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(+)₅₈₉-Λ-Amminebromobis(ethylenediamine-*N,N'*)cobalt(III) Dibromide

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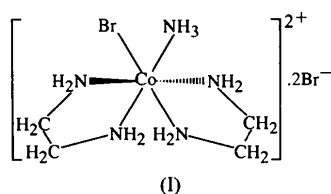
Abstract

The absolute configuration of (+)₅₈₉-*cis*-[CoBr(C₂H₈N₂)₂(NH₃)]²⁺ was confirmed to be Λ. The ethylenediamine five-membered chelate rings take the *lel*₂ conformation. There are N—H···Br intermolecular hydrogen bonds with N···Br distances ranging from 3.267 (9) to 3.715 (8) Å.

Comment

Chiral autocatalysis has been investigated on the reaction of optically inactive [Co(H₂O)₂{(OH)₂Co(en)₂}₂](SO₄)₂ with ammonium bromide in a water suspension to obtain optically active *cis*-[Co(en)₂(NH₃)Br]Br₂ (en is ethylenediamine) (Asakura *et al.*, 1995). The sign of the rotatory power of the product can be controlled by seeding a crystal of the product at the beginning of the reaction and stirring the suspension.

The absolute structure of the (+)₅₈₉ title complex, (I), was determined by the anomalous scattering technique to be Λ, which is in accord with the work on (+)₅₈₉-Λ-*cis*-[Co(en)₂(NH₃)Br]S₄O₆ by Bernal, Cetrullo & Jackson (1993*a*). The absolute configuration of (+)₅₈₉-Λ-*cis*-[Co(en)₂(NH₃)Cl]²⁺ was also determined for the (+)-3-bromocamphor-8-sulfonate salt monohydrate by Kuramoto, Kushi & Yoneda (1978). The structures of the racemates (±)-*cis*-[Co(en)₂(NH₃)Cl]Cl₂ (Harrowfield, Skelton, White & Wilner, 1986) and (±)-*cis*-[Co(en)₂(NH₃)Br]Br₂·2H₂O (Bernal, Cetrullo & Jackson, 1993*b*) have also been reported.



The intermolecular N—H···Br hydrogen bonds form a three-dimensional network. The Br₂ ligand accepts two hydrogen bonds from the adjacent complex cations and the Br₃ and Br₄ anions are each acceptors of five hydrogen bonds. The Co(en)₂ moiety takes the *lel*₂ conformation which has the lowest strain energy. The *lel* ob conformation observed in (+)₅₈₉-Λ-*cis*-[Co(en)₂(NH₃)Br]S₄O₆ may be due to ion-pair formation (Bernal, Cetrullo & Jackson, 1993*a*).

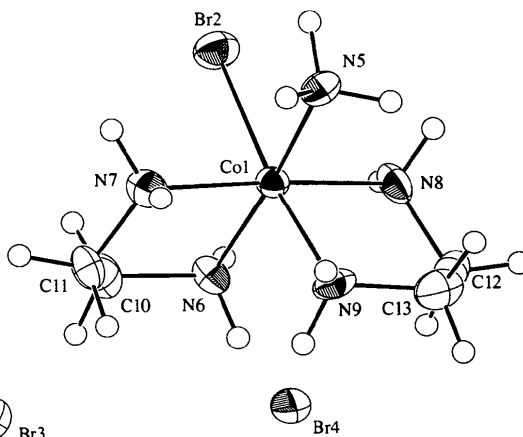


Fig. 1. The molecular structure of (I) with displacement ellipsoids at the 50% probability level. H atoms are represented by circles of radius 0.1 Å.

Experimental

Recrystallization of the (+)₅₈₉ complex was carried out from 5% HBr aqueous solution, in which the racemization does not occur. A large single crystal was cut into several pieces, one of which was shaped into a sphere of 0.6 mm diameter by an Enraf–Nonius spherizer. The rotatory power of (+)₅₈₉ was confirmed using the solution of the remaining part of the single crystal.

Crystal data

[CoBr(C₂H₈N₂)₂(NH₃)]Br₂
M_r = 435.87
 Orthorhombic
*P*2₁2₁
a = 9.339 (2) Å
b = 18.136 (3) Å
c = 7.615 (2) Å
V = 1289.8 (5) Å³
Z = 4
D_x = 2.245 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 14.1–15.0°
 μ = 10.60 mm⁻¹
T = 294 K
 Sphere
 0.30 mm (radius)
 Black

Data collection

Rigaku AFC-5 diffractometer
 θ–2θ scans
 Absorption correction: spherical
T_{min} = 0.023, *T_{max}* = 0.044

1341 reflections with |*F_o*| > 3σ(|*F_o*|)
 θ_{max} = 27.5°
h = 0 → 12
k = 0 → 24
l = 0 → 10

1718 measured reflections	3 standard reflections
1718 independent reflections	every 100 reflections
	intensity decay: 2.6%
Refinement	
Refinement on F	$w = 1/[\sigma^2(F) + 0.000225F^2]$
$R = 0.0448$	$(\Delta/\sigma)_{\max} = 0.015$
$wR = 0.0324$	$\Delta\rho_{\max} = 0.97 \text{ e } \text{\AA}^{-3}$
$S = 1.48$	$\Delta\rho_{\min} = -0.99 \text{ e } \text{\AA}^{-3}$
1341 reflections	Extinction correction: none
135 parameters	Scattering factors from <i>International Tables for X-ray Crystallography</i> (Vol. IV)
Only H-atom U 's refined	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Co1	0.5201 (1)	0.84488 (7)	0.8418 (2)	0.0214 (4)
Br2	0.5430 (1)	0.77576 (6)	1.1102 (2)	0.0359 (4)
Br3	0.2877 (1)	1.15424 (7)	0.9507 (2)	0.0494 (4)
Br4	0.5984 (1)	1.07330 (6)	0.6271 (2)	0.0388 (4)
N5	0.4519 (9)	0.7548 (4)	0.7220 (12)	0.028 (3)
N6	0.5676 (8)	0.9379 (4)	0.9672 (12)	0.024 (3)
N7	0.3191 (8)	0.8717 (4)	0.8905 (15)	0.035 (3)
N8	0.7225 (9)	0.8250 (4)	0.7958 (13)	0.031 (3)
N9	0.5217 (9)	0.8954 (4)	0.6124 (11)	0.030 (3)
C10	0.4385 (12)	0.9624 (6)	1.0671 (16)	0.041 (4)
C11	0.3100 (11)	0.9478 (6)	0.9555 (17)	0.037 (4)
C12	0.7740 (11)	0.8734 (6)	0.6507 (15)	0.035 (4)
C13	0.6530 (13)	0.8765 (6)	0.5188 (15)	0.039 (4)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Co1—Br2	2.407 (2)	N6—C10	1.494 (14)
Co1—N5	1.976 (9)	N7—C11	1.468 (14)
Co1—N6	1.988 (9)	N8—C12	1.491 (15)
Co1—N7	1.974 (8)	N9—C13	1.459 (15)
Co1—N8	1.956 (9)	C10—C11	1.495 (16)
Co1—N9	1.972 (9)	C12—C13	1.514 (17)
Br2—Co1—N9	173.3 (3)	N7—Co1—N8	176.3 (4)
N5—Co1—N6	174.1 (4)	N8—Co1—N9	85.4 (4)
N6—Co1—N7	85.0 (4)		

The U_{iso} parameters of the H7A and H9A atoms were fixed to avoid unreasonable values. The enantiomeric crystal structure gave $R = 0.0547$ and $wR = 0.0413$, which are significantly greater than those of the present structure.

Structure analysis was carried out using *CRYSTAN-GM* software (Edwards, Gilmore, Mackay & Stewart, 1995) on a SUN SPARC10 workstation.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1130). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Chelation of 2,6-Bis(hydroxymethyl)pyridine in *cis*-Dichloro(triphenylphosphine-*P*)[2-(oxymethylene-*O*)-6-(hydroxymethyl)pyridine-*N*]oxorhenium(V)–Water (2/1)

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Abstract

The potentially terdentate dianionic ligand pyridine-2,6-bis(methanol) (H_2L) acts as a bidentate monoanionic N, O^- -donor in the title compound, dichloro(oxo)[pyridine-2,6-bis(methanolato)(1-)-*N, O*](triphenylphosphine-*P*)rhenium(V)–water (2/1), $2[\text{ReCl}_2\text{O}\{\text{C}_5\text{H}_3\text{N}(\text{CH}_2\text{O})(\text{CH}_2\text{OH})\}(\text{PPh}_3)] \cdot \text{H}_2\text{O}$. The asymmetric unit contains two monomeric neutral independent and well separated $[\text{ReOCl}_2(\text{HL})(\text{PPh}_3)]$ moieties per water molecule.

Comment

As part of a program to study the formation of oxorhenium(V) complexes containing mixed di- and terdentate N, O^- -donor ligands (Du Preez, Gerber & Kemp, 1992; Gerber, Kemp, Du Preez & Bandoli, 1993; Bandoli, Gerber, Jacobs & Du Preez, 1994), we isolated the title compound, (I), in which the potentially terdentate 2,6-bis(hydroxymethyl)pyridine ligand (H_2L) acts as a bidentate N, O^- -donor.

