

catena-Poly[cobalt(II)-bis(μ -3,7-dichloroquinoline-8-carboxylato- κ^3 N,O:O')]

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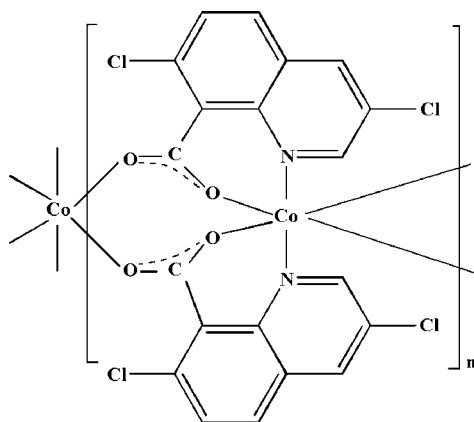
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 Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.034; wR factor = 0.089; data-to-parameter ratio = 12.4.

In the crystal structure of the title compound, $[\text{Co}(\text{C}_{10}\text{H}_4\text{Cl}_2\text{NO}_2)_2]_n$, the Co^{II} cation lies on a twofold rotation axis. Each cation is N,O -chelated by the carboxylate anions of two 3,7-dichloroquinoline-8-carboxylate ligands. The second carboxylate O atom of each ligand coordinates to the Co^{II} cation of an adjacent molecule, linking the cations into a linear chain. Strong interchain π - π stacking interactions are observed in the crystal structure (perpendicular distance 3.42 Å, centroid-to-centroid distance 3.874 Å)

Related literature

For the use of 3,7-dichloro-8-quinolinecarboxylic acid as a herbicide, see: Nuria *et al.* (1997); Pornprom *et al.* (2006); Sunohara & Matsumoto (2004); Tresch & Grossmann (2002). For related vanadium and cadmium complexes, see Chen *et al.* (2001); Yang *et al.* (2005). For related literature, see: Turel *et al.* (2004); Zhang *et al.* (2007).



Experimental

Crystal data

$[\text{Co}(\text{C}_{10}\text{H}_4\text{Cl}_2\text{NO}_2)_2]$	$V = 1987.7$ (5) Å ³
$M_r = 541.01$	$Z = 4$
Orthorhombic, $Pccn$	Mo $K\alpha$ radiation
$a = 13.5109$ (14) Å	$\mu = 1.43$ mm ⁻¹
$b = 15.964$ (2) Å	$T = 298$ (2) K
$c = 9.2157$ (16) Å	$0.49 \times 0.33 \times 0.31$ mm

Data collection

Siemens SMART CCD area-detector diffractometer	9558 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	1752 independent reflections
$T_{\text{min}} = 0.57$, $T_{\text{max}} = 0.64$	1404 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.039$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$	141 parameters
$wR(F^2) = 0.089$	H-atom parameters constrained
$S = 1.11$	$\Delta\rho_{\text{max}} = 0.67$ e Å ⁻³
1752 reflections	$\Delta\rho_{\text{min}} = -0.76$ e Å ⁻³

Table 1

Selected geometric parameters (Å, °).

Co1—O1	2.093 (2)	Co1—N1	2.197 (2)
Co1—O2 ⁱ	2.057 (2)		
O2 ⁱ —Co1—O2 ⁱⁱ	103.60 (12)	O2 ⁱⁱ —Co1—N1	87.24 (9)
O2 ⁱ —Co1—O1	170.96 (9)	O1—Co1—N1	89.82 (9)
O2 ⁱⁱ —Co1—O1	85.43 (8)	O1 ⁱⁱⁱ —Co1—N1	92.31 (9)
O1—Co1—O1 ⁱⁱⁱ	85.55 (12)	N1 ⁱⁱⁱ —Co1—N1	177.10 (14)
O2 ⁱ —Co1—N1	90.97 (9)		

 Symmetry codes: (i) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (ii) $-x + \frac{3}{2}, y, z + \frac{1}{2}$; (iii) $-x + \frac{3}{2}, -y + \frac{3}{2}, z$.

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a); molecular graphics: SHELXTL (Sheldrick, 1997b); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2456).

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***catena*-Poly[cobalt(II)-bis(μ -3,7-dichloroquinoline-8-carboxylato- $\kappa^3N,O:O'$)]**

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Comment

Quinolinecarboxylates generally chelate to metal atoms, and some metal quinolinecarboxylates have been reported such as, for example, bis(6-methyl-4-hydroxy-3-quinolinecarboxylate) mono(oxo)monohydroxyvanadium(V) and Cd(H₂O)(4-quinolinecarboxylato)₂ (Chen *et al.*, 2001; Yang *et al.*, 2005). Quinclorac (3,7-dichloro-8-quinolinecarboxylic acid) is a most effective herbicides (Nuria *et al.*, 1997; Pornprom *et al.*, 2006; Sunohara & Matsumoto, 2004; Tresch & Grossmann, 2002). We have reported a nickel-quinclorac complex in our previous work (Zhang *et al.*, 2007). The title compound is a cobalt(II) derivative (I) (Fig. 1) with the Co^{II} cation located on a twofold rotation axis. The Co^{II} center exhibits a distorted octahedral geometry defined by four carboxylato oxygen atoms from four quinclorac and two nitrogen atoms from two quinclorac units. Each quinclorac ligand chelates to the cobalt atom *via* a quinoline N atom and a carboxylate O atom. Adjacent molecules are linked by carboxylate bridges into a linear chain. The chains are assembled into a three-dimensional supramolecular architecture by strong offset face-to-face π - π stacking interactions (perpendicular distance: 3.42 Å, centroid-centroid distance: 3.874 Å) between the C2-C7 and C2ⁱ-C7ⁱ benzene rings [symmetry code: (i) 2 - x, 1 - y, - z].

Experimental

A mixture of quinclorac (0.5 mmol, 0.121 g), CoCl₂·6H₂O (1 mmol, 0.238 g), Na₂MoO₄·2H₂O (0.5 mmol, 0.121 g) and H₂O (10 ml) was treated with aqueous HCl to a pH of 5. The mixture was placed in a Teflon-lined autoclave; this was heated at 403 K for three days. Red crystals were collected and washed with water. C H & N elemental analysis. Calculated for C₂₀H₈Cl₄N₂O₄Co: C 44.36, H 1.48, N 5.18%; found: C 44.48, H 1.69, N 5.31%. Selected FT-IR (KBr, cm⁻¹): 3301(w), 1581(s), 1553(m), 1482(m), 1402(m), 1383(s), 1232(m), 1139 (m), 1101(s), 761(m), 553(m), 449(m).

Refinement

H atoms were positioned geometrically and refined as riding atoms, with C-H = 0.93Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures

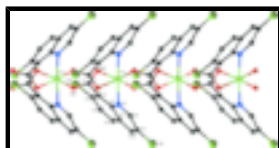


Fig. 1. The structure of (I), with the atomic numbering scheme and displacement ellipsoids at the 50% probability level. H atoms have been omitted for clarity [Symmetry code: (i) $x, -y + 1/2, z + 1/2$.]

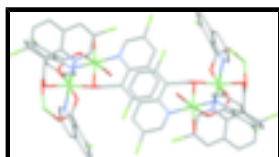


Fig. 2. Three dimensional supramolecular architecture constructed by interchain π - π stacking interactions.

supplementary materials

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Crystal data

[Co(C ₁₀ H ₄ Cl ₂ NO ₂) ₂]	$F_{000} = 1076$
$M_r = 541.01$	$D_x = 1.808 \text{ Mg m}^{-3}$
	$D_m = 1.800 \text{ Mg m}^{-3}$
	D_m measured by not measured
Orthorhombic, <i>Pccn</i>	Mo $K\alpha$ radiation
	$\lambda = 0.71073 \text{ \AA}$
Hall symbol: -P 2ab 2ac	Cell parameters from 9558 reflections
$a = 13.5109 (14) \text{ \AA}$	$\theta = 2.0\text{--}25.0^\circ$
$b = 15.964 (2) \text{ \AA}$	$\mu = 1.43 \text{ mm}^{-1}$
$c = 9.2157 (16) \text{ \AA}$	$T = 298 (2) \text{ K}$
$V = 1987.7 (5) \text{ \AA}^3$	Block, red
$Z = 4$	$0.49 \times 0.33 \times 0.31 \text{ mm}$

Data collection

Siemens SMART CCD area-detector diffractometer	1752 independent reflections
Radiation source: fine-focus sealed tube	1404 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.039$
$T = 298(2) \text{ K}$	$\theta_{\text{max}} = 25.0^\circ$
φ and ω scans	$\theta_{\text{min}} = 2.0^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -16 \rightarrow 13$
$T_{\text{min}} = 0.57, T_{\text{max}} = 0.64$	$k = -18 \rightarrow 18$
9558 measured reflections	$l = -10 \rightarrow 9$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.034$	H-atom parameters constrained
$wR(F^2) = 0.089$	$w = 1/[\sigma^2(F_o^2) + (0.0291P)^2 + 3.6236P]$
$S = 1.11$	where $P = (F_o^2 + 2F_c^2)/3$
1752 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
141 parameters	$\Delta\rho_{\text{max}} = 0.67 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -0.76 \text{ e \AA}^{-3}$
	Extinction correction: none

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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.7500	0.7500	0.25905 (6)	0.02337 (17)
Cl1	0.77826 (7)	0.45967 (6)	-0.08682 (10)	0.0438 (3)
Cl2	1.11100 (8)	0.71113 (7)	0.54570 (14)	0.0641 (4)
N1	0.89374 (19)	0.68581 (16)	0.2651 (3)	0.0271 (6)
O1	0.70392 (16)	0.66997 (13)	0.0924 (2)	0.0296 (5)
O2	0.80139 (16)	0.65857 (13)	-0.1029 (2)	0.0287 (5)
C1	0.7764 (2)	0.64027 (19)	0.0240 (3)	0.0253 (7)
C2	0.8430 (2)	0.57762 (19)	0.0989 (3)	0.0254 (7)
C3	0.8519 (2)	0.4963 (2)	0.0541 (4)	0.0305 (7)
C4	0.9198 (3)	0.4403 (2)	0.1170 (4)	0.0406 (9)
H4	0.9214	0.3846	0.0871	0.049*
C5	0.9831 (3)	0.4674 (2)	0.2212 (4)	0.0405 (9)
H5	1.0300	0.4309	0.2594	0.049*
C6	0.9783 (2)	0.5510 (2)	0.2723 (4)	0.0325 (8)
C7	0.9051 (2)	0.60506 (19)	0.2140 (3)	0.0273 (7)
C8	0.9570 (2)	0.7133 (2)	0.3621 (4)	0.0325 (8)
H8	0.9503	0.7681	0.3949	0.039*
C9	1.0338 (2)	0.6646 (2)	0.4188 (4)	0.0378 (8)
C10	1.0438 (3)	0.5835 (2)	0.3773 (4)	0.0397 (9)
H10	1.0929	0.5499	0.4175	0.048*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0269 (3)	0.0247 (3)	0.0185 (3)	0.0027 (3)	0.000	0.000
Cl1	0.0472 (5)	0.0369 (5)	0.0472 (6)	-0.0042 (4)	-0.0028 (4)	-0.0106 (4)
Cl2	0.0561 (6)	0.0563 (7)	0.0799 (8)	0.0064 (5)	-0.0383 (6)	-0.0098 (6)
N1	0.0271 (14)	0.0274 (14)	0.0268 (15)	0.0037 (11)	-0.0010 (11)	0.0010 (11)
O1	0.0316 (12)	0.0338 (12)	0.0233 (12)	0.0062 (10)	-0.0014 (10)	-0.0035 (10)
O2	0.0344 (12)	0.0307 (12)	0.0211 (12)	0.0016 (10)	0.0015 (9)	0.0020 (10)
C1	0.0322 (17)	0.0217 (15)	0.0220 (16)	-0.0028 (12)	-0.0030 (13)	0.0000 (12)
C2	0.0258 (16)	0.0285 (16)	0.0218 (16)	0.0024 (13)	0.0053 (13)	0.0052 (13)

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C3	0.0331 (17)	0.0261 (17)	0.0323 (18)	-0.0021 (14)	0.0046 (14)	0.0002 (14)
C4	0.051 (2)	0.0242 (18)	0.047 (2)	0.0059 (16)	0.0032 (19)	-0.0001 (16)
C5	0.042 (2)	0.0340 (19)	0.045 (2)	0.0122 (16)	-0.0004 (17)	0.0073 (17)
C6	0.0332 (18)	0.0330 (18)	0.0311 (19)	0.0051 (14)	0.0012 (14)	0.0049 (15)
C7	0.0266 (16)	0.0289 (17)	0.0264 (17)	0.0044 (13)	0.0070 (13)	0.0044 (14)
C8	0.0292 (17)	0.0315 (18)	0.037 (2)	0.0018 (14)	-0.0010 (15)	0.0008 (15)
C9	0.0306 (18)	0.042 (2)	0.041 (2)	0.0018 (15)	-0.0088 (16)	-0.0023 (17)
C10	0.0337 (19)	0.045 (2)	0.040 (2)	0.0106 (16)	-0.0065 (16)	0.0053 (18)

Geometric parameters (Å, °)

Co1—O1	2.093 (2)	C2—C3	1.368 (4)
Co1—O1 ⁱ	2.093 (2)	C2—C7	1.422 (4)
Co1—O2 ⁱⁱ	2.057 (2)	C3—C4	1.406 (5)
Co1—O2 ⁱⁱⁱ	2.057 (2)	C4—C5	1.357 (5)
Co1—N1 ⁱ	2.197 (2)	C4—H4	0.9300
Co1—N1	2.197 (2)	C5—C6	1.416 (5)
Cl1—C3	1.738 (3)	C5—H5	0.9300
Cl2—C9	1.734 (4)	C6—C10	1.410 (5)
N1—C8	1.312 (4)	C6—C7	1.419 (4)
N1—C7	1.381 (4)	C8—C9	1.398 (5)
O1—C1	1.257 (4)	C8—H8	0.9300
O2—C1	1.252 (4)	C9—C10	1.358 (5)
O2—Co1 ^{iv}	2.057 (2)	C10—H10	0.9300
C1—C2	1.512 (4)		
O2 ⁱⁱ —Co1—O2 ⁱⁱⁱ	103.60 (12)	C7—C2—C1	119.2 (3)
O2 ⁱⁱ —Co1—O1	170.96 (9)	C2—C3—C4	122.5 (3)
O2 ⁱⁱⁱ —Co1—O1	85.43 (8)	C2—C3—Cl1	119.6 (3)
O2 ⁱⁱ —Co1—O1 ⁱ	85.43 (8)	C4—C3—Cl1	117.9 (3)
O2 ⁱⁱⁱ —Co1—O1 ⁱ	170.96 (8)	C5—C4—C3	120.0 (3)
O1—Co1—O1 ⁱ	85.55 (12)	C5—C4—H4	120.0
O2 ⁱⁱ —Co1—N1 ⁱ	87.24 (9)	C3—C4—H4	120.0
O2 ⁱⁱⁱ —Co1—N1 ⁱ	90.97 (9)	C4—C5—C6	120.5 (3)
O1—Co1—N1 ⁱ	92.31 (9)	C4—C5—H5	119.8
O1 ⁱ —Co1—N1 ⁱ	89.82 (9)	C6—C5—H5	119.8
O2 ⁱⁱ —Co1—N1	90.97 (9)	C10—C6—C5	123.1 (3)
O2 ⁱⁱⁱ —Co1—N1	87.24 (9)	C10—C6—C7	118.3 (3)
O1—Co1—N1	89.82 (9)	C5—C6—C7	118.6 (3)
O1 ⁱ —Co1—N1	92.31 (9)	N1—C7—C6	121.1 (3)
N1 ⁱ —Co1—N1	177.10 (14)	N1—C7—C2	118.5 (3)
C8—N1—C7	118.2 (3)	C6—C7—C2	120.5 (3)
C8—N1—Co1	115.9 (2)	N1—C8—C9	123.5 (3)
C7—N1—Co1	121.7 (2)	N1—C8—H8	118.2
C1—O1—Co1	111.49 (19)	C9—C8—H8	118.2
C1—O2—Co1 ^{iv}	130.7 (2)	C10—C9—C8	119.9 (3)

O2—C1—O1	126.2 (3)	C10—C9—C12	122.6 (3)
O2—C1—C2	114.9 (3)	C8—C9—C12	117.4 (3)
O1—C1—C2	119.0 (3)	C9—C10—C6	118.8 (3)
C3—C2—C7	117.8 (3)	C9—C10—H10	120.6
C3—C2—C1	122.9 (3)	C6—C10—H10	120.6
O2 ⁱⁱ —Co1—N1—C8	9.9 (2)	C11—C3—C4—C5	176.0 (3)
O2 ⁱⁱⁱ —Co1—N1—C8	-93.6 (2)	C3—C4—C5—C6	3.0 (5)
O1—Co1—N1—C8	-179.1 (2)	C4—C5—C6—C10	-178.1 (4)
O1 ⁱ —Co1—N1—C8	95.4 (2)	C4—C5—C6—C7	1.0 (5)
O2 ⁱⁱ —Co1—N1—C7	166.4 (2)	C8—N1—C7—C6	4.7 (4)
O2 ⁱⁱⁱ —Co1—N1—C7	62.8 (2)	Co1—N1—C7—C6	-151.2 (2)
O1—Co1—N1—C7	-22.7 (2)	C8—N1—C7—C2	-174.0 (3)
O1 ⁱ —Co1—N1—C7	-108.2 (2)	Co1—N1—C7—C2	30.1 (4)
O1 ⁱ —Co1—O1—C1	68.44 (19)	C10—C6—C7—N1	-4.1 (5)
N1 ⁱ —Co1—O1—C1	158.1 (2)	C5—C6—C7—N1	176.6 (3)
N1—Co1—O1—C1	-23.9 (2)	C10—C6—C7—C2	174.5 (3)
Co1 ^{iv} —O2—C1—O1	8.1 (5)	C5—C6—C7—C2	-4.8 (5)
Co1 ^{iv} —O2—C1—C2	-170.54 (19)	C3—C2—C7—N1	-177.0 (3)
Co1—O1—C1—O2	-109.2 (3)	C1—C2—C7—N1	7.7 (4)
Co1—O1—C1—C2	69.4 (3)	C3—C2—C7—C6	4.4 (4)
O2—C1—C2—C3	-65.8 (4)	C1—C2—C7—C6	-170.9 (3)
O1—C1—C2—C3	115.4 (3)	C7—N1—C8—C9	-1.4 (5)
O2—C1—C2—C7	109.2 (3)	Co1—N1—C8—C9	155.8 (3)
O1—C1—C2—C7	-69.6 (4)	N1—C8—C9—C10	-2.3 (6)
C7—C2—C3—C4	-0.3 (5)	N1—C8—C9—C12	179.7 (3)
C1—C2—C3—C4	174.8 (3)	C8—C9—C10—C6	2.8 (6)
C7—C2—C3—C11	-179.7 (2)	C12—C9—C10—C6	-179.4 (3)
C1—C2—C3—C11	-4.6 (4)	C5—C6—C10—C9	179.5 (4)
C2—C3—C4—C5	-3.4 (5)	C7—C6—C10—C9	0.4 (5)

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

Fig. 2

