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Dichloro[(6*R*,7*S*,8*S*,14*S*)-(−)-sparteine-κ^2N,N']nickel(II)

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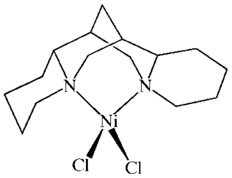
In the title compound, $[NiCl_2(C_{15}H_{26}N_2)]$, the chiral alkaloid (6*R*,7*S*,8*S*,14*S*)-(−)-L-sparteine acts as a bidentate ligand, with two chloride ligands occupying the remaining coordination sites, producing a slightly distorted tetrahedron. The N—Ni—N plane in the title complex is twisted by 81.31 (11)° from the Cl—Ni—Cl plane. Other distortions of the tetrahedron are discussed.

Comment

The majority of four-coordinate Ni^{II} complexes prefer to adopt a square-planar structure as a consequence of the d^8 configuration. In tetrahedral coordination, the occupation of the unique high-energy antibonding $d_{x^2-y^2}$ orbital is unavoidable and so relatively few tetrahedral Ni^{II} complexes are known (Cotton *et al.*, 1999). The tetrahedral Ni^{II} complexes are mainly of the stoichiometric types NiX_4^{2-}, NiX_2L_2 and $Ni(L\text{–}L)_2$, where X is usually a halogen ion, L is a neutral monodentate ligand and $L\text{–}L$ is one of several types of bulky bidentate anion (Ban *et al.*, 1973; Koester & Dunn, 1975; Cruse & Gerloch, 1977).

(−)-Sparteine (sp), a naturally occurring tertiary diamine, has attracted research attention and has been used in medicinal chemistry (Cady *et al.*, 1977), in the asymmetric synthesis of chiral compounds (Kretchmer, 1972; Mason & Peacock, 1973; Beak *et al.*, 1996) and in the preparation of a model compound for the type I copper(II) site in metalloproteins (Kim *et al.*, 2001). The structures of several metal(II) sparteine complexes of type $[MX_2(\mathrm{sp})]$ (M = Co^{II}, Cu^{II} and Zn^{II}, and X = Cl$^-$, Br$^-$ and N_3^-) have been reported, and the metal moieties in these compounds are known, without exception, to have a slightly distorted tetrahedral geometry (Kuroda & Mason, 1979; Lopez *et al.*, 1998; Lee *et al.*, 2000; Kim *et al.*, 2001, 2003; Lee, Kang *et al.*, 2002, 2003; Lee, Kwon *et al.*, 2003). This bidentate ligand contains sufficiently bulky substituents on, and adjacent to, the two N-donor atoms to render the planarity of the $[MX_2(L\text{–}L)]$ molecule sterically impossible, and thus a distorted tetrahedron is generated around the metal centers.

Synthesis of the title compound, (I) (Fig. 1), was prompted by our interest in the preparation of a new paramagnetic and tetrahedral Ni^{II} compound of the type $[\mathrm{Ni}^{II}X_2(L\text{–}L)]$, and our attempt to compare the stability, coordination geometry and bonding parameters of (I) with analogous Co^{II}, Cu^{II} and Zn^{II} (−)-sparteine dichlorides for which the structures are already known (Kuroda & Mason, 1979; Lopez *et al.*, 1998; Lee, Kwon *et al.*, 2003).



(I)

As expected from previous studies (Kuroda & Mason, 1979; Choi *et al.*, 1995; Lopez *et al.*, 1998; Lee *et al.*, 1998, 2000; Kim *et al.*, 2001, 2003; Lee, Kang *et al.*, 2002, 2003; Lee, Kwon *et al.*, 2003), the conformation of the coordinated (−)-sparteine ligand 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) or monoprotonated sparteinium salt (Lee, Shim *et al.*, 2002*b*).

In $[CuCl_2(\mathrm{sp})]$, one consequence of the *endo–exo* configuration is a slight asymmetry in the Cu—N bond lengths; the *endo* ring has a shorter Cu—N bond length [Cu—N1 = 2.003 (3) Å, compared with 2.021 (3) Å for Cu—N9] (Lopez *et al.*, 1998). However, in (I), the two Ni—N bond distances (Table 1) correspond to a more symmetric configuration. The Ni—N bond distances are slightly longer than those in $[CuCl_2(\mathrm{sp})]$ but are shorter than those in $[CoCl_2(\mathrm{sp})]$ [2.040 (7) and 2.068 (8) Å] and $[ZnCl_2(\mathrm{sp})]$ [2.085 (7) and

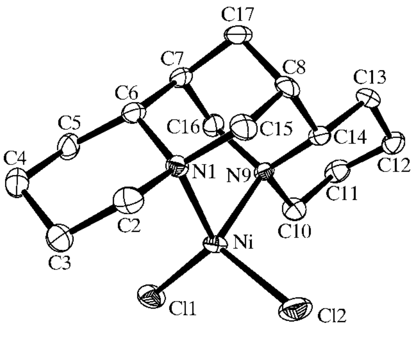


Figure 1
An *ORTEP*-3 (Farrugia, 1997) diagram of (I), showing the atom-numbering scheme and 30% probability ellipsoids. H atoms have been omitted for clarity.

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2.087 (7) Å]. The stability of complexes of the 3*d* metal ions with a given ligand almost invariably follows the order $Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$ (Irving & Williams, 1953). A similar trend is observable in this series of metal(II) sparteine compounds if it is assumed that the stability of the complexes is inversely related to the metal(II)–nitrogen bond distances.

The dihedral angle between the N1—Ni—N9 and Cl1—Ni—Cl2 planes in (I) is 81.31 (11)°, a value which is only ~8.7° less than the perfect tetrahedral angle (90°). The dihedral angles between the N—*M*—N and Cl—*M*—Cl (*M* = Cu^{II} or Zn^{II}) planes in [$CuCl_2$(sp)] and [$ZnCl_2$(sp)] are reported to be 67.0 and 82.2°, respectively (Lopez *et al.*, 1998; Lee, Kang *et al.*, 2003). The dihedral angle in (I) is very close to that of zinc(II) sparteine dichloride but is much larger than that of copper(II) sparteine dichloride. The Zn^{II} atom has a closed-shell electronic structure of d^{10}, and as a result the molecular structure of [$ZnCl_2$(sp)] has to be determined solely by the steric effect. The very similar values in the dihedral angles of the Ni^{II} and Zn^{II} compounds suggest that the electronic effect in the molecular structure of (I) is not as important as that in the analogous Cu^{II} compound, and that the molecular structure is determined by intramolecular steric interactions between the (−)-sparteine ligand and the chloride ions coordinated to the Ni^{II} ion. The smaller dihedral angle of 67.0° reported for [$CuCl_2$(sp)] is a result of the balance of the electronic effect of the d^9 system and the steric effect imposed by a bulky (−)-sparteine ligand (Figgis, 1966).

Another way of looking at the distortion of the tetrahedron is to compare the 'bite angle' and the 'tilt' of the bidentate (−)-sparteine ligand with respect to the Cl—Ni—Cl plane (Lee, Kang *et al.*, 2002, 2003). The mid-point of the N1···N9 line does not lie on the Cl1—Ni—Cl2 plane but is tilted towards atom N1 by 0.193 Å (13.5% of half of the N1···N9 distance). Similarly, the mid-point of the Cl1···Cl2 line is tilted towards atom Cl2 by 0.144 Å (7.4% of half of the Cl1···Cl2 distance). The N1—Ni—Cl1 and N9—Ni—Cl2 angles are similar; however, the N1—Ni—Cl2 and N9—Ni—Cl1 angles differ by more than 10°.

In Ni^{II} complexes, even slight distortion from the perfect tetrahedron reduces the magnetic moment markedly by splitting the orbital degeneracy (Cotton *et al.*, 1999). The room-temperature magnetic moment of (I), estimated from the relation $\mu_{\rm eff} = 2.828(\chi_M \times T)^{1/2}$, is 3.3 BM. This value is much smaller than the value of ~4.2 BM that is usually exhibited by truly tetrahedral Ni^{II} complexes.

Experimental

Complex (I) was prepared by the direct reaction of nickel(II) chloride with a stoichiometric amount of (−)-L-sparteine in an ethanol–triethylorthoformate (5:1 *v*/*v*) solution. The resulting violet precipitate was filtered off, washed with cold absolute ethanol and dried in a vacuum. Single crystals were obtained by recrystallization at room temperature from a dichloromethane–triethylorthoformate (5:1 *v*/*v*) solution. Analysis calculated for $C_{15}H_{26}Cl_2N_2Ni$: C 49.49, H 7.20, N 7.70%; found: C 49.50, H 7.14, N 7.74%.

Crystal data

[$NiCl_2(C_{15}H_{26}N_2)$]
M_r = 363.99
Orthorhombic, $P2_12_12_1$
a = 11.1357 (17) Å
b = 11.8679 (14) Å
c = 12.3278 (19) Å
V = 1629.2 (4) Å^3
Z = 4
D_x = 1.484 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 24 reflections
θ = 11.5–12.6°
μ = 1.51 mm^{-1}
T = 293 (2) K
Block, dark violet
0.30 × 0.30 × 0.26 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled $\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\rm min}$ = 0.612, $T_{\rm max}$ = 0.672
4063 measured reflections
3730 independent reflections
2855 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.037
$\theta_{\rm max}$ = 27.5°
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 16$
3 standard reflections every 400 reflections
intensity decay: 4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.130
S = 1.03
3730 reflections
181 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0655P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.64 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.50 e Å^{-3}
Absolute structure: Flack (1983), 1597 Friedel pairs
Flack parameter = 0.00 (3)

Table 1
Selected geometric parameters (Å, °).

Ni—N1	2.032 (4)	N1—C6	1.498 (6)
Ni—N9	2.027 (4)	N1—C15	1.491 (6)
Ni—Cl1	2.2363 (15)	N9—C10	1.502 (6)
Ni—Cl2	2.2337 (14)	N9—C14	1.506 (6)
N1—C2	1.492 (7)	N9—C16	1.488 (6)
N1—Ni—N9	89.51 (16)	N9—Ni—Cl1	110.35 (12)
N1—Ni—Cl1	103.10 (11)	N9—Ni—Cl2	105.99 (12)
N1—Ni—Cl2	123.85 (12)	Cl1—Ni—Cl2	119.67 (6)

The H atoms of the sparteine ligand were positioned geometrically and constrained to ride on their attached atoms at distances of 0.97–0.98 Å. The $U_{\rm iso}$(H) values were fixed at $1.2U_{\rm eq}$ of the parent atoms.

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: TA1437). Services for accessing these data are described at the back of the journal.

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