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# $(-)_D$-Aquabromo{3,3′-[(1*R*,2*R*)-1,2-bis(2,4,6-trimethylphenyl)ethane-1,2-diylbis(nitrilomethylidyne)]bis(pentane-2,4-dionato)-*N*,*N*′,*O*,*O*′}cobalt(III) tetrahydrofuran solvate

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In the title compound, $(-)_D$-[$CoBr(C_{32}H_{38}N_2O_4)(H_2O)$]·$C_4H_8O$, the benzylic C atoms of the tetradentate ligand have an *R*,*R* configuration. There are two independent complex molecules in the asymmetric unit, essentially of the same geometry and absolute configuration. It was possible to determine the absolute configuration based on the Flack parameter, although the crystal structure has a pseudo-center of symmetry.

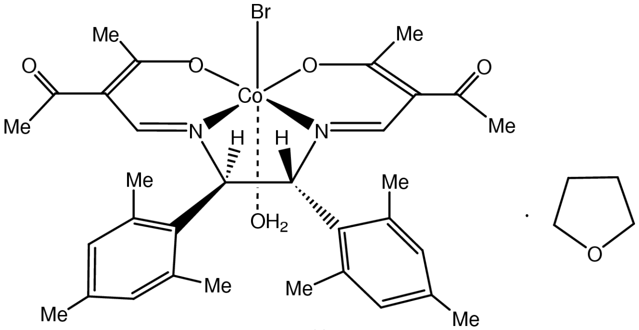
**Key indicators**

Single-crystal X-ray study
$T$ = 297 K
Mean $\sigma$(C–C) = 0.021 Å
*R* factor = 0.064
*wR* factor = 0.186
Data-to-parameter ratio = 15.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

## Comment

The space group of the title $Co^{III}$ complex, (I), is chiral since it was prepared with an optically pure tetradentate ligand. Pseudo-systematic absences $h0l$, $l$ odd, were observed, which corresponds to the fact that the crystal structure has a pseudo-center of symmetry and the space group is approximately $P2_1/c$. However, both of the two independent Co complexes have the chiral ligand in an *R*,*R* configuration, as shown in Figs. 1 and 2, and there is no disorder around the asymmetric C atoms (C24, C25, C56, and C57). Although the values of the s.u.'s of coordinates are relatively high, the geometry is quite normal (Table 1).



(I)

Flack & Bernardinelli (1999) formulated the inversion-distinguishing power, which is not decreased by the pseudo-centrosymmetric arrangement of the heavy atoms if the light-atom substructure is clearly non-centrosymmetric. The title crystal is just such a case and the absolute configuration could be determined definitely based on Flack parameter, 0.04 (2). As seen from Fig. 3, the aromatic rings bonded at the asymmetric C atoms contribute to the non-centrosymmetry.

There are intermolecular O—H···O hydrogen bonds involving the aqua ligands. The structures of the complex molecules have significant C—H···O close contacts (Table 2).

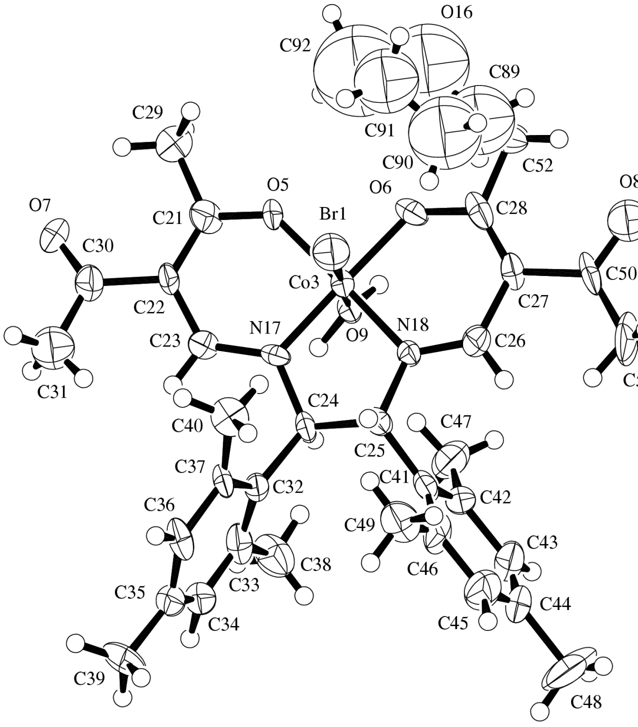


**Figure 1**
The structure of the complex involving the Co3 atom in (I) with displacement ellipsoids at the 50% probability level. A neighboring THF molecule is also shown.

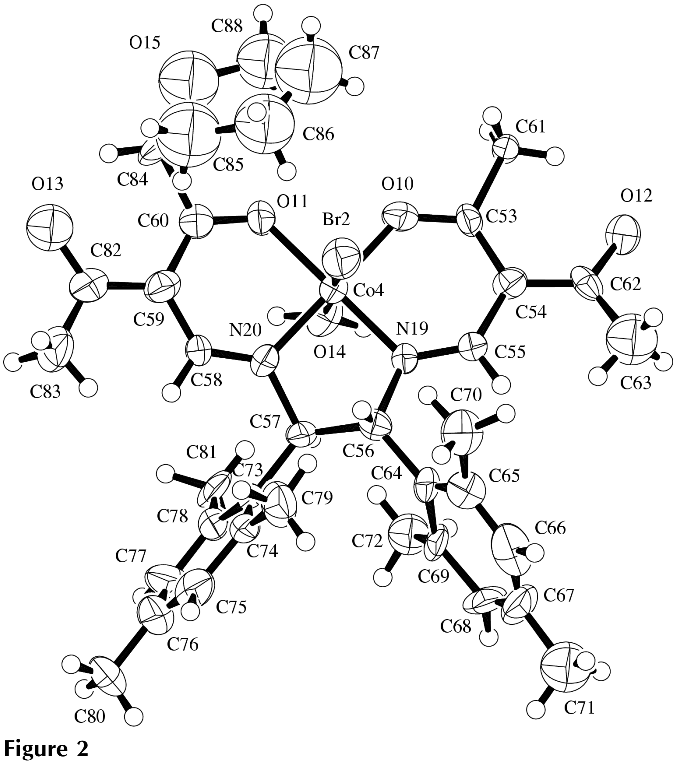


**Figure 2**
The structure of the complex involving the Co4 atom in (I) with displacement ellipsoids at the 50% probability level. A neighboring THF molecule is also shown.

## Experimental

The chiral tetradentate ligand (−)-*L* {*L* = 3,3′-[1,2-bis(2,4,6-trimethylphenyl)ethane-1,2-diylbis(nitrilomethylidyne)]bis(pentane-2,4-dione)} was derived from optically pure (+)-1,2-bis(2,4,6-trimethylphenyl)ethylenediamine prepared according to the literature (Roskamp & Pedersen, 1987; Zhang, 1991). Optical resolution of the racemic diamine with (−)-mandelic acid led to the optically pure (+)-diamine. The specific rotation of *L* and its original diamine, $[\alpha]_D$ at 300 K, are −186° (*c* = 1.02, $CHCl_3$) and +200 ° (*c* = 1.19, $CH_2Cl_2$), respectively. Complex (I) was synthesized according to Yamada *et al.* (1999). To a solution of (−)-*L* in methanol were added aqueous solutions of NaOH and $CoCl_2\cdot6H_2O$ at 323 K under nitrogen bubbling. The $Co^{II}(L)$ complex precipitated from the red–violet solution as an orange solid and was oxidized to the $Co^{III}Br(L)$ complex by adding bromine in $CH_2Cl_2$ under a nitrogen atmosphere. Crystals of (I) were grown from a THF solution by diffusion of a small amount of hexane. The crystal specimen was sealed in a capillary to avoid efflorescence. The specific rotation $[\alpha]_D$ of the title Co complex at 300 K is −1440° (*c* = 0.022, THF).

### *Crystal data*

$[CoBr(C_{32}H_{38}N_2O_4)(H_2O)]\cdot C_4H_8O$
$M_r = 743.62$
Monoclinic, $P2_1$
$a = 13.667$ (2) Å
$b = 15.046$ (2) Å
$c = 17.764$ (2) Å
$\beta = 100.32$ (1)°
$V = 3593.8$ (8) Å$^3$
$Z = 4$

$D_x = 1.374$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 14.6$–15.0°
$\mu = 1.64$ mm$^{-1}$
$T = 297$ K
Plate, brown
0.5 × 0.3 × 0.1 mm

### *Data collection*

Rigaku AFC-7*R* diffractometer
$\theta$–$2\theta$ scans
Absorption correction: by integration (Coppens *et al.*, 1965)
$T_{\min} = 0.619$, $T_{\max} = 0.854$
12 278 measured reflections
11 744 independent reflections
6371 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.046$
$\theta_{\max} = 27.5°$
$h = 0 \rightarrow 18$
$k = -14 \rightarrow 20$
$l = -23 \rightarrow 23$
3 standard reflections every 150 reflections intensity decay: 1.7%

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.186$
$S = 1.04$
11 744 reflections
749 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F_o^2) + (0.0754P)^2 + 8.5404P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.020$
$\Delta\rho_{\max} = 0.70$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.60$ e Å$^{-3}$
Absolute structure: Flack (1983), 3169 Friedel pairs
Flack parameter = 0.04 (2)

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Br1—Co3 | 2.345 (2) | Co3—N18 | 1.88 (1) |
| Br2—Co4 | 2.359 (3) | Co4—O10 | 1.89 (1) |
| Co3—O5 | 1.91 (1) | Co4—O11 | 1.89 (1) |
| Co3—O6 | 1.89 (1) | Co4—O14 | 1.997 (9) |
| Co3—O9 | 2.007 (8) | Co4—N19 | 1.88 (1) |
| Co3—N17 | 1.85 (1) | Co4—N20 | 1.87 (1) |
| | | | |
| Br1—Co3—O9 | 178.6 (4) | Br2—Co4—O14 | 178.6 (4) |
| | | | |
| N17—C24—C25—N18 | −38 (1) | N19—C56—C57—N20 | −51 (1) |

*Acta Cryst.* (2001). E**57**, m124–m126 Ohba *et al.* • $[CoBr(C_{32}H_{38}N_2O_4)(H_2O)]\cdot C_4H_8O$ **m125**

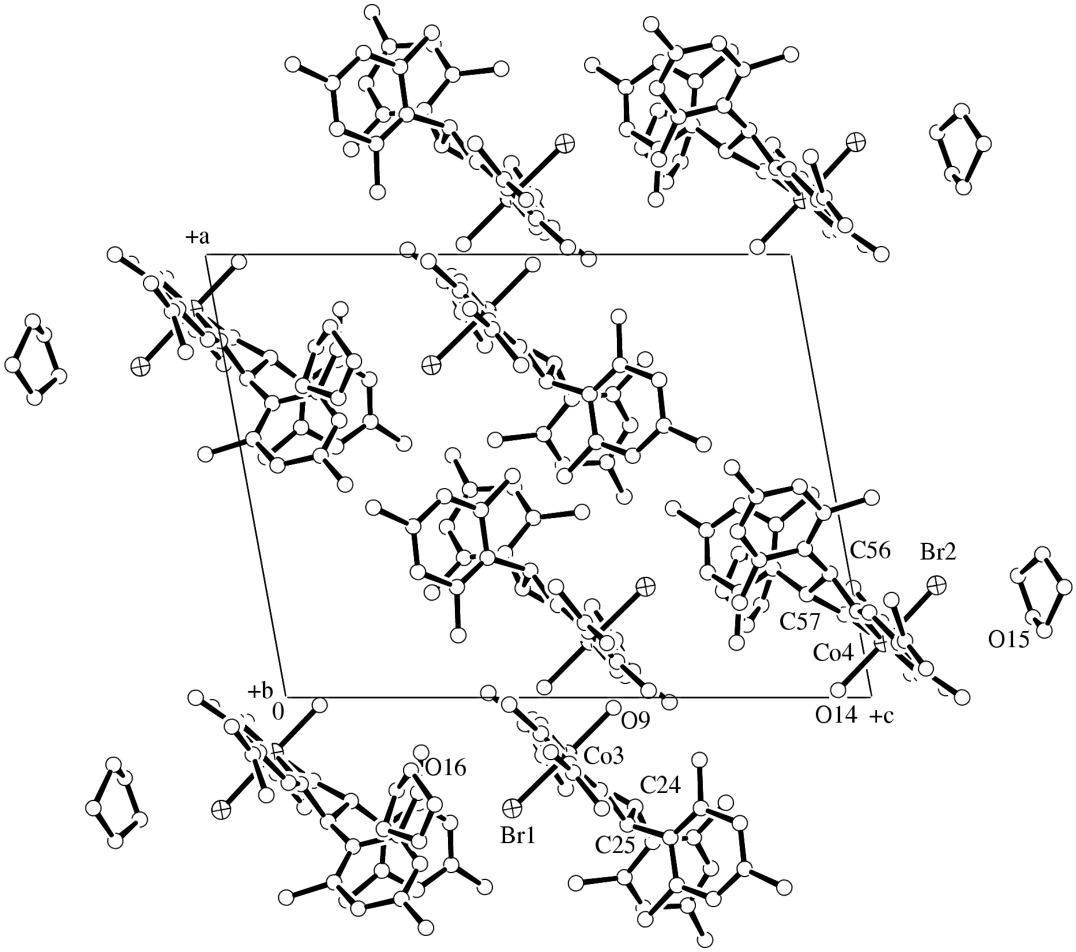


**Figure 3**
The crystal structure of (I) projected along *b*. C24, C25, C56 and C57 are the asymmetric C atoms in the *R* configuration.

**Table 2**
Hydrogen-bonding and short contact geometry (Å, °).

| $D-\mathrm{H}\cdots A$ | $D-\mathrm{H}$ | $\mathrm{H}\cdots A$ | $D\cdots A$ | $D-\mathrm{H}\cdots A$ |
|---|---|---|---|---|
| O9—H9*A*···O7$^{i}$ | 0.95 | 1.94 | 2.69 (2) | 135 |
| O9—H9*B*···O8$^{ii}$ | 0.96 | 2.56 | 2.74 (2) | 91 |
| O14—H14*A*···O12$^{iii}$ | 0.95 | 1.73 | 2.67 (2) | 169 |
| O14—H14*B*···O13$^{iv}$ | 0.96 | 1.97 | 2.73 (2) | 134 |
| C40—H40*A*···N17 | 0.94 | 2.48 | 3.15 (2) | 128 |
| C47—H47*B*···N18 | 0.95 | 2.45 | 3.09 (2) | 125 |
| C29—H29*A*···O7 | 0.96 | 2.11 | 2.82 (2) | 130 |
| C52—H52*C*···O8 | 0.94 | 2.07 | 2.78 (2) | 132 |
| C61—H61*A*···O12 | 0.94 | 1.91 | 2.69 (2) | 139 |
| C84—H84*C*···O13 | 0.96 | 1.89 | 2.70 (2) | 139 |

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

Friedel pairs were measured for the reflections with $\theta < 20°$. The positional parameters of the aqua H atoms were calculated geometrically (assuming $sp^2$ hybridization) based on the corresponding peaks on difference syntheses. The other H-atom positional parameters were also calculated and fixed with $U_{\rm iso}(\mathrm{H}) = 1.2U_{\rm eq}$(parent atom). The non-H atoms of THF molecules (the O15—O16 and C85—C92 atoms) were refined isotropically with restraints of C—C = 1.54 Å (s.u. 0.001 Å) and C—O = 1.43 Å (s.u. 0.001 Å). The O8, O13, C31, C63, C71 and C72 atoms were refined isotropically to avoid non-positive definite parameters or a large max/min ratio (more than 4) of the ADP.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976).

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**m126** Ohba *et al.* • [CoBr($C_{32}H_{38}N_2O_4$)($H_2O$)]·$C_4H_8O$ *Acta Cryst.* (2001). E**57**, m124–m126