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Bis(azido-κN)[(6*R*,7*S*,8*S*,14*S*)-(–)-sparteine-$\kappa^2 N,N'$]copper(II)

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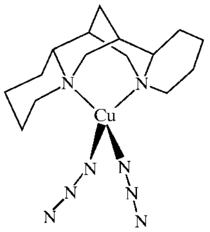
In the title compound, $[Cu(N_3)_2(C_{15}H_{26}N_2)]$, the chiral alkaloid (−)-*l*-sparteine (Sp) acts as a bidentate ligand, with two azide ligands occupying the remaining coordination sites, forming a distorted CuN_4 tetrahedron. The dihedral angle between the $N_{Sp}—Cu—N_{Sp}$ and $N_{azide}—Cu—N_{azide}$ planes is 55.3 (2)°. Principal dimensions include $Cu—N_{Sp}$ = 2.011 (6) and 2.025 (5) Å, and $Cu—N_{azide}$ = 1.939 (6) and 1.934 (7) Å. The mid-point of the $N_{Sp}\cdots N_{Sp}$ line does not lie exactly in the $N_{azide}—Cu—N_{azide}$ plane, but is tilted towards one of the N_{Sp} atoms by 0.026 Å.

Comment

There exist three diastereomers of sparteine, namely (6*R*,7*S*,8*S*,14*S*)-(−)-sparteine, (6*R*,7*S*,8*S*,14*R*)-(−)-α-isosparteine and (6*S*,7*S*,8*S*,14*S*)-(−)-β-isosparteine. These sparteine ligands have attracted research attention and have been intensively utilized in medicinal chemistry (Cady *et al.*, 1977) and the asymmetric synthesis of chiral compounds (Beak *et al.*, 1996; Kretchmer, 1972; Mason & Peacock, 1973). Many crystal structures of copper(II) complexes with neutral alkaloid sparteine diastereomers have been reported (Childers *et al.*, 1975; Choi *et al.*, 1995; Kim *et al.*, 2001, 2002; Lee *et al.*, 1998, 2000; Lopez *et al.*, 1998). The sparteine–copper(II) complexes that have been reported, with one exception (Lee *et al.*, 1998), are four-coordinate and tetrahedrally distorted (Childers *et al.*, 1975; Choi *et al.*, 1995; Kim *et al.*, 2001, 2002; Lee *et al.*, 2000; Lopez *et al.*, 1998) from the ligand-field favorable square-planar geometry (Figgis, 1966). The pseudo-tetrahedral geometry around the Cu^{II} center of these complexes is due to the steric requirements imposed by the bulky sparteine ligand. However, the role of the anionic ligand, *L*, in these complexes, *i.e.* of the type $[CuL_2(C_{15}H_{26}N_2)]$, is also important in the ultimate molecular structure. We determined the crystal structure of the title compound, (I), in order to evaluate the extent of the distortion imposed by the (−)-sparteine ligand compared with that imposed by (−)-α-isosparteine. Actually, the extent of the distortion towards a tetrahedron in (I) was higher than that in the (−)-α-isosparteine complex (Kim *et al.*, 2002).



(I)

In (I), (−)-sparteine acts as a bidentate ligand and two azide ligands occupy the remaining coordination sites, forming a distorted CuN_4 tetrahedron (Fig. 1). The (−)-sparteine ligand consists of one terminal ring folded down over the metal (*endo*) and another terminal ring folded back away from the metal (*exo*). This conformation is identical to that of the free ligand (Boschmann *et al.*, 1974; Wrobleski & Long, 1977). Two azide anions are bound terminally to the Cu^{II} center. The dihedral angle between the N1—Cu—N9 and N18—Cu—N21 planes in (I) is 55.3 (2)°, whereas that in $[Cu(N_3)_2(\alpha\text{-}C_{15}H_{26}N_2)]$ is 50.2 (2)° (Kim *et al.*, 2002). This smaller dihedral angle can be visualized as a balance between the crystal field stabilization effect and the steric effect of (−)-sparteine.

One of the parameters associated with the distortion of the tetrahedron is the 'tilt' of the bidentate sparteine ligand with respect to the N18—Cu—N21 plane. In (I), the mid-point of the N1···N9 line does not lie exactly in the N18—Cu—N21 plane, but is tilted towards atom N1 by 0.026 Å (1.8% of half of the N1···N9 distance). Similarly, the mid-point of the

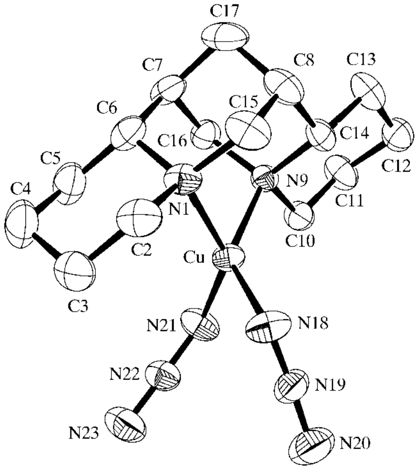


Figure 1
ORTEP-3 (Farrugia, 1997) diagram of (I) showing the atom-numbering scheme and 30% probability ellipsoids. H atoms have been omitted for clarity.

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N18···N21 line is tilted towards atom N18 by 0.045 Å (3.0% of half of the N18···N21 distance). However, in [Cu(N_3)$_2$(α-$C_{15}H_{26}N_2$)], the mid-point of the N1···N9 line is tilted towards atom N1 by 0.103 Å (7.2% of half of the N1···N9 distance) and the mid-point of the N18···N21 line is greatly tilted towards atom N18 by 0.264 Å (17.7% of half of the N18···N21 distance). In (I), the N1—Cu—N18 and N9—Cu—N21 angles differ by 2.1° and, similarly, the N1—Cu—N21 and N9—Cu—N18 angles differ by only 2.2°. These results clearly indicate that the distortion towards a tetrahedron for (I) is quite symmetrically twisted.

The Cu^{II}–azide distances (Table 1) found in (I) agree with the Cu^{II}—N distances found in copper(II) complexes containing a terminally bound azide ligand (Goher *et al.*, 2001; Grove *et al.*, 2001; Kim *et al.*, 2002). The coordinating azide anions are nearly linear, but the (Cu—)N—N bonds are longer than the (Cu—N—)N—N bonds. This result suggests that the covalency in Cu^{II}–azide bonding is appreciable and that the main contribution to the ground-state geometry of the coordinated azide is provided by the two canonical structures $-N{=}N^{+}{=}N^{-} \leftrightarrow -N^{-}-N^{+}{\equiv}N$. This result is quite similar to that found in the [Cu(N_3)$_2$(α-$C_{15}H_{26}N_2$)] complex (Kim *et al.*, 2002).

Experimental

The precursor copper(II) complex [Cu(NO_3)$_2$($C_{15}H_{26}N_2$)] was prepared by mixing an ethanol–triethyl orthoformate (5:1 *v*/*v*) solution of copper(II) nitrate 2.5-hydrate with a stoichiometric amount of (−)-sparteine at room temperature for 2 h. The resulting blue precipitate was filtered off, washed with cold absolute ethanol and then dried in a vacuum. The title complex, (I), was prepared from the substitution reaction of [Cu(NO_3)$_2$($C_{15}H_{26}N_2$)] with a stoichiometric amount of NaN_3 in an ethanol–triethyl orthoformate (5:1 *v*/*v*) solution. The dark-brown precipitate was filtered off, washed with cold absolute ethanol and then dried in a vacuum. Single crystals were obtained by recrystallization at about 278 K from a dichloromethane–triethyl orthoformate (5:1 *v*/*v*) solution. Analysis calculated for $C_{15}H_{26}CuN_8$: C 47.17, H 6.86, N 29.34%; found: C 47.83, H 6.91, N 29.59%.

Crystal data

[Cu(N_3)$_2$($C_{15}H_{26}N_2$)]
$M_r = 381.98$
Orthorhombic, $P2_12_12_1$
$a = 8.2870\ (9)$ Å
$b = 14.061\ (3)$ Å
$c = 14.9685\ (15)$ Å
$V = 1744.2\ (5)$ Å^3
$Z = 4$
$D_x = 1.455$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 40 reflections
$\theta = 5.0$–$12.6°$
$\mu = 1.27$ mm^{-1}
$T = 296\ (2)$ K
Irregular, dark brown
$0.44 \times 0.42 \times 0.32$ mm

Data collection

Bruker *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.882$, $T_{\max} = 0.938$
5383 measured reflections
4004 independent reflections
2061 reflections with $>2\sigma(I)$
$R_{\rm int} = 0.040$
$\theta_{\max} = 27.5°$
$h = -1 \rightarrow 10$
$k = -1 \rightarrow 18$
$l = -19 \rightarrow 19$
3 standard reflections every 97 reflections
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.171$
$S = 1.06$
4004 reflections
218 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0588P)^2 + 0.8943P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.90$ e Å^{-3}
$\Delta\rho_{\min} = -0.52$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0055 (12)
Absolute structure: Flack (1983), 1712 Friedel pairs
Flack parameter = −0.06 (3)

Table 1
Selected geometric parameters (Å, °).

Cu—N1	2.011 (6)	N18—N19	1.175 (8)
Cu—N9	2.025 (5)	N19—N20	1.134 (10)
Cu—N18	1.939 (6)	N21—N22	1.200 (8)
Cu—N21	1.934 (7)	N22—N23	1.140 (9)
N1—Cu—N9	90.2 (2)	N18—Cu—N21	101.1 (3)
N1—Cu—N18	96.8 (3)	Cu—N18—N19	118.7 (6)
N1—Cu—N21	140.6 (3)	N18—N19—N20	172.6 (9)
N9—Cu—N18	138.4 (3)	Cu—N21—N22	120.7 (5)
N9—Cu—N21	98.9 (2)	N21—N22—N23	174.4 (9)

The positional parameters of the H atoms of the sparteine ligand were calculated geometrically and constrained to ride on their attached atoms, with $U_{\rm iso}$ values fixed at 1.2 times the $U_{\rm eq}$ values of their parent atoms. The absolute configuration of (I) was known from the known configuration of the starting material and was confirmed by the value [−0.06 (3)] of the Flack (1983) parameter.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1997); 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: FG1677). Services for accessing these data are described at the back of the journal.

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