

RefinementRefinement on F $R = 0.048$ $wR = 0.052$ $S = 1.94$

8682 reflections

847 parameters

H atoms not refined

Weighting scheme based

on measured s.u.'s;

$$w = 4F^2/\sigma^2(F^2)$$

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

$$\Delta\rho_{\max} = 0.69 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.71 \text{ e } \text{\AA}^{-3}$$

Extinction correction: none

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)Molecular Structure Corporation (1992). *TEXSAN. Single Crystal Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.Steward, O. W., McAfee, R. C., Chang, S.-C., Piskor, S. R., Schreiber, W. J., Jury, C. F., Taylor, C. E., Pletcher, J. F. & Chen, S.-C. (1986). *Inorg. Chem.* **25**, 771–777.*Acta Cryst.* (1998). **C54**, 1083–1085Table 1. Selected geometric parameters (\AA , $^\circ$)

Mn1—O1	2.102 (2)	O3—C3	1.266 (4)
Mn1—O3	2.228 (2)	O4—C3	1.245 (4)
Mn1—O5	2.226 (2)	O5—C5	1.267 (4)
Mn1—O8'	2.065 (2)	O6—C5	1.241 (4)
Mn2—O2	2.100 (3)	O7—C7	1.246 (4)
Mn2—O7	2.127 (2)	O8—C7	1.233 (4)
Mn2—O10	2.210 (3)	C1—C2	1.579 (4)
Mn2—O11	2.174 (3)	C3—C4	1.564 (4)
Mn2—O12	2.189 (3)	C5—C6	1.554 (4)
O1—C1	1.261 (4)	C7—C8	1.589 (4)
O2—C1	1.228 (4)		
O1—Mn1—O3	95.84 (9)	O10—Mn2—O11	88.4 (1)
O1—Mn1—O5	120.77 (9)	O10—Mn2—O12	170.2 (1)
O1—Mn1—O8'	98.3 (1)	O11—Mn2—O12	84.6 (1)
O3—Mn1—O5	132.51 (9)	Mn1—O1—C1	130.5 (2)
O3—Mn1—O8'	97.73 (9)	Mn2—O2—C1	167.5 (3)
O5—Mn1—O8'	104.9 (1)	Mn1—O3—C3	92.9 (2)
O2—Mn2—O7	97.5 (1)	Mn1—O5—C5	95.1 (2)
O2—Mn2—O10	88.22 (10)	Mn2—O7—C7	136.0 (2)
O2—Mn2—O11	165.8 (1)	Mn1 ⁱⁱ —O8—C7	168.5 (3)
O2—Mn2—O12	97.0 (1)	O1—C1—O2	123.7 (3)
O7—Mn2—O10	104.77 (10)	O3—C3—O4	121.0 (3)
O7—Mn2—O11	96.7 (1)	O5—C5—O6	118.6 (3)
O7—Mn2—O12	82.90 (10)	O7—C7—O8	124.4 (3)

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

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1373). Services for accessing these data are described at the back of the journal.

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Absolute Configuration of (+)₅₈₉-(4,4'-Dimethoxy-2,2'-bipyridine 1,1'-dioxide-O,O')bis(ethylenediamine-N,N')cobalt(III) Triperchlorate

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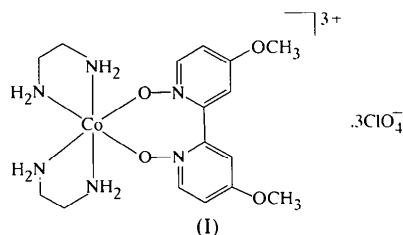
Abstract

The complex ion of the title molecule, (+)₅₈₉-[Co(C₂H₈N₂)₂(C₁₂H₁₂N₂O₄)](ClO₄)₃, has twofold symmetry and the absolute configuration is Λ . The seven-membered chelate ring of the 4,4'-dimethoxy-2,2'-bipyridine 1,1'-dioxide ligand adopts a δ chiral skew conformation, which forms a *lel* structure in the complex ion. The dihedral angle between the two pyridine rings is 61.2 (2)°, and the O—Co—O bite angle is 91.3 (2)°. The ethylenediamine chelates take a δ -*gauche* conformation in the complex ion.

Comment

2,2'-Bipyridine 1,1'-dioxide (bpdo) forms a skewed seven-membered chelate ring with a metal ion (Al-Karaghoulis *et al.*, 1978; Alcock & Roberts, 1987; Koman *et al.*, 1991; Baran *et al.*, 1991). Since the skew conformation produces a pair of enantiomers, δ and λ , a tris(bpdo) complex has four possible racemic pairs of diastereomers. Recently, it was reported that a tris[4,4'-(MeO)₂bpdo]chromium(III) complex gave two of four possible diastereomers, where 4,4'-(MeO)₂bpdo is the 4,4'-dimethoxy derivative of bpdo (Kanno *et al.*, 1996). However, the molecular structures of optically active complexes with bpdo have not been reported. A new bis(en)cobalt(III) complex with 4,4'-(MeO)₂bpdo was thus prepared, where en is ethylenediamine. The complex, (I), was found to form only one diastereomer in solution (¹³C NMR spectrum), though the complex has two

possible racemic pairs of diastereomers, *lel* [$\Delta(\lambda), \Lambda(\delta)$] and *ob* [$\Delta(\delta), \Lambda(\lambda)$], where the symbols *lel* and *ob* denote the structures of diastereomers with the skewed 4,4'-(MeO)₂bpdo chelate ring viewed along the pseudo-C₃ symmetry axis of the complex ion. The racemic pair was completely resolved by column chromatography. The present work was undertaken in order to determine the absolute configuration and the structure of the complex, which gives a positive rotation at 589 nm.



Since the central metal ion in the title complex lies on a crystallographic twofold axis, the complex ion, (+)₅₈₉-[Co{4,4'-(MeO)₂bpdo}(en)₂]³⁺, has twofold symmetry. The absolute configuration of the complex was designated as Λ by the absolute structure determination using all Bijvoet pairs of reflections, as shown in Fig. 1. The 4,4'-(MeO)₂bpdo chelate ring takes a δ skew conformation. Thus, the complex forms only a *lel* isomer stereoselectively with respect to the 4,4'-(MeO)₂bpdo ligand. The selective formation of a *lel* isomer has also been reported for [Cr(bpdo)(en)₂]³⁺ (Kanno *et al.*, 1979) and [Co(bpdo)(en)₂]³⁺ (Kanno *et al.*, 1997). The dihedral angle between the two pyridine rings in the 4,4'-(MeO)₂bpdo ligand is 61.2 (2)°, which is close to those in the bpdo complexes reported previously (Al-Karaghoulis *et al.*, 1978; Alcock & Roberts, 1987; Koman *et al.*, 1991; Baran *et al.*, 1991). The Co^{III} atom is in an octahedral environment formed by two O atoms of the 4,4'-(MeO)₂bpdo ligand and four N atoms of the two ethylenediamine ligands. The Co—O bond distance [1.910 (3) Å] is shorter than the La—O distance (2.506 Å) in [La(bpdo)₄](ClO₄)₃ (Al-Karaghoulis *et al.*, 1978), which is attributable to the difference in ionic radius of the central metal ions. The δ -*gauche* conformation of the ethylenediamine chelate ring in the present complex is the same as that in (+)₅₈₉-[Co(en)₃]Cl₃ (Iwata *et al.*, 1969). The Co—N bond distances [1.976 (4) and 1.953 (4) Å] and the N—Co—N angle [85.6 (2)°] are in good agreement with the corresponding ones in [Co(en)₃]Cl₃ [1.978 Å and 85.3°, respectively]. There are six perchlorate ions in the unit cell, and two of these are located in special positions with twofold symmetry. Although the displacement parameters of the perchlorate ions located in general positions were normal, those of the O atoms attached to the Cl atoms in the special positions were abnormally large, which seems to indicate disorder of the perchlorate ions occupying the special positions.

The maximum residual electron density, $\Delta\rho_{\max}$, is also located around the Cl atom at the special position. Further refinement was not carried out. There are no abnormally short distances between the complexes and the counterions.

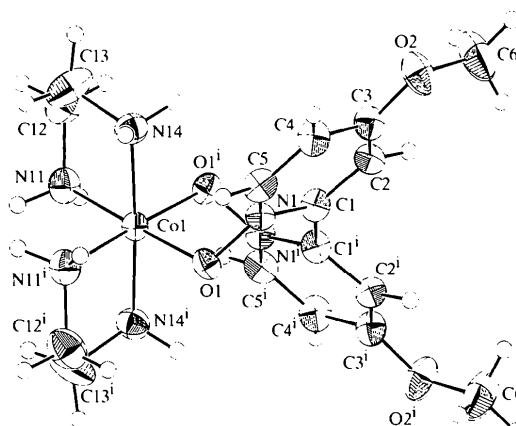


Fig. 1. ORTEP drawing (Johnson, 1965) of (+)₅₈₉-[Co{4,4'-(MeO)₂bpdo}(en)₂]³⁺ with the atomic numbering scheme. Displacement ellipsoids of non-H atoms are shown at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

Experimental

The title complex, (I), was prepared from *cis*-[CoCl₂(en)₂]Cl and 4,4'-(MeO)₂bpdo by a method similar to that used for the preparation of [Co(bpdo)(en)₂](ClO₄)₃ (Kanno *et al.*, 1997). The complex was completely resolved into a pair of enantiomers by SP-Sephadex C-25 column chromatography using an eluent of Na₂[Sb₂{(+)₅₈₉-tartrate}₂]. The (+)₅₈₉-isomer was eluted faster from the column. Purple crystals of the optically active perchlorate were obtained by recrystallization from a dilute perchloric acid solution.

Crystal data

[Co(C₂H₈N₂)₂(C₁₂H₁₂N₂O₄)](ClO₄)₃

M_r = 725.7

Orthorhombic

*P*2₁2₁

a = 11.280 (3) Å

b = 13.417 (2) Å

c = 8.986 (2) Å

V = 1360.0 (5) Å³

Z = 2

D_x = 1.772 Mg m⁻³

D_m = 1.80 Mg m⁻³

D_m measured by flotation in a mixture of chloroform and 1,2-dibromoethane

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 22 reflections

θ = 15.6–17.5°

μ = 1.012 mm⁻¹

T = 298 K

Block

0.35 × 0.28 × 0.18 mm

Purple

Data collection

MacScience MXC3 diffractometer

3180 reflections with *I* > 2σ(*I*)

2 θ / ω scans
 Absorption correction:
 ψ scan (North *et al.*,
 1968)
 $T_{\min} = 0.749$, $T_{\max} = 0.833$
 3618 measured reflections
 3618 independent reflections

$\theta_{\max} = 26.47^\circ$
 $h = -14 \rightarrow 14$
 $k = 0 \rightarrow 17$
 $l = 0 \rightarrow 11$
 3 standard reflections
 every 100 reflections
 intensity decay: <1%

Refinement

Refinement on F
 $R = 0.056$
 $wR = 0.070$
 $S = 1.433$
 3180 reflections
 192 parameters
 H atoms not refined
 $w = 1/[\sigma^2(F) + 0.005F^2]$
 $(\Delta/\sigma)_{\max} = 0.0029$
 $\Delta\rho_{\max} = 1.11 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.52 \text{ e } \text{Å}^{-3}$
 Extinction correction: none

Scattering factors from
*International Tables for
 Crystallography* (Vol. C)
 Absolute structure: all
 Bijvoet pairs of reflections
 were measured and used
 for determination of the
 absolute structure; the
 final absolute structure is
 the one which converged
 the Rogers parameter, η ,
 to 1.01 (6)

Table 1. Selected geometric parameters (Å , $^\circ$)

Co1—O1	1.910 (3)	C2—C3	1.408 (6)
Co1—N11	1.976 (4)	C3—C4	1.401 (6)
Co1—N14	1.953 (4)	C3—O2	1.337 (6)
O1—N1	1.365 (4)	C4—C5	1.364 (6)
N1—C1	1.342 (5)	O2—C6	1.456 (7)
N1—C5	1.361 (5)	N11—C12	1.492 (7)
C1—C1'	1.478 (5)	C12—C13	1.461 (8)
C1—C2	1.381 (6)	C13—N14	1.484 (7)
O1—Co1—O1'	91.3 (2)	N1—C1—C2	120.8 (4)
O1—Co1—N11	177.1 (2)	C1'—C1—C2	120.3 (4)
O1—Co1—N11'	85.8 (2)	C1—C2—C3	118.5 (4)
O1—Co1—N14	94.6 (2)	C2—C3—C4	119.4 (4)
O1—Co1—N14'	87.6 (2)	C2—C3—O2	124.0 (4)
N11—Co1—N11'	97.1 (2)	C4—C3—O2	116.7 (4)
N11—Co1—N14	85.6 (2)	C3—C4—C5	119.3 (4)
N11—Co1—N14'	92.3 (2)	N1—C5—C4	120.5 (4)
N14—Co1—N14'	176.9 (2)	C3—O2—C6	118.3 (4)
Co1—O1—N1	115.8 (3)	Co1—N11—C12	107.6 (3)
O1—N1—C1	119.6 (3)	N11—C12—C13	106.3 (5)
O1—N1—C5	118.8 (3)	C12—C13—N14	107.9 (5)
C1—N1—C5	121.4 (4)	Co1—N14—C13	108.1 (3)
N1—C1—C1'	118.9 (4)		

Symmetry code: (i) $x, -y, -z$.

The title structure was solved by direct methods and refined by full-matrix least-squares calculations using *CRYSTAN-GM* (Gilmore & Brown, 1988). H atoms were placed in geometrically idealized positions, with distances of 0.96 Å, and the equivalent isotropic displacement parameters were fixed at 0.06 Å^{-2} .

Data collection: *MXC Operation Manual* (MacScience Co. Ltd, 1989). Cell refinement: *MXC Operation Manual*. Data reduction: *CRYSTAN-GM*. Program(s) used to solve structure: *CRYSTAN-GM*. Program(s) used to refine structure: *CRYSTAN-GM*. Molecular graphics: *CRYSTAN-GM*. Software used to prepare material for publication: *CRYSTAN-GM*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1050). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). **C54**, 1085–1087

Carbonyl(1,3-diphenyl-1,3-propanedionato-*O,O'*)(4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-*P*)rhodium(I)

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Abstract

The bicyclic phosphite 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane reacts in a 1:1 molar ratio with dicarbonyl(1,3-diphenyl-1,3-propanedionato-*O,O'*)-rhodium(I) to yield the title compound, $[\text{Rh}(\text{C}_{15}\text{H}_{11}\text{O}_2)(\text{C}_5\text{H}_9\text{O}_3\text{P})(\text{CO})]$, with square-planar geometry about the Rh atom. The Rh—P bond distance is 2.1690 (11) Å.

Comment

The syntheses, structure and reactivity of complexes of the type $[\text{Rh}(\beta\text{-diketonato})(\text{CO})(P)]$, where P = phosphine and/or phosphite, form part of a study mainly focused upon relating the chemical and electrochemical oxidation behaviour of the rhodium centre. In order to manipulate the Lewis basicity of the rhodium centre