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Dibromo[(−)-sparteine-κ^2N,N']zinc(II)

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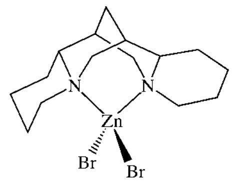
In the title compound, dibromo[(6*R*,7*S*,8*S*,14*S*)-1,3,4,7,7a,8,9,10,11,13,14,14a-dodecahydro-7,14-methano-2*H*,6*H*-dipyrido[1,2-*a*:1′,2′-*e*][1,5]diazocine-κ^2N,N']zinc(II), [$ZnBr_2(C_{15}H_{26}N_2)$], the chiral nitrogen-chelating alkaloid (−)-L-sparteine acts as a bidentate ligand, with two bromide ligands occupying the remaining coordination sites, producing a slightly distorted tetrahedral structure. The dihedral angle between the N—Zn—N and Br—Zn—Br planes is 82.4 (1)°. The distortion of the tetrahedral coordination is demonstrated by the fact that the midpoint of the N···N line does not lie in the Br—Zn—Br plane, but is tilted towards one of the N atoms by 0.164 Å. Similarly, the midpoint of the Br···Br line is tilted towards one of the Br atoms by 0.117 Å.

Comment

Many structural studies of transition metal(II) complexes with (−)-sparteine have been reported (Choi *et al.*, 1995; Kim *et al.*, 2001; Kuroda & Mason, 1979; Lee *et al.*, 2000; Lopez *et al.*, 1998), but, to date, relatively little is known about the structural characteristics of the corresponding Zn^{II} complexes. The crystal structure of a 1:1 adduct of dimethylzinc and (−)-sparteine is a rare example (Motevalli *et al.*, 1993). Like other four-coordinate (−)-sparteine copper(II) complexes, this adduct is monomeric, with pseudo-tetrahedral coordination at the metal center, and the N—Zn—N bond angle of 80.4 (2)° is the smallest among the N—*M*—N angles found in four-coordinate (−)-sparteine metal(II) complexes (Choi *et al.*, 1995; Kim *et al.*, 2001; Kuroda & Mason, 1979; Lee *et al.*, 2000; Lopez *et al.*, 1998). The title Zn^{II} complex, (I), was prepared and its crystal structure determined in order to evaluate the steric effects imposed by a bulky (−)-sparteine ligand and to determine the role of the coordinating anionic ligands and the metal ions in these complexes. It is well known that the crystal-field stabilization effect favors a square-planar coordination geometry for four-coordinate Cu^{II} complexes (Figgis, 1966). However, due to the closed-shell electronic structure of Zn^{II}, the coordination geometry around the Zn^{II} center in (I) will be determined solely by the steric effects of the coordinating ligands, and the dihedral angle between the N—Zn—N and Br—Zn—Br planes is expected to be larger than those observed in other (−)-sparteine copper(II) complexes.



(I)

All four six-membered rings in the (−)-L-sparteine moiety, which is one of three sparteine diastereoisomers, adopt a chair conformation (Fig. 1). The conformation of the coordinated (−)-sparteine ligand in (I) consists of one terminal ring folded down over the metal (*endo*) and a second terminal ring folded back away from the metal (*exo*), identical to the conformation of the free ligand (Boschmann *et al.*, 1974; Wrobleski & Long, 1977). The coordination geometry around the metal center in the known four-coordinate (−)-sparteine metal(II) complexes is distorted tetrahedral (Choi *et al.*, 1995; Kim *et al.*, 2001; Kuroda & Mason, 1979; Lee *et al.*, 2000; Lopez *et al.*, 1998). The dihedral angles between the N—Cu—N and *X*—Cu—*X* (*X* = Cl or O) planes in [$CuCl_2(C_{15}H_{26}N_2)$], [$Cu(NO_3)_2(C_{15}H_{26}N_2)$] and [$Cu(C_2H_3O_2)_2(C_{15}H_{26}N_2)$] are 67.0, 31.7 and 45.8°, respectively (Choi *et al.*, 1995; Lopez *et al.*, 1998; Lee *et al.*, 2000). The dihedral angle between the N1—Zn—N9 and Br1—Zn—Br2 planes in (I) is 82.4 (1)°, so that the geometry around the Zn^{II} center is almost ideal tetrahedral. The smaller dihedral angle of 67.0° reported for the corresponding copper(II) dichloride complex can be visualized as a balance between the crystal-field stabilization effect and the steric effect of (−)-sparteine.

Another parameter associated with the distortion of the tetrahedron is the 'tilt' of the bidentate (−)-sparteine ligand with respect to the Br1—Zn—Br2 plane. The midpoint of the N1···N9 line does not lie on the Br1—Zn—Br2 plane, but is tilted towards atom N1 by 0.164 Å (11.2% of half of the

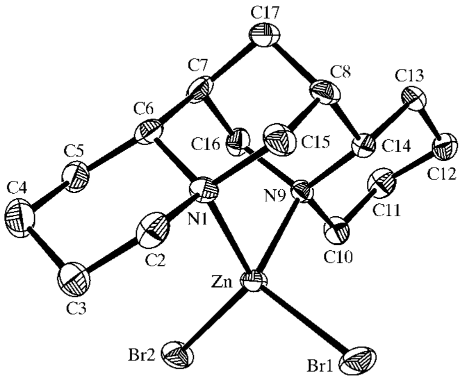


Figure 1
A view of the molecule of (I), showing the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

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N1···N9 distance). Similarly, the midpoint of the Br1···Br2 line is tilted towards atom Br2 by 0.117 Å (5.9% of half of the Br1···Br2 distance). The N1—Zn—Br1 and N9—Zn—Br2 angles are quite similar; however, the N1—Zn—Br2 and N9—Zn—Br1 angles differ by more than 10°. These results clearly indicate that the reduction of the dihedral angles by about 8° from the perfect tetrahedral value of 90° in (I) is caused by intramolecular steric interactions between the (−)-sparteine moiety and the bromide ions coordinated to the Zn^{II} atom.

The Zn^{II}—N bond lengths in (I) (Table 1) are significantly shorter than those found in $[Zn(CH_3)_2(C_{15}H_{26}N_2)]$ [2.222 (5) and 2.256 (6) Å; Motevalli *et al.*, 1993] and, consequently, the N—Zn—N bite angle in (I) is larger than the corresponding bite angle of 80.4 (2)° found in the dimethylzinc(II) complex. This result strongly suggests that the nature of the coordinating anions in (−)-sparteine zinc(II) complexes plays an important role in the ultimate molecular structure of the complexes. The smaller N—Zn—N bite angle and the longer Zn—N bond distances found in $[Zn(CH_3)_2(C_{15}H_{26}N_2)]$ can be attributed to the presence of the coordinating methyl ligand, which is a very strong Lewis base and which has a small C-donor atom. The average Zn—C bond distance [2.012 (8) Å] in $[Zn(CH_3)_2(C_{15}H_{26}N_2)]$ is about 0.35 Å shorter than the average Zn—Br bond distance in (I). Assuming that the steric demands of the methyl group and the bromide anion are similar, the elongation of the Zn—N bond distances in the (−)-sparteine–dimethylzinc(II) complex is probably caused by the reduction in the Lewis acidity of Zn^{II} upon formation of strong Zn—C bonds.

Experimental

The title complex was prepared by the direct reaction of zinc(II) bromide with a stoichiometric amount of (−)-sparteine in an ethanol–triethylorthoformate (5:1 *v*/*v*) solution. The resulting colorless precipitate was filtered off, washed with cold absolute ethanol and dried under vacuum. Single crystals of (I) were obtained by recrystallization at room temperature from a dichloromethane–triethylorthoformate (4:1 *v*/*v*) solution under CCl_4 vapor.

Crystal data

$[ZnBr_2(C_{15}H_{26}N_2)]$
$M_r = 459.57$
Orthorhombic, $P2_12_12_1$
$a = 11.1770\ (14)$ Å
$b = 12.0378\ (18)$ Å
$c = 12.7533\ (9)$ Å
$V = 1715.9\ (4)$ Å^3
$Z = 4$
$D_x = 1.779$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 25 reflections
$\theta = 11.4–12.6°$
$\mu = 6.08$ mm^{-1}
$T = 293\ (2)$ K
Block, colorless
0.40 × 0.33 × 0.30 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled $\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.104$, $T_{max} = 0.161$
4912 measured reflections
3928 independent reflections
2729 reflections with $I > 2\sigma(I)$

$R_{int} = 0.029$
$\theta_{max} = 27.5°$
$h = -14 \rightarrow 14$
$k = -15 \rightarrow 15$
$l = -16 \rightarrow 16$
3 standard reflections
frequency: 300 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.104$
$S = 1.03$
3928 reflections
181 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0474P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.69$ e Å^{-3}
$\Delta\rho_{min} = -0.57$ e Å^{-3}
Absolute structure: Flack (1983), 1689 Friedel pairs
Flack parameter = −0.02 (2)

Table 1
Selected geometric parameters (Å, °).

Zn—N9	2.078 (5)	Zn—Br2	2.3580 (10)
Zn—N1	2.086 (5)	Zn—Br1	2.3628 (10)
N9—Zn—N1	88.9 (2)	N9—Zn—Br1	112.60 (14)
N9—Zn—Br2	107.95 (14)	N1—Zn—Br1	107.12 (13)
N1—Zn—Br2	123.31 (14)	Br2—Zn—Br1	114.25 (4)

The absolute configuration was confirmed crystallographically to agree with that expected for (−)-sparteine. The positional parameters of the H atoms were calculated geometrically (C—H = 0.97–0.98 Å) and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1140). Services for accessing these data are described at the back of the journal.

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