	Co1—N1	2.0463 (18)
C4—H4A	0.9700	Co1—N1 ⁱⁱ	2.0463 (18)
C4—H4B	0.9700	Co1—O2	2.3444 (19)
C5—C10	1.377 (3)	Co1—O2 ⁱⁱ	2.3444 (19)
C5—C6	1.380 (3)	N1—N2	1.364 (2)
C6—C7	1.386 (3)	N3—O3	1.216 (2)
C6—H6	0.9300	N3—O2	1.256 (2)
C7—C8	1.384 (3)	N3—O1	1.275 (2)
N1—C1—C2	110.92 (18)	C5—C10—C9	121.14 (19)
N1—C1—H1	124.5	C5—C10—H10	119.4
C2—C1—H1	124.5	C9—C10—H10	119.4
C3—C2—C1	105.08 (19)	O1—Co1—O1 ⁱⁱ	133.02 (10)
C3—C2—H2	127.5	O1—Co1—N1	105.33 (6)
C1—C2—H2	127.5	O1 ⁱⁱ —Co1—N1	105.37 (7)
N2—C3—C2	108.24 (17)	O1—Co1—N1 ⁱⁱ	105.37 (7)
N2—C3—H3	125.9	O1 ⁱⁱ —Co1—N1 ⁱⁱ	105.33 (6)
C2—C3—H3	125.9	N1—Co1—N1 ⁱⁱ	96.74 (10)
N2—C4—C5	114.35 (17)	O1—Co1—O2	57.99 (6)
N2—C4—H4A	108.7	O1 ⁱⁱ —Co1—O2	86.45 (7)
C5—C4—H4A	108.7	N1—Co1—O2	162.95 (6)
N2—C4—H4B	108.7	N1 ⁱⁱ —Co1—O2	91.76 (8)
C5—C4—H4B	108.7	O1—Co1—O2 ⁱⁱ	86.45 (7)
H4A—C4—H4B	107.6	O1 ⁱⁱ —Co1—O2 ⁱⁱ	57.99 (6)
C10—C5—C6	118.75 (18)	N1—Co1—O2 ⁱⁱ	91.76 (8)
C10—C5—C4	119.24 (19)	N1 ⁱⁱ —Co1—O2 ⁱⁱ	162.95 (6)

C6—C5—C4	121.82 (19)	O2—Co1—O2 ⁱⁱ	84.08 (10)
C5—C6—C7	120.29 (19)	C1—N1—N2	105.32 (15)
C5—C6—H6	119.9	C1—N1—Co1	124.84 (13)
C7—C6—H6	119.9	N2—N1—Co1	129.07 (13)
C8—C7—C6	120.99 (19)	C3—N2—N1	110.44 (16)
C8—C7—H7	119.5	C3—N2—C4	130.38 (16)
C6—C7—H7	119.5	N1—N2—C4	119.18 (15)
C7—C8—C9	118.34 (17)	O3—N3—O2	123.31 (18)
C7—C8—C8 ⁱ	121.46 (14)	O3—N3—O1	121.13 (18)
C9—C8—C8 ⁱ	120.19 (13)	O2—N3—O1	115.56 (18)
C10—C9—C8	120.40 (19)	N3—O1—Co1	100.08 (12)
C10—C9—H9	119.8	N3—O2—Co1	86.31 (11)
C8—C9—H9	119.8		

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

Fig. 1

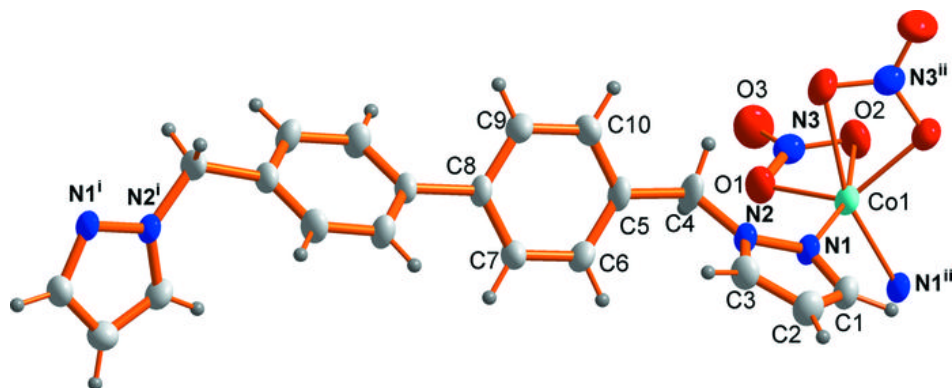


Fig. 2

