

# Bis(2,4-dichlorophenoxyacetato- $\kappa^2O^1, O^1'$ )(5,5'-dimethyl-2,2'-bipyridine- $\kappa^2N, N'$ )cobalt(II)

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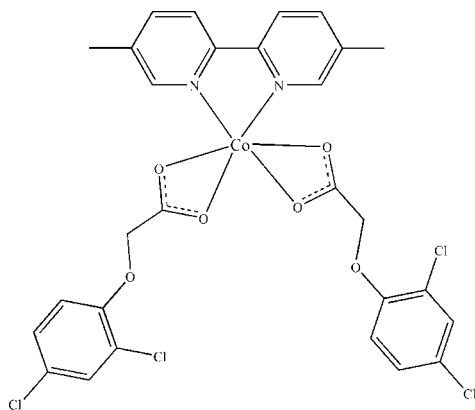
Received 18 March 2011; accepted 22 March 2011

Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(C-C) = 0.006$  Å;  $R$  factor = 0.034;  $wR$  factor = 0.106; data-to-parameter ratio = 13.7.

In the title compound,  $[Co(C_8H_5Cl_2O_3)(C_{12}H_{12}N_2)]$ , the  $Co^{II}$  atom, lying on a twofold rotation axis, is coordinated by four O atoms from two chelating 2,4-dichlorophenoxyacetate ligands and two N atoms from a 5,5'-dimethyl-2,2'-bipyridine ligand, displaying a distorted octahedral geometry. A three-dimensional supramolecular structure is formed through intermolecular  $C-H \cdots O$  hydrogen bonds and  $\pi-\pi$  stacking interactions between the pyridine and benzene rings [centroid-centroid distance =  $3.779(2)$  Å].

## Related literature

For related structures with 2,4-dichlorophenoxyacetate ligands, see: Liu (2010); Song & Xi (2006).



## Experimental

### Crystal data

$[Co(C_8H_5Cl_2O_3)(C_{12}H_{12}N_2)]$   
 $M_r = 683.21$   
Monoclinic,  $P2_1/c$   
 $a = 13.397(2)$  Å  
 $b = 8.4152(14)$  Å  
 $c = 13.752(2)$  Å  
 $\beta = 112.570(3)^\circ$

$V = 1431.7(4)$  Å<sup>3</sup>  
 $Z = 2$   
Mo  $K\alpha$  radiation  
 $\mu = 1.02$  mm<sup>-1</sup>  
 $T = 296$  K  
 $0.30 \times 0.28 \times 0.21$  mm

### Data collection

Bruker APEXII CCD diffractometer  
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{min} = 0.756$ ,  $T_{max} = 0.819$

10343 measured reflections  
2567 independent reflections  
2229 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.028$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$   
 $wR(F^2) = 0.106$   
 $S = 1.14$   
2567 reflections

187 parameters  
H-atom parameters constrained  
 $\Delta\rho_{max} = 0.28$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.37$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C7-H7B \cdots O3^i$	0.97	2.49	3.391(3)	154
$C12-H12 \cdots O2^ii$	0.93	2.40	3.157(4)	139

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

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008) and DIAMOND (Brandenburg, 1999); software used to prepare material for publication: SHELXTL.

The authors acknowledge Donghua University for supporting this work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2417).

## References

- Brandenburg, K. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.  
Bruker (2007). *APEX2* and *SAINTE*. Bruker AXS Inc., Madison, Wisconsin, USA.  
Liu, S.-Z. (2010). *Acta Cryst.* **E66**, m199.  
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.  
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.  
Song, W.-D. & Xi, D.-L. (2006). *Acta Cryst.* **E62**, m2594–m2596.

**supplementary materials**

*Acta Cryst.* (2011). E67, m493 [ doi:10.1107/S1600536811010579 ]

## Bis(2,4-dichlorophenoxyacetato- $\kappa^2O^1,O^1'$ )(5,5'-dimethyl-2,2'-bipyridine- $\kappa^2N,N'$ )cobalt(II)

L.-L. Ji, J.-S. Liu and W.-D. Song

### Comment

In the structural investigation of 2,4-dichlorophenoxyacetate complexes, it has been found that 2,4-dichlorophenoxyacetic acid functions as a multidentate ligand (Liu, 2010; Song & Xi, 2006), with versatile binding and coordination modes. In this paper, we report the crystal structure of the title compound, a new Co(II) complex obtained by the reaction of 2,4-dichlorophenoxyacetic acid, 5,5'-dimethyl-2,2'-bipyridine and cobalt nitrate hexahydrate in an alkaline aqueous solution.

As illustrated in Fig. 1, the Co<sup>II</sup> atom, lying on a twofold rotation axis, exists in a distorted octahedral environment defined by four carboxylate O atoms from two different bidentate 2,4-dichlorophenoxyacetate ligands and two N atoms from one 5,5'-dimethyl-2,2'-bipyridine ligand. Intermolecular C—H $\cdots$ O hydrogen bonds (Table 1) and  $\pi$ – $\pi$  stacking interactions are observed (Fig. 2). The centroid–centroid distance between a pyridine ring and a benzene ring at (1-*x*, 1-*y*, -*z*) is 3.779 (2) Å, thus indicating a weak  $\pi$ – $\pi$  stacking interaction.

### Experimental

A mixture of 2,4-dichlorophenoxyacetic acid (0.110 g, 0.5 mmol), 5,5'-dimethyl-2,2'-bipyridine (0.092 g, 0.5 mmol), cobalt nitrate hexahydrate (0.145 g, 0.5 mmol), NaOH (0.08 g, 0.2 mmol) and H<sub>2</sub>O (10 ml) was placed in a 23 ml Teflon-lined reactor, which was heated to 423 K for 3 days, and then cooled to room temperature at a rate of 10 K h<sup>-1</sup>. The block purple crystals obtained were washed with water and dried in air (yield: 45% based on Co).

### Refinement

H atoms were positioned geometrically and treated as riding atoms, with C—H = 0.93 (atomic), 0.96 (CH<sub>3</sub>) and 0.97 (CH<sub>2</sub>) Å and with  $U_{\text{iso}}(\text{H}) = 1.2(1.5 \text{ for methyl})U_{\text{eq}}(\text{C})$ . The highest peak is located 0.86 Å from Cl1 and the deepest hole is located 0.73 Å from Cl1.

### Figures

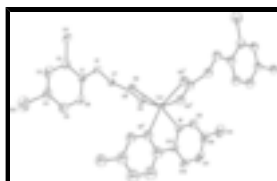


Fig. 1. The molecular structure of the title compound, showing 50% probability displacement ellipsoids. [Symmetry code: (i) 1-*x*, *y*, 1/2-*z*.]

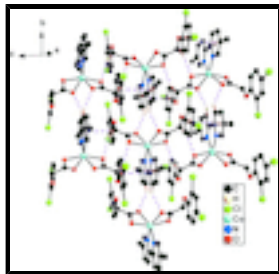


Fig. 2. Packing diagram of the title compound. C—H...O hydrogen bonds and  $\pi$ - $\pi$  interactions are shown as dashed lines. H atoms not involved in hydrogen bonds have been omitted for clarity.

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### Crystal data

[Co(C<sub>8</sub>H<sub>5</sub>Cl<sub>2</sub>O<sub>3</sub>)(C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>)]

$M_r = 683.21$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2yc

$a = 13.397 (2) \text{ \AA}$

$b = 8.4152 (14) \text{ \AA}$

$c = 13.752 (2) \text{ \AA}$

$\beta = 112.570 (3)^\circ$

$V = 1431.7 (4) \text{ \AA}^3$

$Z = 2$

$F(000) = 694$

$D_x = 1.585 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 5837 reflections

$\theta = 2.8\text{--}27.9^\circ$

$\mu = 1.02 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Block, purple

$0.30 \times 0.28 \times 0.21 \text{ mm}$

### Data collection

Bruker APEXII CCD  
diffractometer

Radiation source: fine-focus sealed tube  
graphite

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(*SADABS*; Sheldrick, 1996)

$T_{\min} = 0.756$ ,  $T_{\max} = 0.819$

10343 measured reflections

2567 independent reflections

2229 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.028$

$\theta_{\max} = 25.2^\circ$ ,  $\theta_{\min} = 1.7^\circ$

$h = -16 \rightarrow 16$

$k = -10 \rightarrow 9$

$l = -16 \rightarrow 16$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.106$

$S = 1.14$

2567 reflections

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0443P)^2 + 1.0781P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

187 parameters

$$\Delta\rho_{\max} = 0.28 \text{ e } \text{\AA}^{-3}$$

0 restraints

$$\Delta\rho_{\min} = -0.37 \text{ e } \text{\AA}^{-3}$$

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.7163 (2)	0.1694 (3)	0.0470 (2)	0.0440 (7)
C2	0.7908 (3)	0.0498 (4)	0.0494 (2)	0.0514 (7)
C3	0.8966 (3)	0.0881 (5)	0.0701 (3)	0.0670 (10)
H3	0.9462	0.0089	0.0732	0.080*
C4	0.9289 (3)	0.2447 (5)	0.0861 (3)	0.0689 (10)
C5	0.8566 (3)	0.3634 (5)	0.0807 (3)	0.0693 (10)
H5	0.8790	0.4689	0.0900	0.083*
C6	0.7503 (3)	0.3250 (4)	0.0612 (3)	0.0563 (8)
H6	0.7013	0.4052	0.0577	0.068*
C7	0.5307 (2)	0.2314 (3)	0.0072 (2)	0.0426 (6)
H7A	0.4623	0.1799	-0.0321	0.051*
H7B	0.5408	0.3142	-0.0373	0.051*
C8	0.5240 (2)	0.3081 (3)	0.1036 (2)	0.0363 (6)
C9	0.2940 (3)	0.6310 (4)	0.2236 (2)	0.0543 (8)
H9	0.2643	0.5303	0.2203	0.065*
C10	0.2281 (3)	0.7617 (5)	0.2140 (3)	0.0638 (9)
C11	0.2754 (4)	0.9083 (5)	0.2190 (3)	0.0766 (12)
H11	0.2344	0.9995	0.2134	0.092*
C12	0.3815 (4)	0.9229 (4)	0.2320 (2)	0.0644 (10)
H12	0.4123	1.0226	0.2343	0.077*
C13	0.4424 (3)	0.7856 (3)	0.2417 (2)	0.0446 (7)
C14	0.1122 (3)	0.7418 (6)	0.2007 (4)	0.0932 (14)
H14A	0.0665	0.7517	0.1276	0.140*
H14B	0.0937	0.8222	0.2404	0.140*
H14C	0.1025	0.6387	0.2257	0.140*
Cl1	0.74751 (8)	-0.14382 (10)	0.02104 (8)	0.0675 (3)
Cl2	1.06334 (9)	0.28906 (19)	0.11140 (13)	0.1133 (5)
Co1	0.5000	0.45028 (5)	0.2500	0.03575 (17)
N1	0.3975 (2)	0.6418 (3)	0.23719 (18)	0.0429 (6)
O1	0.61468 (16)	0.1179 (2)	0.02776 (17)	0.0482 (5)
O2	0.59131 (17)	0.2812 (2)	0.19438 (15)	0.0471 (5)
O3	0.44679 (16)	0.4039 (2)	0.08733 (15)	0.0460 (5)

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0543 (17)	0.0405 (15)	0.0426 (15)	0.0081 (13)	0.0248 (13)	-0.0017 (12)
C2	0.0608 (19)	0.0482 (17)	0.0496 (17)	0.0134 (15)	0.0261 (15)	0.0016 (14)
C3	0.055 (2)	0.081 (3)	0.067 (2)	0.0212 (18)	0.0251 (17)	0.0001 (19)
C4	0.0500 (19)	0.084 (3)	0.074 (2)	-0.0019 (18)	0.0245 (17)	-0.013 (2)
C5	0.064 (2)	0.071 (2)	0.080 (3)	-0.0110 (19)	0.0352 (19)	-0.019 (2)
C6	0.061 (2)	0.0475 (18)	0.069 (2)	0.0053 (15)	0.0347 (17)	-0.0076 (16)

## supplementary materials

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C7	0.0504 (16)	0.0378 (14)	0.0447 (15)	0.0063 (12)	0.0239 (13)	-0.0020 (12)
C8	0.0499 (15)	0.0237 (12)	0.0429 (15)	-0.0003 (11)	0.0262 (13)	0.0016 (11)
C9	0.0608 (19)	0.0546 (19)	0.0493 (17)	0.0114 (15)	0.0232 (15)	-0.0006 (14)
C10	0.079 (2)	0.067 (2)	0.0501 (19)	0.0319 (19)	0.0292 (17)	0.0086 (16)
C11	0.110 (3)	0.068 (3)	0.057 (2)	0.049 (2)	0.038 (2)	0.0093 (18)
C12	0.110 (3)	0.0374 (17)	0.0464 (18)	0.0194 (18)	0.0307 (19)	0.0019 (13)
C13	0.0789 (19)	0.0252 (13)	0.0302 (13)	0.0057 (12)	0.0217 (14)	-0.0008 (10)
C14	0.079 (3)	0.116 (4)	0.087 (3)	0.045 (3)	0.035 (2)	0.009 (3)
Cl1	0.0849 (6)	0.0432 (5)	0.0889 (7)	0.0162 (4)	0.0495 (5)	0.0002 (4)
Cl2	0.0555 (6)	0.1306 (11)	0.1526 (12)	-0.0124 (6)	0.0388 (7)	-0.0322 (9)
Co1	0.0512 (3)	0.0227 (3)	0.0400 (3)	0.000	0.0248 (2)	0.000
N1	0.0590 (15)	0.0341 (13)	0.0390 (13)	0.0066 (11)	0.0225 (11)	-0.0005 (10)
O1	0.0547 (12)	0.0372 (10)	0.0628 (13)	0.0063 (9)	0.0338 (10)	-0.0038 (9)
O2	0.0657 (13)	0.0352 (10)	0.0421 (11)	0.0102 (9)	0.0227 (10)	0.0026 (8)
O3	0.0540 (11)	0.0430 (11)	0.0456 (11)	0.0099 (9)	0.0242 (9)	-0.0030 (9)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

C1—O1	1.355 (4)	C9—H9	0.9300
C1—C6	1.375 (4)	C10—C11	1.377 (6)
C1—C2	1.408 (4)	C10—C14	1.500 (6)
C2—C3	1.374 (5)	C11—C12	1.368 (6)
C2—Cl1	1.723 (3)	C11—H11	0.9300
C3—C4	1.378 (6)	C12—C13	1.391 (4)
C3—H3	0.9300	C12—H12	0.9300
C4—C5	1.372 (5)	C13—N1	1.342 (4)
C4—Cl2	1.739 (4)	C13—C13 <sup>i</sup>	1.470 (6)
C5—C6	1.383 (5)	C14—H14A	0.9600
C5—H5	0.9300	C14—H14B	0.9600
C6—H6	0.9300	C14—H14C	0.9600
C7—O1	1.419 (3)	Co1—N1 <sup>i</sup>	2.080 (2)
C7—C8	1.508 (4)	Co1—N1	2.080 (2)
C7—H7A	0.9700	Co1—O3	2.1073 (19)
C7—H7B	0.9700	Co1—O3 <sup>i</sup>	2.1074 (19)
C8—O2	1.249 (3)	Co1—O2	2.1963 (19)
C8—O3	1.262 (3)	Co1—O2 <sup>i</sup>	2.1963 (19)
C9—N1	1.329 (4)	Co1—C8 <sup>i</sup>	2.467 (3)
C9—C10	1.385 (4)		
O1—C1—C6	125.8 (3)	C13—C12—H12	120.7
O1—C1—C2	115.2 (3)	N1—C13—C12	120.5 (3)
C6—C1—C2	119.0 (3)	N1—C13—C13 <sup>i</sup>	115.62 (16)
C3—C2—C1	120.2 (3)	C12—C13—C13 <sup>i</sup>	123.9 (2)
C3—C2—Cl1	120.0 (3)	C10—C14—H14A	109.5
C1—C2—Cl1	119.8 (2)	C10—C14—H14B	109.5
C2—C3—C4	119.5 (3)	H14A—C14—H14B	109.5
C2—C3—H3	120.3	C10—C14—H14C	109.5
C4—C3—H3	120.3	H14A—C14—H14C	109.5

C5—C4—C3	121.1 (3)	H14B—C14—H14C	109.5
C5—C4—C12	120.6 (3)	N1 <sup>i</sup> —Co1—N1	78.44 (14)
C3—C4—C12	118.3 (3)	N1 <sup>i</sup> —Co1—O3	100.17 (8)
C4—C5—C6	119.5 (4)	N1—Co1—O3	96.32 (8)
C4—C5—H5	120.2	N1 <sup>i</sup> —Co1—O3 <sup>i</sup>	96.32 (8)
C6—C5—H5	120.2	N1—Co1—O3 <sup>i</sup>	100.17 (8)
C1—C6—C5	120.7 (3)	O3—Co1—O3 <sup>i</sup>	158.67 (11)
C1—C6—H6	119.7	N1 <sup>i</sup> —Co1—O2	95.37 (9)
C5—C6—H6	119.7	N1—Co1—O2	155.51 (8)
O1—C7—C8	115.0 (2)	O3—Co1—O2	61.12 (7)
O1—C7—H7A	108.5	O3 <sup>i</sup> —Co1—O2	104.07 (8)
C8—C7—H7A	108.5	N1 <sup>i</sup> —Co1—O2 <sup>i</sup>	155.51 (8)
O1—C7—H7B	108.5	N1—Co1—O2 <sup>i</sup>	95.37 (9)
C8—C7—H7B	108.5	O3—Co1—O2 <sup>i</sup>	104.07 (8)
H7A—C7—H7B	107.5	O3 <sup>i</sup> —Co1—O2 <sup>i</sup>	61.12 (7)
O2—C8—O3	121.4 (2)	O2—Co1—O2 <sup>i</sup>	99.27 (11)
O2—C8—C7	122.5 (2)	N1 <sup>i</sup> —Co1—C8 <sup>i</sup>	126.52 (9)
O3—C8—C7	116.1 (2)	N1—Co1—C8 <sup>i</sup>	98.99 (9)
N1—C9—C10	123.5 (3)	O3—Co1—C8 <sup>i</sup>	132.83 (9)
N1—C9—H9	118.2	O3 <sup>i</sup> —Co1—C8 <sup>i</sup>	30.76 (8)
C10—C9—H9	118.2	O2—Co1—C8 <sup>i</sup>	103.57 (8)
C11—C10—C9	116.2 (4)	O2 <sup>i</sup> —Co1—C8 <sup>i</sup>	30.36 (8)
C11—C10—C14	122.8 (3)	C9—N1—C13	119.5 (3)
C9—C10—C14	121.0 (4)	C9—N1—Co1	125.3 (2)
C12—C11—C10	121.5 (3)	C13—N1—Co1	115.1 (2)
C12—C11—H11	119.2	C1—O1—C7	118.9 (2)
C10—C11—H11	119.2	C8—O2—Co1	86.89 (15)
C11—C12—C13	118.7 (3)	C8—O3—Co1	90.57 (16)
C11—C12—H12	120.7		

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

*Hydrogen-bond geometry* ( $\text{\AA}, ^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C7—H7B $\cdots$ O3 <sup>ii</sup>	0.97	2.49	3.391 (3)	154
C12—H12 $\cdots$ O2 <sup>iii</sup>	0.93	2.40	3.157 (4)	139

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

Fig. 1

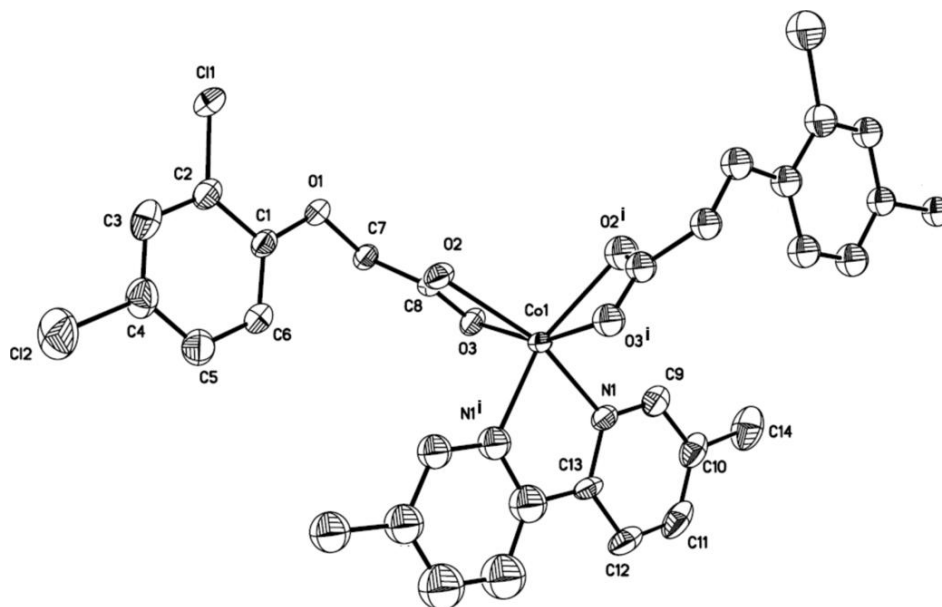




Fig. 2

