metal-organic compounds

Bis[2,4-dibromo-6-(ethyliminomethyl)-phenolato-κ^2N,O]cobalt(II)

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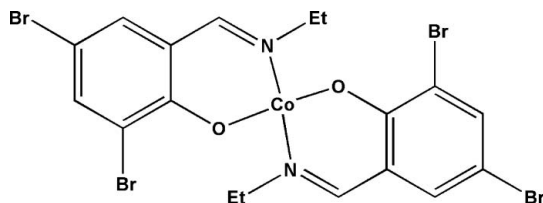Correspondence e-mail: lichunyan2009@yahoo.com.cn

In the title compound, [Co($C_9H_8Br_2NO$)$_2$], the Co^{II} atom, located on a twofold axis, is in a pseudo-tetrahedral environment, with two bidentate 2,4-dibromo-6-(ethyliminomethyl)phenolate Schiff base ligands acting as chelates through their phenolate O and azomethine N atoms. C—H···O hydrogen bonds link the complex molecules to form a chain parallel to the b axis.

Related literature

For related Lewis base adducts, see: Akitsu *et al.* (2005); Bahron *et al.* (1994); Bermejo *et al.* (1996); Elerman *et al.* (1996); Groombridge *et al.* (1992); Li *et al.* (2008); Maneiro *et al.* (2001); Qiu *et al.* (2007). For a related structure, see: Jiang *et al.* (2008). For standard bond-distance values, see: Allen *et al.* (1987).

Experimental

Crystal data

[Co($C_9H_8Br_2NO$)$_2$]	V = 2081.9 (4) Å^3
M_r = 670.90	Z = 4
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
a = 22.116 (3) Å	μ = 8.52 mm^{-1}
b = 4.8645 (5) Å	T = 298 K
c = 19.652 (2) Å	0.30 × 0.21 × 0.11 mm
β = 100.038 (3)°	

Data collection

Bruker SMART CCD area-detector diffractometer	6537 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)	2028 independent reflections
T_{min} = 0.089, T_{max} = 0.392	1607 reflections with $I > 2\sigma(I)$
	R_{int} = 0.099

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.060	124 parameters
$wR(F^2)$ = 0.161	H-atom parameters constrained
S = 1.00	$\Delta\rho_{max}$ = 1.39 e Å^{-3}
2028 reflections	$\Delta\rho_{min}$ = −1.08 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C8—H8A···O1^i	0.97	2.49	3.389 (8)	154

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996), *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2009).; software used to prepare material for publication: *SHELXL97*.

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supporting information

Bis[2,4-dibromo-6-(ethyliminomethyl)phenolato-*κ²N,O*]cobalt(II)

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S1. Comment

The Lewis base adducts of the 3,5-dibromosalicylidene group that are derived from the condensation of 3,5-dibromo-salicylaldehyde and various primary amine are very interesting in a large number of transition metal complexes (Qiu *et al.*, 2007; Akitsu *et al.*, 2005; Maneiro *et al.*, 2001; Bermejo *et al.*, 1996). Recently, some mononuclear cobalt(II) compounds of Schiff base ligands derived from the condensation of salicylaldehyde with ethyl-, propyl- and butylamine have been structurally characterized (Li *et al.*, 2008; Elerman *et al.*, 1996; Bahron *et al.*, 1994; Groombridge *et al.*, 1992). As an extension of this work, the crystal structure of the title compound, (I), is reported here.

In (I), the Co atoms, located on a two fold axis, have pseudo-tetrahedral coordination environments with two bidentate Schiff base ligands,derived from the condensation of 3,5-dibromosalicylaldehyde and ethylamine, acting as chelates through their phenolate O and azomethine N atoms (Fig. 1). The structure is closely related to the Bis{2-[(*E*)-benzyl-iminomethyl]-4,6-dibromophenolato-*κ²N, O*}cobalt(II) compound (Jiang *et al.*, 2008). The C7═N1 bond length of 1.287 (7) Å is similar to that of 1.288 (7) Å observed in the previously reported compound of Schiff base ligand, which was derived from the condensation of salicylaldehyde and isopropylamine (Elerman *et al.*, 1996). The angle between the two O1—Co1—N1 planes of the molecule is equal to 82.80°. All bond lengths are within normal ranges (Allen *et al.*, 1987).

In the crystal structure, the molecules are linked *via* intermolecular C—H···O hydrogen bonds forming a chain parallel to the b axis (Table 1, Fig. 2).

S2. Experimental

3,5-Dibromosalicyladehyde (560 mg, 2 mmol) and ethylamine (90 mg, 2 mmol) were dissolved in methanol (25 ml). The mixture was stirred for 30 min to give an orange solution, which was added to a methanol solution (15 ml) of $Co(NO_3)_2.6H_2O$ (280 mg, 1 mmol). The mixture was stirred for another 20 min at room temperature to give a red solution and then filtered. The filtrate was kept in air for 5 d, forming red blocky crystals. The crystals were isolated, washed three times with distilled water and dried in a vacuum desiccator containing anhydrous $CaCl_2$ (yield 66%). Analysis calculated for $C_{18}H_{16}Br_4CoN_2O_2$: C 32.23, H 2.40, N 4.18%; found: C 32.11, H 2.55, N 4.00%. IR (KBr, cm⁻¹): 3447, 2956, 2925, 2868, 2363, 1736, 1616, 1581, 1505, 1436, 1406, 1343, 1309, 1210, 1156, 1090, 1058, 974, 863, 840, 750, 708, 606, 534, 477.

S3. Refinement

All the H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.93–0.97 Å, and with $U_{iso}(H) = 1.2U_{eq}$(carrier) or $1.5U_{eq}$(methyl groups).
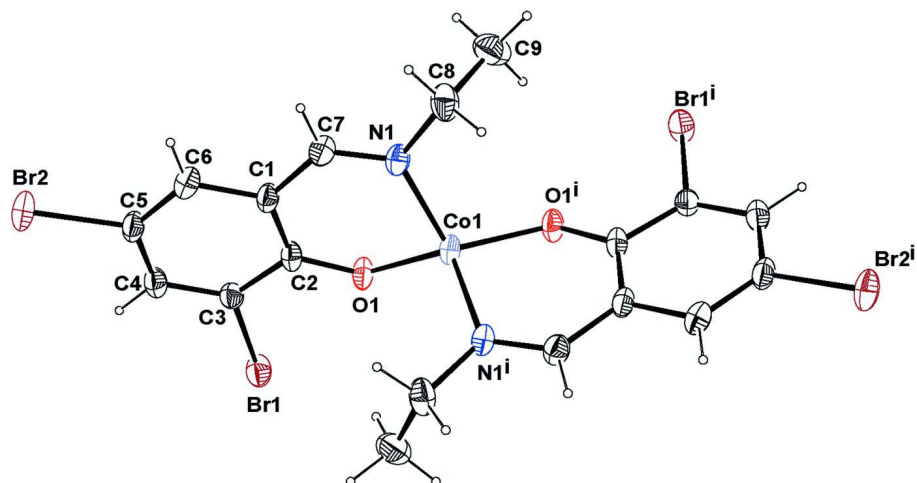
Figure 1

The structure of the title compound (I), with the atom labeling scheme. Ellipsoids are drawn at the 30% probability level.
H atoms are represented as small spheres of arbitrary radii. [Symmetry code: (i) 1 - x, y, 1/2 - z.]
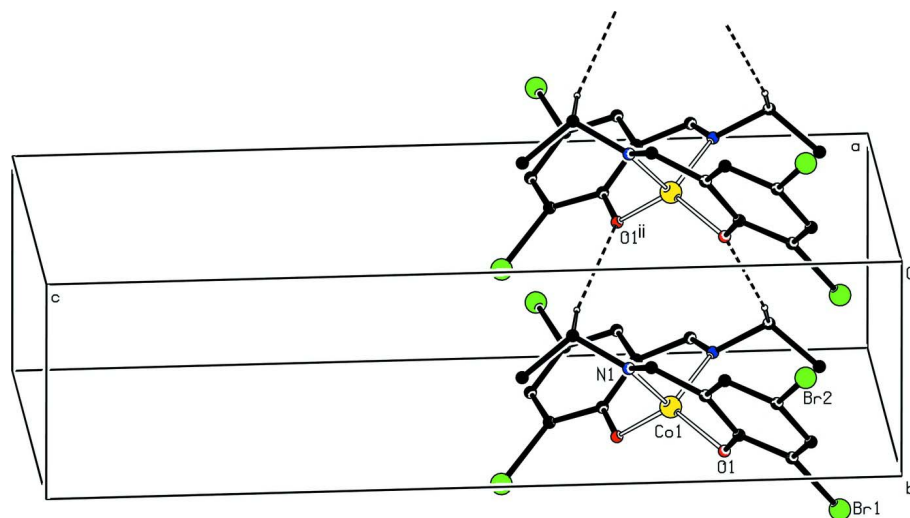

Figure 2

Partial packing view showing the chain formed through C—H⋯O hydrogen bonds. H atoms not involved in hydrogen
bondings have been omitted for clarity. H bonds are shown as dashed lines. [Symmetry code: (ii) -x + 1, y - 1, -z + 1/2.]

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Crystal data

[Co(C₉H₈Br₂NO)₂]	$F(000) = 1284$
$M_r = 670.90$	$D_x = 2.140$ Mg m⁻³
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 2472 reflections
$a = 22.116$ (3) Å	$\theta = 2.6–27.2°$
$b = 4.8645$ (5) Å	$\mu = 8.52$ mm⁻¹
$c = 19.652$ (2) Å	$T = 298$ K
$\beta = 100.038$ (3)°	Block, red
$V = 2081.9$ (4) Å³	$0.30 \times 0.21 \times 0.11$ mm
$Z = 4$	

Data collection

Bruker SMART CCD area-detector diffractometer	6537 measured reflections
Radiation source: fine-focus sealed tube	2028 independent reflections
Graphite monochromator	1607 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.099$
Absorption correction: multi-scan	$\theta_{max} = 26.0°, \theta_{min} = 1.9°$
(*SADABS*; Bruker, 2000)	$h = -26 \rightarrow 26$
$T_{min} = 0.089, T_{max} = 0.392$	$k = -6 \rightarrow 5$
	$l = -24 \rightarrow 22$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.060$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.161$	
$S = 1.00$	H-atom parameters constrained
2028 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0865P)^2]$
124 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 1.39$ e Å^{-3}
	$\Delta\rho_{min} = -1.08$ 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.

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 (Å²)

	x	y	z	$U_{iso}*/U_{eq}$
Co1	0.5000	0.9495 (3)	0.2500	0.0396 (3)
N1	0.44643 (19)	0.7331 (11)	0.3012 (2)	0.0394 (11)
O1	0.43303 (17)	1.1213 (9)	0.1898 (2)	0.0423 (10)
Br1	0.36561 (3)	1.36837 (14)	0.05745 (3)	0.0477 (3)
Br2	0.18010 (3)	0.63810 (17)	0.10502 (4)	0.0595 (3)
C1	0.3544 (2)	0.8138 (12)	0.2155 (3)	0.0354 (12)
C2	0.3778 (2)	1.0161 (13)	0.1750 (3)	0.0343 (12)
C3	0.3371 (3)	1.1041 (12)	0.1146 (3)	0.0354 (13)
C4	0.2796 (2)	0.9972 (13)	0.0949 (3)	0.0398 (13)
H4	0.2549	1.0568	0.0544	0.048*
C5	0.2587 (2)	0.8016 (14)	0.1352 (3)	0.0405 (14)
C6	0.2942 (3)	0.7099 (14)	0.1949 (3)	0.0438 (14)
H6	0.2789	0.5792	0.2219	0.053*
C7	0.3891 (3)	0.6970 (13)	0.2770 (3)	0.0406 (13)
H7	0.3677	0.5820	0.3023	0.049*
C8	0.4728 (3)	0.5890 (14)	0.3657 (3)	0.0508 (16)

H8A	0.5098	0.4929	0.3593	0.061*	
H8B	0.4437	0.4538	0.3767	0.061*	
C9	0.4878 (4)	0.7869 (17)	0.4243 (3)	0.064 (2)	
H9A	0.5131	0.9319	0.4116	0.096*	
H9B	0.5094	0.6928	0.4642	0.096*	
H9C	0.4505	0.8634	0.4349	0.096*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0224 (5)	0.0503 (8)	0.0437 (6)	0.000	−0.0009 (4)	0.000
N1	0.026 (2)	0.043 (3)	0.048 (3)	0.006 (2)	0.0011 (19)	0.001 (2)
O1	0.0245 (19)	0.047 (3)	0.051 (2)	−0.0072 (16)	−0.0047 (17)	0.0032 (19)
Br1	0.0393 (4)	0.0488 (5)	0.0511 (4)	−0.0047 (2)	−0.0036 (3)	0.0089 (3)
Br2	0.0276 (4)	0.0697 (6)	0.0769 (5)	−0.0128 (3)	−0.0030 (3)	−0.0035 (4)
C1	0.022 (2)	0.040 (3)	0.043 (3)	0.002 (2)	0.000 (2)	−0.006 (2)
C2	0.026 (2)	0.032 (3)	0.042 (3)	0.003 (2)	−0.004 (2)	−0.006 (2)
C3	0.029 (3)	0.041 (4)	0.035 (3)	0.002 (2)	0.003 (2)	−0.002 (2)
C4	0.031 (3)	0.043 (4)	0.043 (3)	0.003 (2)	−0.003 (2)	−0.005 (3)
C5	0.022 (2)	0.051 (4)	0.046 (3)	0.000 (2)	−0.001 (2)	−0.008 (3)
C6	0.029 (3)	0.044 (4)	0.059 (4)	−0.003 (3)	0.010 (3)	−0.002 (3)
C7	0.032 (3)	0.041 (4)	0.048 (3)	−0.002 (2)	0.007 (2)	0.003 (3)
C8	0.039 (3)	0.049 (4)	0.058 (4)	0.006 (3)	−0.007 (3)	0.010 (3)
C9	0.071 (5)	0.077 (6)	0.044 (4)	0.016 (4)	0.009 (3)	0.009 (4)

Geometric parameters (Å, º)

Co1—O1[i]	1.918 (4)	C3—C4	1.366 (8)
Co1—O1	1.918 (4)	C4—C5	1.370 (9)
Co1—N1[i]	1.985 (5)	C4—H4	0.9300
Co1—N1	1.985 (5)	C5—C6	1.367 (9)
N1—C7	1.287 (7)	C6—H6	0.9300
N1—C8	1.477 (8)	C7—H7	0.9300
O1—C2	1.310 (6)	C8—C9	1.493 (10)
Br1—C3	1.886 (6)	C8—H8A	0.9700
Br2—C5	1.909 (5)	C8—H8B	0.9700
C1—C6	1.414 (8)	C9—H9A	0.9600
C1—C2	1.419 (8)	C9—H9B	0.9600
C1—C7	1.432 (8)	C9—H9C	0.9600
C2—C3	1.424 (8)		
O1[i]—Co1—O1	128.3 (3)	C6—C5—C4	121.4 (5)
O1[i]—Co1—N1[i]	94.52 (17)	C6—C5—Br2	119.2 (5)
O1—Co1—N1[i]	112.53 (19)	C4—C5—Br2	119.4 (4)
O1[i]—Co1—N1	112.53 (19)	C5—C6—C1	120.0 (6)
O1—Co1—N1	94.52 (17)	C5—C6—H6	120.0
N1[i]—Co1—N1	116.0 (3)	C1—C6—H6	120.0
C7—N1—C8	118.0 (5)	N1—C7—C1	127.3 (6)

C7—N1—Co1	121.5 (4)	N1—C7—H7	116.3
C8—N1—Co1	120.4 (4)	C1—C7—H7	116.3
C2—O1—Co1	123.9 (4)	N1—C8—C9	110.9 (6)
C6—C1—C2	120.3 (5)	N1—C8—H8A	109.5
C6—C1—C7	116.0 (6)	C9—C8—H8A	109.5
C2—C1—C7	123.7 (5)	N1—C8—H8B	109.5
O1—C2—C1	124.3 (5)	C9—C8—H8B	109.5
O1—C2—C3	119.8 (5)	H8A—C8—H8B	108.0
C1—C2—C3	115.9 (5)	C8—C9—H9A	109.5
C4—C3—C2	122.9 (6)	C8—C9—H9B	109.5
C4—C3—Br1	118.8 (4)	H9A—C9—H9B	109.5
C2—C3—Br1	118.3 (4)	C8—C9—H9C	109.5
C3—C4—C5	119.5 (5)	H9A—C9—H9C	109.5
C3—C4—H4	120.2	H9B—C9—H9C	109.5
C5—C4—H4	120.2		

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

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
C8—H8A···O1[ii]	0.97	2.49	3.389 (8)	154

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