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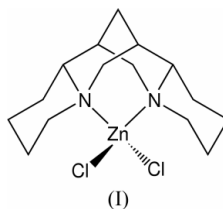
Key indicators

Single-crystal X-ray study
T = 296 K
Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$
R factor = 0.032
wR factor = 0.065
Data-to-parameter ratio = 15.8For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Dichloro[(6*R*,7*S*,8*S*,14*R*)-(–)- α -
isosparteine- $\kappa^2\text{N},\text{N}'$]zinc(II)

The title compound, $[\text{ZnCl}_2(\text{C}_{15}\text{H}_{26}\text{N}_2)]$, was obtained as a by-product during the synthesis of the corresponding complex of the naturally occurring ligand (6*R*,7*S*,8*S*,14*S*)-(–)-sparteine, as a result of impurity of the starting material. The molecule lies on a twofold axis. The geometry around the Zn^{II} ion is highly distorted from tetrahedral, with a dihedral angle between the ZnN_2 and ZnCl_2 planes of $71.58(6)^\circ$.

Comment

Our interest in studying magnetic lattices and their structural and electronic properties, for modeling type 1 blue copper proteins, has led us to prepare a series of sparteine-containing derivatives. A general strategy consists of isolating isostructural Cu^{II} and Zn^{II} complexes; the former is intended for modeling and the latter is used as a magnetic diluting agent, in order to measure accurate spectroscopic data, mainly through ESR and ^1H NMR studies. Numerous derivatives of this kind, including those with naturally occurring (6*R*,7*S*,8*S*,14*S*)-(–)-sparteine, have been reported, with a pseudo-tetrahedral metal ion environment (Mason & Peacock, 1973; Choi *et al.*, 1975; Kuroda & Mason, 1979*a*; Motevalli *et al.*, 1993; Lopez *et al.*, 1998; Gutiérrez *et al.*, 2001; Lee *et al.*, 2002; Alcántara-Flores *et al.*, 2003). In contrast, only a few complexes have been obtained with the diastereoisomers of this alkaloid, namely (6*R*,7*S*,8*S*,14*R*)-(–)- α -isosparteine (Kuroda & Mason, 1979*b*; Kim *et al.*, 2002) and (6*S*,7*S*,8*S*,14*S*)-(–)- β -isosparteine (Childers *et al.*, 1975).



We report here the unexpected synthesis of the title compound, (I), when attempting a direct synthesis of [(–)-sparteine] ZnCl_2 , using metallic zinc as a starting material (see *Experimental*). It is important to mention that the reaction conditions used in the direct synthesis route (Gutiérrez *et al.*, 2001) are totally different from those reported for the synthesis of (–)- α -isosparteine (Okamoto *et al.*, 1982). We assume that no isomerization at C14 is possible in the direct synthesis. Thus, the crystallization of a complex containing (–)- α -isosparteine should rather be attributed to the presence of this diastereoisomer in the (–)-sparteine obtained from Aldrich and used for the synthesis. This company provides (–)-spar-

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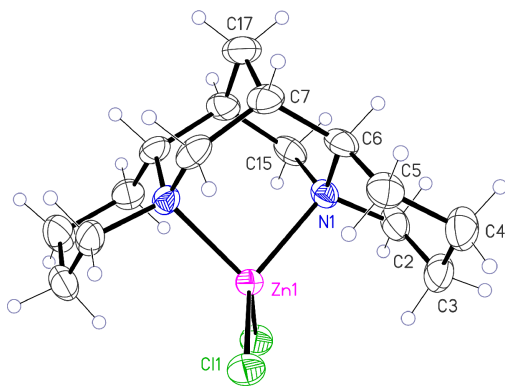


Figure 1
The structure of (I), with displacement ellipsoids at the 30% probability level.

teine with a 99% chemical purity, without specifying what are the expected impurities.

The title compound, (I), is almost isostructural with the Co^{II} complex previously reported with the same ligands (Kuroda & Mason, 1979*b*). The asymmetric unit contains one-half of the molecule ($Z' = \frac{1}{2}$) with the metal center and atom C17 lying on a twofold axis (Wyckoff position $4a$ in space group $P4_32_12$) and the remaining atoms in general positions. Therefore, the whole molecule (Fig. 1 and Table 1) displays exact C_2 symmetry, consistent with the $RSSR$ configuration of the chiral ligand. The $(-)\text{-}\alpha$ -isosparteine shows an all-chair conformation, with the two tertiary N atoms each shared by two six-membered rings, coordinated to Zn^{II} . The coordination of Zn^{II} is completed by two chloride anions. The *endo-endo* configuration for the terminal rings of $(-)\text{-}\alpha$ -isosparteine generates a highly hindered structure, preventing the coordination of two sparteine ligands at the same metal ion, as occurs in a recently reported dinuclear copper-dioxygen complex (Funahashi *et al.*, 2003).

The dihedral angle between the planes $\text{N1}-\text{Zn}-\text{N1}^i$ and $\text{Cl1}-\text{Zn}-\text{Cl1}^i$ [symmetry code: (i) $y, x, -z$] of $71.58(6)^\circ$ is significantly different from that observed for the complex containing natural sparteine (Lee *et al.*, 2003) of 82.2° , reflecting the greater steric hindrance of $(-)\text{-}\alpha$ -isosparteine compared to natural sparteine. This behavior is also observed with other transition metals for which both complexes have been crystallographically characterized: for the Co^{II} -containing complexes, dihedral angles are 70.8° with $(-)\text{-}\alpha$ -isosparteine and 82.2° with natural sparteine (Kuroda & Mason, 1979*b,a*, respectively). With Cu^{II} as metal center and azide as ancillary ligands, the observed dihedral angles are $50.0(2)$ and $55.3(2)^\circ$ (Kim *et al.*, 2002, 2003, respectively). As expected, this angle is increased when Co is replaced by Zn, and this effect is larger for natural sparteine than for $(-)\text{-}\alpha$ -isosparteine.

Numerous compounds including natural sparteine have been reported, in accord with its natural availability and its high versatility for coordinating different ions. Its less constrained structure allowed the synthesis of a Pd^{II} -based complex (Jensen *et al.*, 2001). In this case, the slightly distorted square-planar structure shows a small dihedral angle of 8.9°

between the PdN_2 and PdCl_2 planes. The largest reported value for this dihedral angle is 82.4° , which is found in a Zn^{II} -containing complex (Lee *et al.*, 2002). On substituting the metal center by a transition metal with a very different electronic configuration, such as Fe^{II} (Lorber *et al.*, 2002), the observed dihedral angle of 78.8° remains in the same range. In contrast, for $(-)\text{-}\alpha$ -isosparteine, there are few reports of its coordination compounds (Kuroda & Mason, 1979*b*; Kim *et al.*, 2002). This is due to the lack of a known natural source for this diastereoisomer and to its rigid conformation, limiting its coordinating ability. This structural feature correlates well with the chemical reactivity reported for each diastereoisomer. For instance, it was reported that the doubly shielded stereochemistry of $(-)\text{-}\alpha$ -isosparteine in its CuCl_2 complex produces the slowest hydrolysis process, with respect to the $(-)\text{-}\beta$ -isosparteine complex (fastest) and to the $(-)$ -sparteine complex (intermediate) (Boschmann *et al.*, 1974).

These observations lead to the following conclusions for this kind of compound: (i) small changes in the dihedral angle between the MX_2 ($X = \text{Cl}, \text{Br}$) and MN_2 planes should be correlated with spectroscopic features, such as A_{\parallel} values in ESR (electron spin resonance) spectra and ligand-field transitions (Lee *et al.*, 2003); (ii) in these studies, the purity of samples should be carefully checked, since it is possible to crystallize mixtures of different complexes, depending on the sparteine diastereoisomers present in the starting material; (iii) concerning the type 1 blue copper modeling, it seems that the rigidity observed for the three diastereoisomers of sparteine which stabilize coordination compounds is a natural restriction for the achievement of accurate structural, electronic and magnetic models.

Experimental

The title compound was prepared by a direct synthetic route, using zinc (0.47 mmol), benzoyl chloride (0.47 mmol), 99% pure $(-)$ -sparteine (0.47 mmol) and dimethyl sulfoxide (5 ml). The reaction mixture was stirred at 333 K for 10 h and then filtered. Two different crystalline compounds were collected after 9 d. The title compound was obtained with a very low yield (<1%), and was separated on the basis of its regular crystalline shape, compared to the main product.

Crystal data

$[\text{ZnCl}_2(\text{C}_{15}\text{H}_{26}\text{N}_2)]$
 $M_r = 370.65$
 Tetragonal, $P4_32_12$
 $a = 8.0474(7) \text{ \AA}$
 $c = 25.518(3) \text{ \AA}$
 $V = 1652.6(3) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.490 \text{ Mg m}^{-3}$

$\text{Mo K}\alpha$ radiation
 Cell parameters from 60 reflections
 $\theta = 3.9\text{--}12.4^\circ$
 $\mu = 1.80 \text{ mm}^{-1}$
 $T = 296(1) \text{ K}$
 Prism, colorless
 $0.28 \times 0.28 \times 0.20 \text{ mm}$

Data collection

Bruker *P4* diffractometer
 $2\theta/\omega$ scans
 Absorption correction: ψ scan
 (XSCANS; Siemens, 1996)
 $T_{\min} = 0.597, T_{\max} = 0.697$
 6151 measured reflections
 1467 independent reflections
 1184 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -9 \rightarrow 9$
 $k = -9 \rightarrow 9$
 $l = -30 \rightarrow 30$
 3 standard reflections every 97 reflections
 intensity decay: 1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.065$
 $S = 1.11$
 1467 reflections
 93 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0202P)^2 + 0.647P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.18 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$
 Extinction correction:
SHELXTL-Plus
 Extinction coefficient: 0.0014 (4)
 Absolute structure: Flack (1983),
 535 Friedel pairs
 Flack parameter = 0.02 (5)

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

Zn1–N1	2.093 (2)	N1–C2	1.487 (4)
Zn1–N1 ⁱ	2.093 (2)	N1–C15	1.494 (4)
Zn1–Cl1 ⁱ	2.2359 (9)	N1–C6	1.500 (4)
Zn1–Cl1	2.2359 (9)		
N1–Zn1–N1 ⁱ	87.79 (15)	C2–N1–C6	109.0 (2)
N1–Zn1–Cl1 ⁱ	103.09 (8)	C15–N1–C6	110.0 (3)
N1 ⁱ –Zn1–Cl1 ⁱ	126.02 (7)	C2–N1–Zn1	110.2 (2)
N1–Zn1–Cl1	126.02 (7)	N1–C6–C5	110.0 (3)
N1 ⁱ –Zn1–Cl1	103.09 (8)	N1–C6–C7	110.2 (3)
Cl1 ⁱ –Zn1–Cl1	111.17 (6)	C5–C6–C7	115.2 (3)
C2–N1–C15	108.3 (3)		

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

H atoms were positioned geometrically and treated as riding atoms with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{parent})$. Constrained distances: methine C–H = 0.98 \AA and methylene C–H = 0.97 \AA .

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

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