

(-)- α -Isosparteine copper(II) diazide¹**Bun-Joo Kim,^a Yong-Min Lee,^a Eun Hee Kim,^b Sung Kwon Kang^b and Sung-Nak Choi^{a*}**^aDepartment of Chemistry and Chemistry Institute for Functional Materials, Pusan National University, Pusan 609-735, South Korea, and ^bDepartment of Chemistry, Chungnam National University, Daejeon 305-764, South Korea
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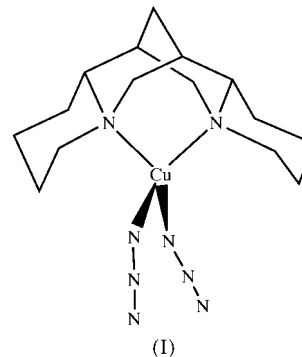
In the title complex, $[\text{Cu}(\text{N}_3)_2(\text{C}_{15}\text{H}_{26}\text{N}_2)]$, the Cu atom is surrounded by the two N atoms of the chelating (-)- α -isosparteine ligand and another two N atoms from the two azide anions, forming a distorted CuN_4 tetrahedron. The two azide anions are terminally bound to the Cu^{II} atom, and the dihedral angle between the $\text{N}_{\text{sparteine}}-\text{Cu}-\text{N}_{\text{sparteine}}$ and $\text{N}_{\text{azide}}-\text{Cu}-\text{N}_{\text{azide}}$ planes is $50.0(2)^\circ$.

Comment

The crystal structures of several copper(II) complexes with the neutral alkaloid (-)-sparteine ($\text{C}_{15}\text{H}_{26}\text{N}_2$) and its diastereomer, (-)- β -isosparteine, have been determined by several workers (Childers *et al.*, 1975; Choi *et al.*, 1995; Kim *et al.*, 2001; Lee *et al.*, 1998, 2000; Lopez *et al.*, 1998). It has been recognized that, with one exception (Lee *et al.*, 1998), sparteine copper(II) complexes are four-coordinate and tetrahedrally distorted (Childers *et al.*, 1975; Choi *et al.*, 1995; Kim *et al.*, 2001; Lee *et al.*, 2000; Lopez *et al.*, 1998). The pseudo-tetrahedral geometry around the Cu^{II} centre of these complexes is due to the steric requirements imposed by the bulky chelating sparteine ligand. However, the anionic ligands *L* in complexes of the type $[\text{Cu}(\text{L})_2(\text{C}_{15}\text{H}_{26}\text{N}_2)]$ are also important in controlling the molecular structures. The X-ray crystallographic structures of sparteine-copper(II) complexes have shown that the average dihedral angles between the L_2Cu and N_2Cu planes in these complexes are in the range $31.7\text{--}87.3^\circ$ (Childers *et al.*, 1975; Choi *et al.*, 1995; Kim *et al.*, 2001; Lee *et al.*, 2000; Lopez *et al.*, 1998). (-)- α -Isosparteine, one of three diastereomers of sparteine, has been reported to react with Cu^{II} halides to produce the corresponding stable complexes (Boschmann *et al.*, 1974), although no structures of (-)- α -isosparteine copper(II) complexes have been reported. The present investigation of (-)- α -isosparteine copper(II) diazide, (I), was also prompted by the possibility of the complex having

¹ Alternative name: bis(azido- κN){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-*N,N'*}copper(II).

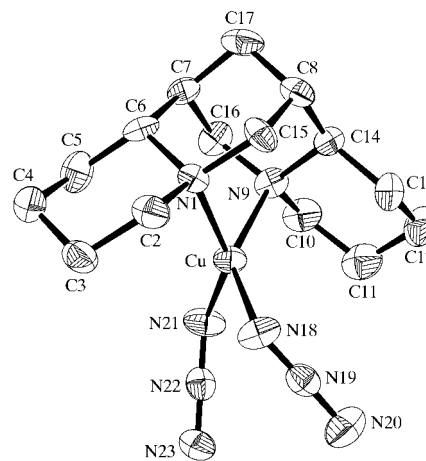
a tetrahedrally distorted $\text{Cu}^{\text{II}}\text{N}_4$ chromophore, and the likely influence of the azide anion on the molecular structure.



In complex (I), the Cu atom is surrounded by two N atoms (N1 and N9) of the chelating (-)- α -isosparteine ligand and by two N atoms (N18 and N21) of the two azide anions, forming a distorted CuN_4 tetrahedron. All four of the six-membered rings in the coordinated (-)- α -isosparteine have a chair conformation. The conformation of the coordinated (-)- α -isosparteine in (I) consists of two terminal rings folded down over the Cu^{II} atom (*endo*), identical to the conformation of the free ligand (Boschmann *et al.*, 1974; Wroblewski & Long, 1977).

The molecule of (I) possesses a nearly perfect twofold axis of rotation along a line through atoms C17 and Cu. Two azide anions are bound terminally to the Cu^{II} atom. The N1-Cu-N9 plane is twisted by $50.0(2)^\circ$ from the N18-Cu-N21 plane.

The Cu^{II} -azide distances (Table 1) found in (I) are similar to the $\text{Cu}^{\text{II}}-\text{N}$ distances found in other copper(II) complexes containing a terminally bound azide ligand (Goher *et al.*, 2001; Grove *et al.*, 2001). $\text{Cu}-\text{N}_{\text{sparteine}}$ bond lengths of approximately 2.0 Å have previously been established for several other sparteine copper(II) complexes (Childers *et al.*, 1975; Choi *et al.*, 1995; Kim *et al.*, 2001; Lee *et al.*, 1998, 2000; Lopez *et al.*, 1998).

**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.

The coordinating azide anions are nearly linear, but the (Cu)—N—N bonds are longer than the (Cu—N)—N—N bonds. This result, together with the non-linear M—N—N angle, suggests that the covalency in copper(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 $\text{—N}=\text{N}^+=\text{N}^- \leftrightarrow \text{—N}^--\text{N}^+=\text{N}$.

Experimental

(-)- α -Isosparteine was derived from commercially available (-)-sparteine according to the literature method of Leonard & Beyler (1950). The precursor copper(II) complex, $[\text{Cu}(\text{NO}_3)_2(\text{C}_{15}\text{H}_{26}\text{N}_2)]$, was prepared in a glove-box by mixing a solution of copper(II) nitrate in ethanol-triethylorthoformate (5:1 v/v) with a stoichiometric amount of (-)- α -isosparteine. The resulting blue precipitate was filtered off, washed with cold absolute ethanol and dried in a vacuum. Complex (I) was prepared by the reaction of $[\text{Cu}(\text{NO}_3)_2(\text{C}_{15}\text{H}_{26}\text{N}_2)]$ with a stoichiometric amount of NaN_3 in an ethanol-triethylorthoformate (5:1 v/v) solution. Single crystals of (I) were obtained by recrystallization at about 278 K from a solution in dichloromethane-triethylorthoformate (5:1 v/v) under carbon tetrachloride vapour.

Crystal data

$[\text{Cu}(\text{N}_3)_2(\text{C}_{15}\text{H}_{26}\text{N}_2)]$	Mo $K\alpha$ radiation
$M_r = 381.98$	Cell parameters from 40 reflections
Orthorhombic, $P2_12_12_1$	$\theta = 6.2\text{--}12.6^\circ$
$a = 8.1517(16) \text{ \AA}$	$\mu = 1.30 \text{ mm}^{-1}$
$b = 13.4955(12) \text{ \AA}$	$T = 296(2) \text{ K}$
$c = 15.486(2) \text{ \AA}$	Block, dark brown
$V = 1703.6(4) \text{ \AA}^3$	$0.38 \times 0.22 \times 0.20 \text{ mm}$
$Z = 4$	
$D_x = 1.489 \text{ Mg m}^{-3}$	

Data collection

Bruker P4 diffractometer	$R_{\text{int}} = 0.023$
$2\theta/\omega$ scans	$\theta_{\text{max}} = 27.5^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = -1 \rightarrow 10$
$T_{\text{min}} = 0.717, T_{\text{max}} = 0.772$	$k = -1 \rightarrow 17$
2930 measured reflections	$l = -1 \rightarrow 20$
2741 independent reflections	3 standard reflections
1431 reflections with $I > 2\sigma(I)$	frequency: 97 min
	intensity decay: none

Table 1

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

Cu—N21	1.931 (5)	N18—N19	1.200 (7)
Cu—N18	1.958 (6)	N19—N20	1.161 (8)
Cu—N1	2.039 (5)	N21—N22	1.186 (8)
Cu—N9	2.050 (5)	N22—N23	1.164 (8)
N21—Cu—N18	99.6 (2)	N1—Cu—N9	89.0 (2)
N21—Cu—N1	146.1 (3)	N19—N18—Cu	118.1 (5)
N18—Cu—N1	96.2 (2)	N20—N19—N18	175.7 (8)
N21—Cu—N9	96.9 (2)	N22—N21—Cu	122.5 (5)
N18—Cu—N9	141.2 (3)	N23—N22—N21	177.0 (7)

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.052$	$\Delta\rho_{\text{max}} = 0.68 \text{ e \AA}^{-3}$
$wR(F^2) = 0.087$	$\Delta\rho_{\text{min}} = -0.42 \text{ e \AA}^{-3}$
$S = 1.08$	Extinction correction: <i>SHELXL97</i> (Sheldrick, 1997)
2741 reflections	Extinction coefficient: 0.0032 (3)
218 parameters	Absolute structure: Flack (1983), 497 Friedel pairs
H-atom parameters constrained	Flack parameter = 0.00 (3)
$w = 1/[\sigma^2(F_o^2) + (0.0101P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	

The positional parameters of the H atoms of the sparteine ligand were calculated geometrically and they were then constrained to ride on their attached atoms, with C—H = 0.97–0.98 \AA and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1202). Services for accessing these data are described at the back of the journal.

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