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[(6*R*,7*S*,8*S*,14*R*)-(–)-*α*-Isosparteine-κ^2N,N']-bis(nitrito-κ^2O,O')copper(II)

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean *σ*(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.040
wR factor = 0.083
Data-to-parameter ratio = 16.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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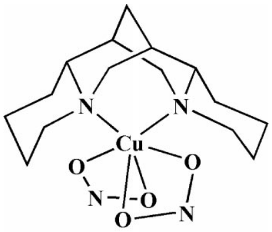
In the title complex, $[Cu(NO_2)_2(\alpha\text{-}C_{15}H_{26}N_2)]$, chiral (6*R*,7*S*,8*S*,14*R*)-(−)-*α*-isosparteine acts as a bidentate ligand, with two nitrite ligands occupying the remaining coordination sites as η^2-chelating groups, producing a pseudo-octahedral coordination complex. The molecule of the title complex possesses a crystallographic twofold axis of rotation along a line through the central C atom of the (−)-*α*-isosparteine ligand and the Cu^{II} atom. However, as a result of the Jahn–Teller effect operating on the d^9 configuration of the copper(II) ion, each nitrite ligand coordinates asymmetrically to the copper(II) centre in a bidentate fashion.

Comment

In recent years, a large number of copper(II) complexes with (−)-sparteine ligands have been reported. The copper(II) (−)-sparteine complexes are usually four-coordinate and tetrahedrally distorted around the approximately square-planar copper(II) ion, as a result of the steric requirements imposed by the bulky chelating (−)-sparteine ligand (Choi *et al.*, 1995, 2004; Kim *et al.*, 2001, 2002, 2003; Lee *et al.*, 2000, 2003; Lopez *et al.*, 1998). The chiral diamine alkaloid, (−)-sparteine, has three diastereomers, namely (−)-L-sparteine ($C_{15}H_{26}N_2$), (−)-*α*-isosparteine ($\alpha\text{-}C_{15}H_{26}N_2$) and (−)-*β*-isosparteine ($\beta\text{-}C_{15}H_{26}N_2$), and has been utilized extensively in medicinal chemistry (Cady *et al.*, 1977), in the asymmetric synthesis of chiral compounds (Beak *et al.*, 1996) and in the preparation of a model compound of the type I copper(II) sites in copper proteins (Kim *et al.*, 2001). Although four-coordinate copper(II) compounds with (−)-L-sparteine, (−)-*α*-isosparteine and (−)-*β*-isosparteine have similar tetrahedrally distorted square-planar structures, the different conformations of three (−)-sparteine diastereomers in these compounds impose different degrees of steric effect on the geometry around the copper(II) centre. For example, in the crystal structure of [(−)-*α*-isosparteine]dinitratocopper(II), $[Cu(NO_3)_2(\alpha\text{-}C_{15}H_{26}N_2)]$ (Choi *et al.*, 2004), the degree of distortion from planarity towards a perfect tetrahedron is not as severe as that found in the corresponding copper(II) (−)-L-



(I)

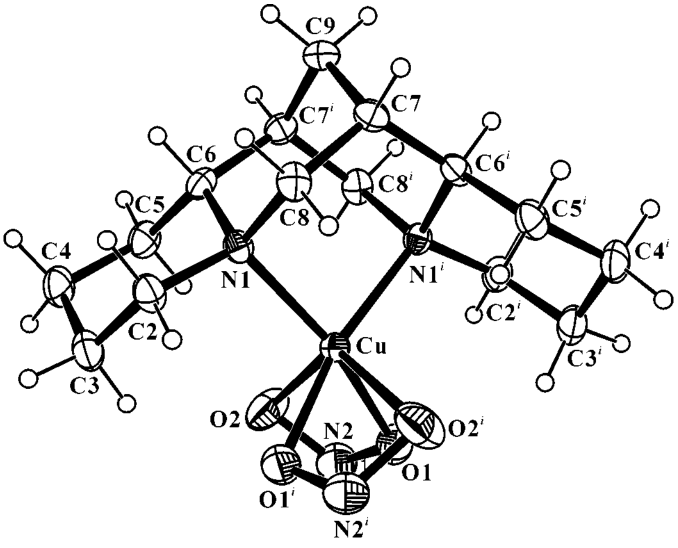


Figure 1
ORTEP-3 (Farrugia, 1997) diagram of (I), showing the atom-numbering scheme and 30% probability displacement ellipsoids. Atom O2 is disordered over two positions (O2 and O2*A*), but atom O2*A* has been omitted for clarity. [Symmetry code: (i) *y*, *x*, −*z*.]

sparteine compound $[Cu(NO_3)_2(C_{15}H_{26}N_2)]$ (Choi *et al.*, 1995).

Whereas many structural studies of four-coordinate copper(II) complexes with (−)-sparteine have been reported, to date, relatively little is known about the structural characteristics of copper(II) (−)-sparteine compounds with a higher coordination number of five or six. The compound $[Cu(NO_2)_2(C_{15}H_{26}N_2)]$ is one of the few copper(II) (−)-sparteine compounds reported to have a five-coordinate square-pyramidal structure, in which (−)-L-sparteine and one nitrite [Cu—O = 2.025 (5) and 2.402 (6) Å] act as bidentate ligands and the other nitrite [Cu—O = 2.002 (5) and 2.637 (5) Å] is bound only through one O atom (Lee *et al.*, 1998).

In this work, we introduced the (−)-α-isosparteine ligand, instead of (−)-L-sparteine, to the $Cu(NO_2)_2$ salt to prepare the title complex, (I) (Fig. 1), and determined its crystal structure. The purpose of this work was to compare the extent of the steric effect imposed by the two different (−)-sparteine diastereomers in copper(II) (−)-sparteine compounds with a coordination number higher than four.

The (−)-α-isosparteine ligand reacts with $Cu(NO_2)_2$ in ethanol to form (I). Two nitrite groups and one (−)-α-isosparteine group in (I) coordinate to the copper(II) ion in a bidentate fashion to produce a six-coordinate and pseudo-octahedral complex, (I). The bonding parameters and coordination geometry of (I) are quite different from those of the previously reported five-coordinate copper(II) (−)-L-sparteine dinitrite $[Cu(NO_2)_2(C_{15}H_{26}N_2)]$ (Lee *et al.*, 1998) complex. One O atom of each nitrite ligand in (I) occupies an axial position, and the other two O atoms of the nitrite ligands constitute, with two N atoms of (−)-α-isosparteine, the equatorial plane.

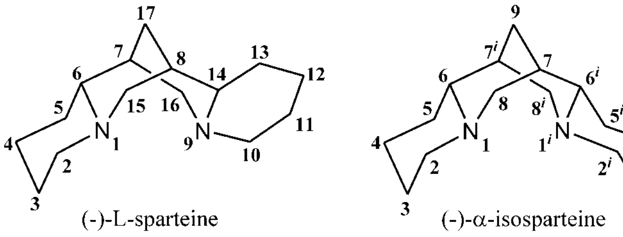


Figure 2
The conformations of (−)-L-sparteine and (−)-α-isosparteine.

The conformation of the coordinated (−)-α-isosparteine in (I) consists of both terminal rings folded down over the metal (*endo–endo*), identical to the conformation of the free ligand (Boschmann *et al.*, 1974; Wrobleski & Long, 1977). The molecule possesses a twofold axis of rotation along a line through atom C9 of (−)-α-isosparteine and the Cu atom. The Cu—O2 and Cu—O2^i distances (see Table 1) are significantly longer than the Cu—O1 and Cu—O1^i distances; each nitrite ion is asymmetrically chelated to copper(II) as a result of the severe Jahn—Teller effect operating on the d^9 configuration of copper(II). The difference in the coordination structures of $[Cu(NO_2)_2(C_{15}H_{26}N_2)]$ and (I) is attributable to the different ring conformations of the two (−)-sparteine diastereomers; the conformation of the coordinated (−)-L-sparteine in $[Cu(NO_2)_2(C_{15}H_{26}N_2)]$ consists of one terminal ring folded down over the Cu atom (*endo*) and a second terminal ring folded back away from the Cu atom (*exo*), whereas both terminal rings in (I) are folded down over the Cu atom (*endo-endo*). The nitrite in the *endo* site can coordinate to the Cu atom in a bidentate fashion, but in the case of the nitrite in the *exo* site, only one O atom can bond to the Cu atom. In the *exo* site of the coordinated (−)-L-sparteine, the H atoms bonded to atom C10 (see Fig. 2) do not allow the access of a second nitrite O atom to the Cu atom [2.637 (5) Å] within a bonding distance. As a result, the copper(II) (−)-L-sparteine compound adopts a five-coordinate square-pyramidal structure, whereas (I) adopts a six-coordinate and pseudo-octahedral structure.

Experimental

(−)-α-Isosparteine (α–$C_{15}H_{26}N_2$) was derived from commercially available (−)-L-sparteine ($C_{15}H_{26}N_2$) according to the literature method (Leonard & Beyler, 1950). The precursor copper(II) complex $[Cu(NO_3)_2(\alpha\text{–}C_{15}H_{26}N_2)]$ was prepared by mixing an ethanol–triethylorthoformate (5:1, *v*/*v*) solution of copper(II) nitrate 2.5-hydrate with a stoichiometric amount of (−)-α-isosparteine at room temperature for 3 h, as has been reported (Choi *et al.*, 2004). The resulting blue precipitate was filtered off, washed with cold absolute ethanol and then dried in a vacuum. The title complex, (I), was prepared by the substitution reaction of $[Cu(NO_3)_2(\alpha\text{–}C_{15}H_{26}N_2)]$ with a stoichiometric amount of $NaNO_2$ in an ethanol–triethylorthoformate (5:1, *v*/*v*) solution. Single crystals of (I) were obtained by recrystallization at 278 K from a dichloromethane–triethylorthoformate (5:1, *v*/*v*) solution under CCl_4 vapour. Analysis calcu-

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lated for $CuC_{15}H_{26}N_4O_4$: C 46.20, H 6.72, N 14.37%; found: C 46.27, H 6.75, N, 14.31%.

Crystal data

$[Cu(NO_2)_2(C_{15}H_{26}N_2)]$
$M_r = 389.94$
Tetragonal, $P4_12_12$
$a = 8.2446$ (5) Å
$c = 25.088$ (4) Å
$V = 1705.3$ (3) Å^3
$Z = 4$
$D_x = 1.519$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 22 reflections
$\theta = 11.4$–14.1°
$\mu = 1.31$ mm^{-1}
$T = 293$ (2) K
Block, dark green
0.30 × 0.23 × 0.23 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled $\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.622$, $T_{\max} = 0.730$
4231 measured reflections
1956 independent reflections
1445 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.061$
$\theta_{\max} = 27.5^\circ$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 32$
3 standard reflections every 400 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.083$
$S = 1.00$
1956 reflections
120 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0297P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.44$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}
Absolute structure: Flack (1983), 737 Friedel pairs
Flack parameter = 0.01 (2)

Table 1

Selected geometric parameters (Å, °).

Cu—N1	2.043 (3)	N2—O1	1.264 (4)
Cu—O1	2.019 (3)	N2—O2	1.30 (5)
Cu—O2	2.50 (3)		
N1—Cu—N1^{i}	89.01 (16)	O1—Cu—O1^{i}	85.23 (18)
N1—Cu—O1	162.78 (9)	O1—Cu—O2	55.0 (11)
N1—Cu—O1^{i}	95.43 (12)	O1—Cu—O2^{i}	90.3 (15)
N1—Cu—O2	107.8 (11)	O2—Cu—O2^{i}	135 (3)
N1—Cu—O2^{i}	104.2 (14)	O1—N2—O2	112.4 (13)

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

H atoms on the (−)-α-isosparteine 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 their parent atoms. Atom O2 was disordered over two positions (O2 and O2*A*). The final occupancy factors for the disordered atom were 0.50 (2) for both sites. The absolute configuration of (I) was known from the configuration of the starting material and was confirmed by the value [0.01 (2)] of the Flack (1983) parameter.

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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